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Critically Evaluated Rate Constants for Gaseous Reactions of Several Electronically Excited Species

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An extensive evaluation is presented of the available gas phase chemical kinetic rate constants for the interactions of the low lying electronic states of several atoms and molecules with numerous collision partners. These include the following excited states: $C(2^1D_2,2^1S_0)$, $N(2^2D_{3/2,5/2}, 2^2P_{1/2,3/2})$, $P(3^2D_{3/2,5/2},3^2P_{1/2,3/2})$, $S(3^1D_2,3^1S_0)$, $Se(4^3P_0, 4^1D_2,4^1S_0)$, $Te(5^3P_{1,0},5^1D_2,5^1S_0)$, $CO(a\,^3\Pi, a'\,^3\Sigma^+,d\,^3\Delta,e\,^3\Sigma^-,A\,^1\Pi)$, $CS(a\,^3\Pi, A\,^1\Pi)$, $OH(A\,^2\Sigma^+)$, $OD(A\,^2\Sigma^+)$, $O_2(c\,^1\Sigma_u^-,C\,^3\Delta_u,A\,^3\Sigma_u^+,B\,^3\Sigma_u^-)$, and $S_2(a\,^1\Delta_g,b\,^1\Sigma_g^+,A\,^3\Sigma_u^+,B\,^3\Sigma_u^-)$. Wherever possible, recommended values are suggested. Much of the data refers only to room temperature. To facilitate the evaluation, collision-free radiative lifetimes often have been required. These also have been evaluated and are presented. The mechanisms of the interactions and the various potential kinetic channels are discussed. These include such processes as chemical reactions, electronic quenching to the ground electronic state, electronic cross relaxation to an adjacent excited state, and for molecules, vibrational and rotational relaxation processes within the excited state. A complete coverage of the literature published prior to 1978 has been attempted.

Key words: Activation energies; electronically excited states; evaluation; gaseous interactions; molecular correlations; quenching; radiative lifetimes; rate constants; reactive channels; recommended data; relaxation processes; review.

Contents

1. Introduction

As we derive the ability to look at the chemistry of various systems in much greater detail, the need for the inclusion of electronically excited state chemistry in kinetic models is increasingly being found necessary. Obvious examples concern atmospheric modeling of regions of normal or perturbed atmospheres and laser chemistry. However, their inclusion in any energetic non-equilibrated system also requires assessing.

Whenever energy is deposited or released in a chemical system knowledge of its transfer and redistribution processes becomes important. The characterization of these relaxation mechanisms and the energy storage potential of metastable states has become a primary goal of gas phase kinetics. This broad interest in spin states and their influence on reaction path has flourished very rapidly, partly as a result of technological developments in experimental methods but also to meet the greater level of sophistication in kinetic modeling of chemical systems. As a consequence, much new data are available that appear to offer a severe challenge to our theoretical understanding.

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It is very necessary to understand the relationships between electronic structure and reactivity for the low lying states of series of atoms and molecules and also to establish quantitatively the stability of the various states to radiative and collisional relaxation processes. Ultimately, a systematic examination and explanation of their behavior is required. The present study is an initial effort to facilitate such an ambition. Additional efforts are planned to include, in time, coverage of the remaining 40 to 50 electronically excited species for which large amounts of reliable data now are available.

1.1. Present Status of Evaluated Chemical Kinetic Data

The past decade has observed the introduction and general availability of tables of critically evaluated chemical kinetic data. The beneficial consequences are difficult to assess, however, it has undoubtedly upgraded the quality of user input data and begun the necessary process of standardizing a set of recommended values.

Available evaluations now are becoming too numerous to list in an introduction such as this, however, it must be noted that they largely emphasize gaseous reactions of neutrals or ions in their ground electronic state configurations. With the exception of those reactions of electronically excited atomic and molecular oxygen pertinent to stratospheric aeronomy (Wayne, 1969; Kearns, 1971; Hampson et al., 1973; Cvetanovic, 1974; Hampson & Garvin, 1975; CIAP Monograph, 1975; Schofield, 1978), the whole field of excited state chemistry has not been collectively evaluated since Laidler (1955) published "The Chemical Kinetics of Excited States" twenty years ago at a time when scarcely any quantitative data existed. Consequently much of the published data are still fragmented over the many different scientific journals that accept chemical kinetic papers. Fortunately, reviews have appeared occasionally (Donovan & Husain, 1970, 1971; Husain and Donovan, 1971; Donovan et al., 1972; Donovan & Gillespie, 1975; King & Setser, 1976; Husain, 1977; Golde, 1977) and have served as surrogate although incomplete source documents particularly for reactions of electronically excited atoms.

This publication is an initial attempt to correct this severe deficiency; it critically evaluates all the currently available chemical kinetic data for gaseous reactions of several commonly encountered electronically excited atoms and molecules of importance to aeronomy, photochemistry, and chemical laser systems.

1.2. Correlation Concepts

Whereas the interaction of C($^1D_2$) with H_2 is very fast, that with the more energetic C($^1S_0$) is quite slow. This typifies the act that energy and spin considerations alone are insuffiient to predict reactive behavior. Both these reactants might have been expected to produce CH and H products, C($^1S_0$) even more exothermically. However, their differing nature can be understood rather satisfactorily in terms of the adiabatic correlations of reactants and products. For example, there are no reactive exothermic potential energy surfaces for C($^1S_0$) and the interaction must proceed via a nonadiabatic curve crossing process. It might be noted though that the predictive power of such correlation rules for a priori assessment of preferred reaction pathways is somewhat limited, requiring information concerning the nature of the collision complex and the magnitude of any activation energy barriers.

Correlation diagrams express the consequences of the laws of symmetry. As normally presented they are constructed within definite constraints, namely the geometrical symmetry of the intermediate, the separation of spin and orbital motion, and the non-crossing rule. Thus, while in many cases the diagrams appear to offer sufficient explanation for the mechanism of many interactions, particularly of the lighter elements, clearly higher approximations and where possible the detailed electronic structure of the intermediate in some instances have to be taken into account. Generally this has not been necessary in the present work.

The application of the linear correlation diagrams in C_s symmetry, well exemplified by the work of Donovan and Husain (1970), is a necessary and valuable first step in understanding the reactions of electronically excited states. This has been very apparent in the present work where many of the interactions involve species of low atomic number.

The necessary information on the low lying spectroscopic states is usually available (Rosen, 1970; Barrow, 1973, 1975). If not, it can generally be sufficiently well assessed by comparison with isoelectronic species to facilitate the necessary ordering of the correlating surfaces. Silver (1974) has discussed in detail these symmetry conservation rules. Carrington (1974) has summarized the characteristics of intersecting potential energy surfaces. The nature of nonadiabatic transitions is not yet clearly understood although such processes may be more common than might be supposed and appear in some cases to occur with surprisingly high efficiencies. Nikitin (1974) has made significant contributions to our understanding in this area and has discussed and reviewed the present status for the case of simple atom-diatom bimolecular reactions.

2. Presentation of the Data

Although a considerable amount of kinetic data are available for electronically excited species, it is still largely limited to room temperature values and little if any information exists on temperature dependences. Also, in a majority of cases the interaction products have not been determined, often leaving some doubt as to whether the collision induces chemical reaction or solely physical relaxation.

Sometimes, the measured quantity is the product of the particular rate coefficient and the radiative lifetime of the state involved. Consequently it has been necessary, particularly in molecular systems, to assess the available radiative lifetime data and adjust the kinetic values to a mutually consistent set.

The collision free radiative lifetimes of the atomic states generally have been evaluated elsewhere and are sufficiently well established. This is not the case for the corresponding molecular states, and an evaluation of their lifetimes has been necessary to facilitate the kinetic analysis. Although somewhat uncertain in some instances it has not been an impediment to the program.

Molecular systems are necessarily more complex owing to the multitude of potential relaxation processes. In some cases, where a system has been characterized more thoroughly, information may be available, for example, on chemical reactions, electronic quenching to the ground state, electronic cross relaxation to neighboring electronic states, and for vibrational and rotational relaxation within the state.

For each atomic or molecular species all the low lying electronic states have been included. These are generally less than about 450 kJ mol^{-1} but in the cases of O_2 and CO lie at or below 600 or 780 kJ mol^{-1}, respectively. Invariably, the majority are metastable.

For each species evaluated, the arrangement consists initially of some illustration of the energy levels concerned, with some discussion as to their nature and radiative lifetimes. This is followed by a listing of the recommended or suggested rate constant values that have been derived from the evaluation, with some indication of accuracy. The technique used to derive these error bars varies according to the extent and nature of the available data. The basis for any evaluation is firstly to ensure that all measurements refer to the same situation and are directly comparable. This may require some correction or reanalysis incorporating parameters that have since been improved upon. Measurements at odds with the general trends or otherwise obviously in error then can be identified and discarded. Error bars have then been set to encompass all the apparently reliable data and are consequently broader than a single deviation. In cases where data are very limited, consisting of possibly only a single or two measures, the confidence level has to be based to a large extent on the reliability of any other measurements made in the same study, on the technique used and on the reputation of the investigators. Such values are obviously subject to a greater uncertainty and the error limits here set are consequently somewhat debatable. No particular weight has been given to individually published error limits. It is very apparent from these summaries of recommended data where values are missing or additional efforts are necessary to improve accuracy.

The presentation then consists of a figure illustrating the available data together with a table which also includes a description of the technique and conditions used, with appropriate comments. Because of the lack of temperature dependent data and also the large number of interactions that have been investigated for some of the states, the room temperature values are plotted as a function of the various interacting species. This better illustrates their relative efficiencies although it produces an unusual style kinetic plot.

The tables then are followed by a discussion of the data which includes an assessment of the processes involved in the interactions and often invokes the use of correlation diagrams to indicate the availability or absence of reactive surfaces. For convenience, references pertaining to each species are listed separately at the end of each such subsection.

Wherever quoted, enthalpy information is nearly always derived from the JANAF Thermochemical Tables and Supplements (Stull & Prophet, 1971; Chase et al., 1974, 1975).

A complete coverage of all the available kinetic data for these species has been attempted including all values published before 1978, and illustrates the full extent of our present understanding.

3. Symbols and Conversion Factors

C_s	Planar symmetry of the collision complex; assumed in most of the correlation diagrams presented here. This is the lowest symmetry case for reactions of atoms and diatomics
$CO^{\dagger}$	Represents vibrationally excited species
D_0°	Dissociation energy as measured from zeroth vibrational level
E_A	Activation energy in the Arrhenius exponent, $\exp(-E_A/8.3143\ T)$, J mol^{-1}. A quoted activation energy implies the value of E_A.
E_T	Activation energy equivalent temperature, units of T, equal to $E_A/8.3143$.
k	Rate coefficient, expressed in cm^3 molecule^{-1} s^{-1} units. The format $A\ \exp(-E_T \pm \text{error}/T)$ has been used instead of the mathematically explicit expression $A\ \exp((-E_T \pm \text{error})/T)$
k_{elect}	Rate coefficient for processes involving a change of electronic state
k_M	Rate coefficient with M as a collision partner
k_{rot}	Rate coefficient for rotational relaxation within the electronically excited state
k_{vib}	Rate coefficient for vibrational relaxation within the electronically excited state
τ	Collision free radiative lifetime, s
T_e	Absolute minimum electronic term, cm^{-1}
T_0	Minimum electronic term of zeroth vibrational state, cm^{-1}

1 cal = 4.1840 J

1 cm^{-1} = 11.9628 J mol^{-1}

1 eV = 96.485 kJ mol^{-1}

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5. Detailed Rate Coefficient Evaluations

5.1. Atomic Carbon $C(2^1D_2, 2^1S_0)$

The lowest lying electronic energy states of atomic carbon, listed in table 1, are metastable as indicated by their long radiative lifetimes. Owing to the closeness of the ^3P_J levels, their populations are rapidly equilibrated and studies of their individual nature are not possible and, moreover, are of little value other than in problems concerning interstellar chemistry (Yau & Dalgarno, 1976). Limited chemical kinetic data are available for interactions of the $C(^1S_0)$ and $C(^1D_2)$ electronic states.

5.1.1. Recommended Rate Constant Values

$C(2^1D_2)$

Chemically reactive collisions probably occur with N_2O, CH_4, C_2H_4, C_3H_6, CO_2?, NO, O_2?, and H_2.

Physical relaxation processes with H_2O, CO, N_2, He, Ne, Ar, Kr and Xe.

All rate constants are $>10^{-11}$ cm^3 molecule^{-1} s^{-1} with the exceptions of N_2, He, Ne, Ar and Kr (table 2). Those for reactive collisions, with the exceptions of O_2 and Xe, appear consistently larger than values for physical quenching.

$C(2^1S_0)$

Physical relaxation processes appear dominant. Rates are generally much slower than for the corresponding interactions of $C(^1D_2)$.

Insufficient data exist to permit establishing a set of recommended values (table 3).

5.1.2. Discussion

Studies of electronically excited states of atomic carbon have been limited by the practical difficulty of their production in systems that are appropriate for kinetic analyses. The only recognized technique is that developed by Braun et al. (1969) who showed that vacuum ultraviolet photolysis of C_3O_2 yields $C(^3P_J, ^1D_2)$ as primary and $C(^1S_0)$ as a minor secondary product. The reaction rates for each of these states are such that their individual interactions can be characterized. However, the methods can be applied in a simple manner only to relatively few collision partners which do not themselves absorb the incident vacuum uv flash, otherwise additional care has to be taken in the interpretation and the data become somewhat questionable. Whereas the yield of $C(^1S_0)$ by this technique is very low, that of $C(^1D_2)$ is a reasonable fraction of the ground state $C(^3P_J)$ concentration.

a. Atomic Carbon, $C(2^3P_{2,1})$

Levels of the ground state triplet are so closely spaced, within kT for normally encountered temperatures, to make a study of their individual natures of little value. As expected, the multiplet levels appear to be rapidly equilibrated, requiring only a few collisions (Braun et al., 1969). Measured reaction rates for ground state carbon atoms therefore are invariably an integral measure for all three components (^3P_J).

Table 1. Energies and radiative lifetimes of low-lying electronic states of atomic carbon

Electronic State	Energy[a] Level (cm^{-1})	Radiative[b] Lifetime (s)
$^1S_0$	21,648.01	2.0
$^1D_2$	10,192.63	3230
$^3P_2$	43.40	3.7×10^6
$^3P_1$	16.40	1.3×10^7
$^3P_0$	0.00	-

[a] Moore, 1970

[b] Wiese et al., 1966

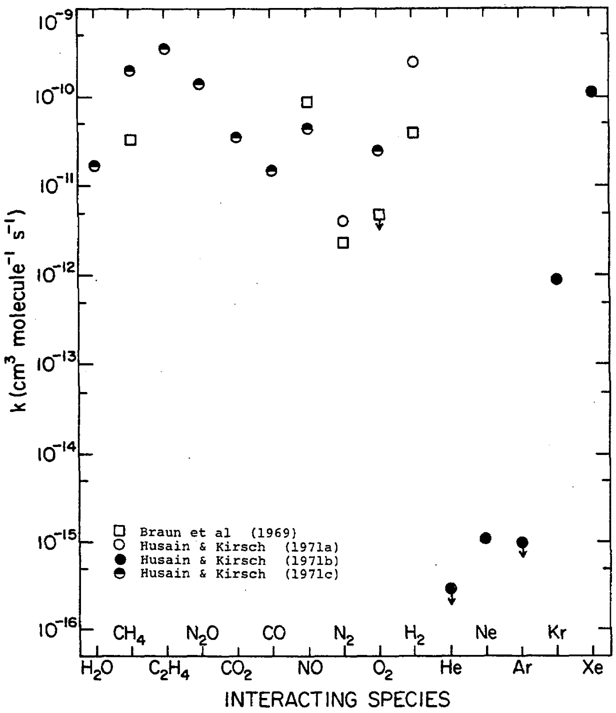

FIGURE 1. Rate constants for the various interactions of $C(2^1D_2)$, 300 K.

b. Atomic Carbon, $C(2^1D_2,2^1S_0)$

Only two research groups have obtained absolute rate constants for the decay of $C(^1D_2)$ in the presence of various molecules. Of these, only Braun et al. (1969) report monitoring some of the products if any, resulting from some of the interactions. Owing to the experimental difficulty of producing $C(^1S_0)$ and its study in the presence of the larger concentrations of $C(^3P_J,^1D_2)$, only limited and probably approximate data are available.

$C(^1D_2)$ + H_2O

A single value, ≅ 1.7×10^{-11}, of limited accuracy has been reported. The uncertainty arises due to the extent of H_2O photolysis that may occur in the original flash. The only reasonable chemical reaction

$$C(^1D_2) + H_2O = CH + OH \quad \Delta H^\circ_{298\,K} = +38.5 \text{ kJ mol}^{-1}$$
$$(+9.20 \text{ kcal mol}^{-1})$$

is endothermic. Exothermic production of CO + H_2 in a single step is kinetically very unlikely. The rate probably describes the physical, spin forbidden relaxation process

$$C(^1D_2) + H_2O = C(^3P_J) + H_2O.$$

$C(^1D_2,^1S_0)$ + N_2O

The interaction with $C(^1D)$ is rapid. The single reported value for the rate constant is $1.4(\pm0.5)\times10^{-10}$ and reaction probably proceeds via either or both of the allowed exothermic channels

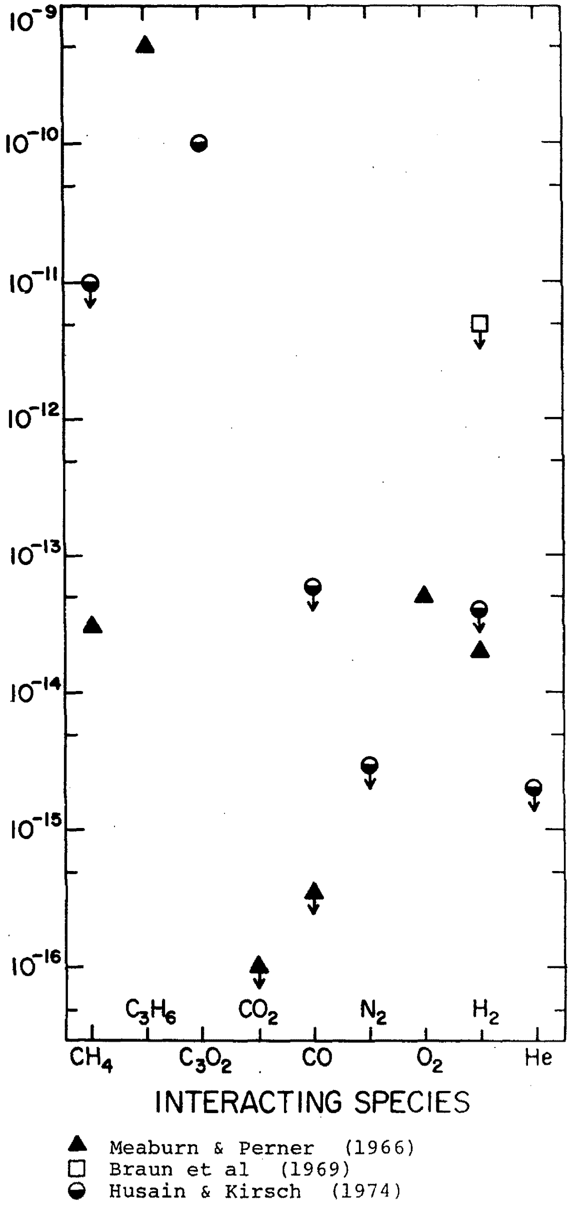

FIGURE 2. Rate constants for the various interactions of $C(2^1S_0)$, 300 K.

$$C(^1D_2) + N_2O = CN + NO \quad \Delta H^\circ_{298\,K} = 393.6 \text{ kJ mol}^{-1}$$
$$(94.1 \text{ kcal mol}^{-1})$$
$$= CO + N_2 \quad 1030 \text{ kJ mol}^{-1}$$
$$(246 \text{ kcal mol}^{-1})$$

These have sufficient energy either to populate excited states of CN or excited singlet states of CO or N_2.

The reaction of N_2O with $C(^1S_0)$ has not been reported but exothermic adiabatic potential energy surfaces are available to both sets of products (Husain and Kirsch, 1971c).

$C(^1D_2,^1S_0)$ + $CH_4,C_2H_6,C_2H_4,C_3H_6$

The two measured rate constants for $C(^1D_2)$ with CH_4 differ, for no obvious reason, by a factor of six; only a single

Table 2. Rate constants for interactions of $C(^1D_2)$.

M	k_M, cm^3 $molecule^{-1}s^{-1}$			
H_2O				$\approx 1.7 \times 10^{-11}$
CH_4	3.2×10^{-11}			$2.1(\pm 0.5) \times 10^{-10}$
C_2H_4				$\approx 3.7 \times 10^{-10}$
N_2O				$1.4(\pm 0.5) \times 10^{-10}$
CO_2				$3.7(\pm 1.7) \times 10^{-11}$
CO				$1.6(\pm 0.6) \times 10^{-11}$
NO	9.2×10^{-11}			$4.7(\pm 1.3) \times 10^{-11}$
N_2	$\approx 2.5 \times 10^{-12}$	$4.2(\pm 1.2) \times 10^{-12}$		
O_2	$< 5 \times 10^{-12}$			$\approx 2.6 \times 10^{-11}$
H_2	$4.1_5 \times 10^{-11}$	$2.6(\pm 0.3) \times 10^{-10}$		
He			$< 3 \times 10^{-16}$	
Ne			$1.1(\pm 0.4) \times 10^{-15}$	
Ar			$\leq 1 \times 10^{-15}$	
Kr			$9.4(\pm 1.6) \times 10^{-13}$	
Xe			$1.1(\pm 0.3) \times 10^{-10}$	
Exp. Temp. K	300	300	300	300
Method	Vacuum uv flash photolysis 1.3 Pa C_3O_2 in excess 7-70 kPa Ar. Plate photometry of 193.1 nm $C(^1D_2)$ absorption line, continuum source.	Vacuum uv flash photolysis (λ>105 nm),		
		1125 J	1125 J	1125, 1280 J,
		0.13 Pa C_3O_2 in excess He diluent; pressures		
		He 6.65 kPa	He 6.65 kPa	He 6.65 kPa, NO, $CO_2 \leq 0.8$ Pa
		$N_2 \leq 12$ Pa	$Xe \leq 0.8$, $Kr \leq 50$ Pa	O_2, $CO \leq 1.5$, CH_4, $N_2O \leq 0.25$ Pa
		$H_2 \leq 0.15$ Pa	$Ar \leq 28$, $Ne \leq 38$ kPa	$C_2H_4 \leq 0.11$, $H_2O \leq 4.4$ Pa
		$C(^1D_2)$ monitored via 193.1 nm atomic absorption using C line microwave discharge source.		
Comments	Decay rates independent of flash lamp intensity over factor of 3.	Same technique used in all three studies by Husain and Kirsch. Error limits are their quoted estimates.		
Reference	Braun et al., 1969	Husain & Kirsch 1971a	Husain & Kirsch 1971b	Husain & Kirsch 1971c

value has been reported for C_2H_4. Data for (C^1S_0) are rather indefinite owing to the questionable results of Meaburn and Perner (1966). These are undoubtedly affected by the large amount of energy deposited into their system which can markedly affect the nature of the species in the mixture. However, the available data does illustrate the more highly reactive nature of $C(^1D_2)$ particularly towards saturated hydrocarbons.

A fast chemical reaction appears to characterize the interaction of $C(^1D_2)$ with CH_4. This is presumably typical of all $C(^1D_2)$/hydrocarbon cases. Braun et al. (1969) measured quantitatively the formation of C_2H_2 via its 151 nm absorption band, suggesting a mechanism proceeding through a short lived excited state of ethylene

$$C(^1D_2) + CH_4 \rightarrow C_2H_4^* \rightarrow C_2H_2 + H_2$$
$$\Delta H^\circ_{298\,K} = -535.3 \text{ kJ mol}^{-1} \, (-127.9 \text{ kcal mol}^{-1}).$$

The reaction is sufficiently exothermic to dissociate either of the products. The acetylene yield was independent of pressure over an order of magnitude change, indicating that collisional physical quenching is not a competitive process. CH_4 can be photodissociated by the flash, however, the reaction with $C(^1D_2)$ was further confirmed by noting no difference in decay rates for reduced flashlamp intensities (Braun et al., 1969). Similarly, in a 147 nm Xe low intensity photolysis study of C_3O_2 in the presence of CH_4, Tschuikow-Roux et al. (1972) have concluded that this reaction is responsible for the C_2H_2 detected gas chromatographically. Using Xe and Ne, respectively, to selectively quench and kinetically moderate hot "recoil" carbon atoms Taylor et al. (1976) also have found evidence for C_2H_2 formation in the $C(^1D) + C_2H_6$ interaction.

Reaction of CH_4 with $C(^1S_0)$ is much slower than with $C(^1D_2)$ but is not yet measured precisely.

The single value for $C(^1D_2) + C_2H_4$ indicates a fast interaction, essentially at every collision, and likewise is presumably chemical in nature proceeding via a stable triangular singlet adduct intermediate (Husain and Kirsch, 1971c).

The value for $C(^1S_0) + C_2H_6$ is questionable and cannot be accepted at present without additional data.

Table 3. Rate constants for interactions of $C(2^1S_0)$.

M	k_M, cm^3 $molecule^{-1}$ s^{-1}		
CH_4	$\approx 3.0 \times 10^{-14}$		$<1 \times 10^{-11}$
C_3H_6	$\approx 5.0 \times 10^{-10}$		
C_3O_2			1×10^{-10}
CO_2	$\leq 1.0 \times 10^{-16}$		
CO	$\leq 3.5 \times 10^{-16}$		$\leq 6 \times 10^{-14}$
N_2			$\leq 3 \times 10^{-15}$
O_2	$\approx 5.0 \times 10^{-14}$		
H_2	$\approx 2 \times 10^{-14}$	$<5 \times 10^{-12}$	$\leq 4 \times 10^{-14}$
He			$<2 \times 10^{-15}$
Exp. Temp. K	300	300	300
Method	Pulsed 250kV e-beam excitation of CO_2, CO or CH_4. Total pressure 60-130 kPa. Analytical absorption flash, White cell, 247.8 nm line analyzed.	Vacuum uv flash photolysis 1.3 Pa C_3O_2 in excess 7 kPa Ar. Plate photometry of 175.2 nm $C(^1S_0)$ absorption line, continuum source.	Vacuum uv flash photolysis $\lambda \geq 110$ nm. 1125-1620 J, 0.27 Pa C_3O_2, He diluent 6.65 kPa, pressures $CH_4 \leq 3.5$, C_3O_2 0.1-0.5, $CO \leq 600$, $H_2 \leq 700$, $N_2 \leq 6000$ Pa. $C(^1S_0)$ 247.8 nm absorption line using C line microwave discharge source.
Comments	Measure approximate half life of $C(^1S_0)$. Reanalyzed by Donovan & Husain (1971) assuming first order kinetics in atom concentration. Questionable values owing to large amount of energy deposited into the system.		
Reference	Meaburn & Perner, 1966	Braun et al., 1969	Husain & Kirsch, 1974

Such reactions with olefins may proceed by insertion into the double bond to form allenes (Marshall et al. 1964; Skell and Engel, 1967).

$C(^1D_2,^1S_0) + CO, CO_2, C_3O_2$

$C(^1D_2)$ is quite rapidly relaxed by CO as measured by Husain and Kirsch (1971c) and implied from the data of Tschuikow-Roux et al. (1972). No chemical reactions are open to either singlet carbon state and decay must be via nonadiabatic physical relaxation channels. The process with $C(^1S_0)$ is inefficient.

The rates for CO_2 are rather similar to those for CO, however, in this case, adiabatic, exothermic reaction pathways are possible

$$C(^1D_2) + CO_2 = CO + CO \quad \Delta H^{\circ}_{298\,K} = -664.5 \text{ kJ mol}^{-1} \; (-158.8 \text{ kcal mol}^{-1})$$

$$C(^1S_0) + CO_2 = CO(A\,^1\Pi) + CO \quad = -26.96 \text{ kJ mol}^{-1} \; (-6.44 \text{ kcal mol}^{-1}).$$

The former is sufficiently exothermic to excite the CO product to high vibrational levels. However, the relative importance of reaction to physical quenching remains unknown.

The rate constant 1×10^{-10}, has been very tentatively reported for $C(^1S_0) + C_3O_2$, presumably indicating a chemical interaction.

$C(^1D_2,^1S_0) + NO$

The two measures of this rate constant for $C(^1D_2)$ differ by a factor of two and indicate a high collision efficiency. Although reaction channels are thermodynamically and adiabatically possible to both CN + O and CO + $N(^2P)$ the former reaction appears preferred. Braun et al. (1969) found no increase in CO yield on adding NO to a system containing all three states of carbon which placed a limit of ≤ 15% on the CO producing channel. Also, CN was detected as a product by its 388.3 nm absorption. The correlating potential energy surfaces for CO + N products may involve activation energies since this reaction is observed only with hot carbon atoms (Husain & Kirsch, 1971c). The surfaces connecting to

CN + O products are illustrated in figure 3. They indicate for C(^{1}D$_2$) the possible formation of either excited CN($A\,^2\Pi$) ($\Delta H^\circ_{298\,\mathrm{K}}$ = -133.8 kJ mol^{-1}, -32.0 kcal mol^{-1}) or O(^{1}D$_2$) ($\Delta H^\circ_{298\,\mathrm{K}}$ = -53.07 kJ mol^{-1}, -12.68 kcal mol^{-1}).

C(^{1}S$_0$) + NO has not been measured. Reactive surfaces leading to CO + N are endothermic, correlating with excited states of CO, and are not expected to occur (Donovan and Husain, 1970). Rather, reaction should yield CN($A\,^2\Pi$) + O(^{1}D) ($\Delta H^\circ_{298\,\mathrm{K}}$ = -81.0 kJ mol^{-1}, -19.4 kcal mol^{-1}).

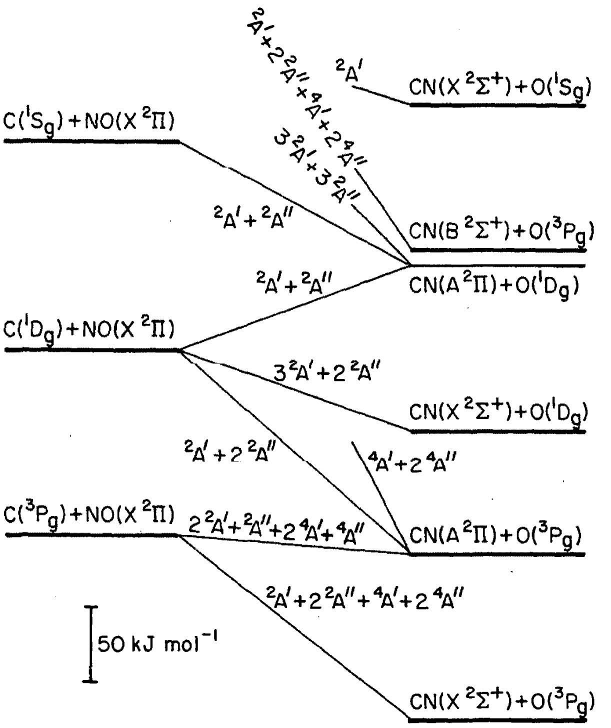

FIGURE 3. Correlation diagram connecting the states of C + NO and CN + O

C(^{1}D$_2$,^{1}S$_0$) + N$_2$

The two independent values for C(^{1}D$_2$) indicate a rate constant of (2.5 − 4.2) × 10^{-12}, rather efficient considering the spin forbidden nature of the non-adiabatic physical quenching transition, figure 4. It must involve a favorable crossing of singlet and triplet surfaces similar to the case for O(^{1}D$_2$).

C(^{1}S$_0$) quenching by N$_2$ is inefficient, $k \le 3 \times 10^{-15}$, and is similarly non-adiabatic in character. However the nature of the products remains in doubt. It is interesting to note that figure 4 does predict the possible chemical reaction between C(^{5}S$_2$) and N$_2$.

C(^{1}D$_2$,^{1}S$_0$) + O$_2$

The two measures of the rate constant for C(^{1}D$_2$) + O$_2$ differ by about a factor of 5, but must be considered with caution owing to the photolysis of O$_2$ in these flash photolysis systems. Decay can proceed via the formation of CO($a'\,^3\Sigma^+$ or $a\,^3\Pi$) + O, as illustrated by the correlation diagram, figure 5. However, these surfaces may or may not involve activation energy barriers (Husain and Kirsch, 1971c) and the quenching mechanism remains uncertain. Meaburn & Perner's (1966) value for C(^{1}S$_0$), ≅ 5.0 × 10^{-14}, if valid, would indicate an activation energy for the allowed transition to CO($d\,^3\Delta$) + O. Experimental results tend to indicate that terminal attack on O$_2$ is preferred to insertion (Donovan & Husain, 1970).

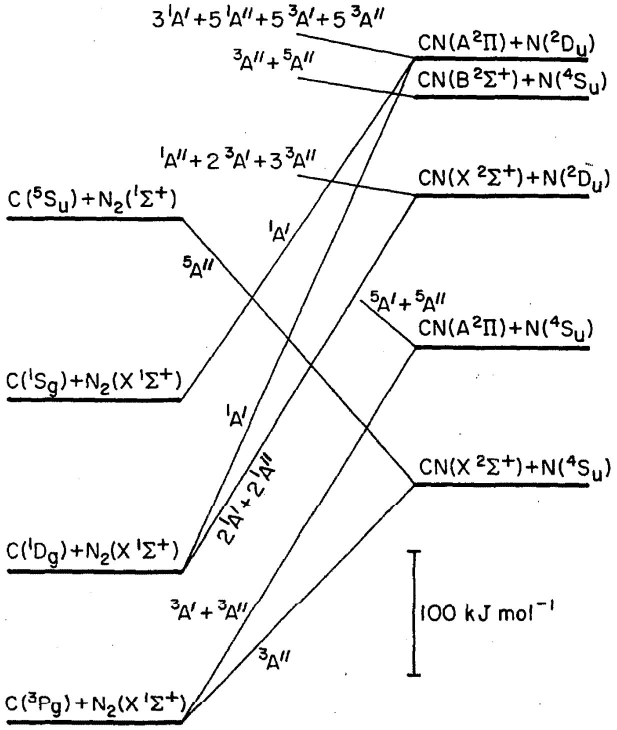

FIGURE 4. Correlation diagram connecting the states of C + N$_2$ and CN + N.

C(^{1}D$_2$,^{1}S$_0$) + H$_2$

The interaction of H$_2$ with C(^{1}D) is very efficient, approaching unit collision frequency and presumably proceeding via the reaction,

$$\mathrm{C(^1D_2) + H_2 = CH + H} \quad \Delta H^\circ_{298\,\mathrm{K}} = -24.8\ \mathrm{kJ\ mol^{-1}}\ (-5.93\ \mathrm{kcal\ mol^{-1}})$$

as indicated in figure 6. Theoretical calculations indicate that the mechanism will be one of insertion with no apparent barrier (Blint and Newton, 1975). The slower nature of the reaction with C(^{1}S$_0$) arises from its nonadiabatic mechanism; the absolute value is still somewhat uncertain.

C(^{1}D$_2$,^{1}S$_0$) + OH

No data are available concerning the interactions of C(^{1}D$_2$,^{1}S$_0$) with OH or its various possible chemical channels. Although reactions to ground state products are exothermic, for example,

$$\mathrm{C(^1D) + OH \rightarrow CO + H} \quad \Delta H^\circ_{298\,\mathrm{K}} = -769.2\ \mathrm{kJ\ mol^{-1}}\ (-183.8\ \mathrm{kcal\ mol^{-1}})$$

$$\rightarrow \mathrm{CH + O} \quad = -33.3\ \mathrm{kJ\ mol^{-1}}\ (-8.0\ \mathrm{kcal\ mol^{-1}})$$

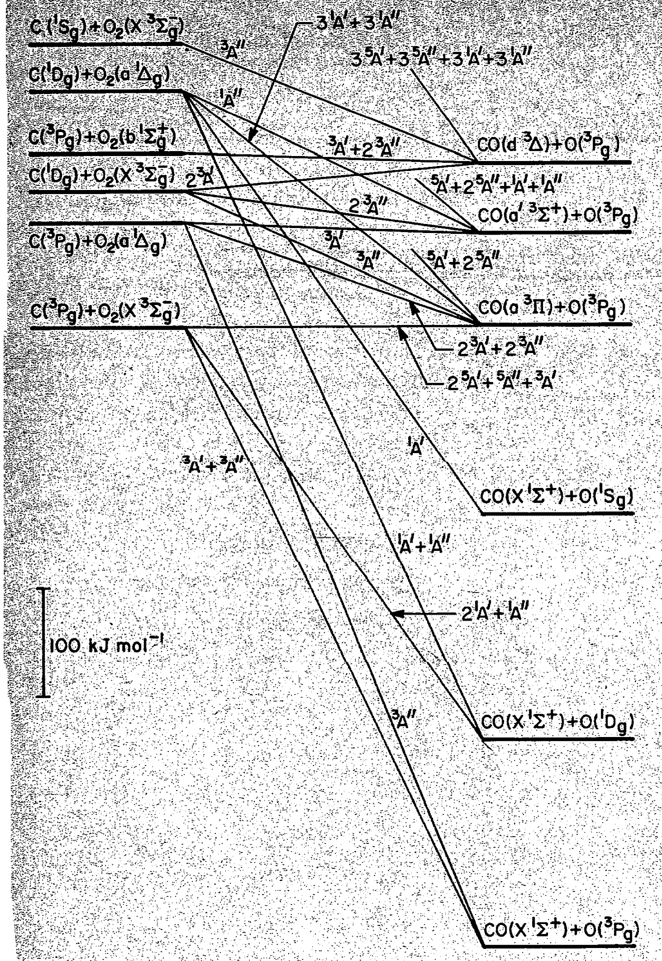

FIGURE 5. Correlation diagram connecting the states of C + O_2 and CO + O (after Donovan & Husain, 1970).

the correlation of electronic states, figure 7, favors the former for C(^{1}D) producing either CO ($d\,^3\Delta, I\,^1\Sigma^-$ or $A\,^1\Pi$) ($\Delta H^\circ_{298\,\mathrm{K}} = -44, +3.0, +5.4$ kJ mol^{-1}, respectively). There are no exothermic adiabatic channels to CH + O products.

Although more energetic, direct reaction between C(^{1}S) and OH appears possible only on endothermic surfaces. That to CH + O(^{1}D) is the least energy deficient, $\Delta H^\circ_{298\,\mathrm{K}} = +19.4$ kJ mol^{-1}.

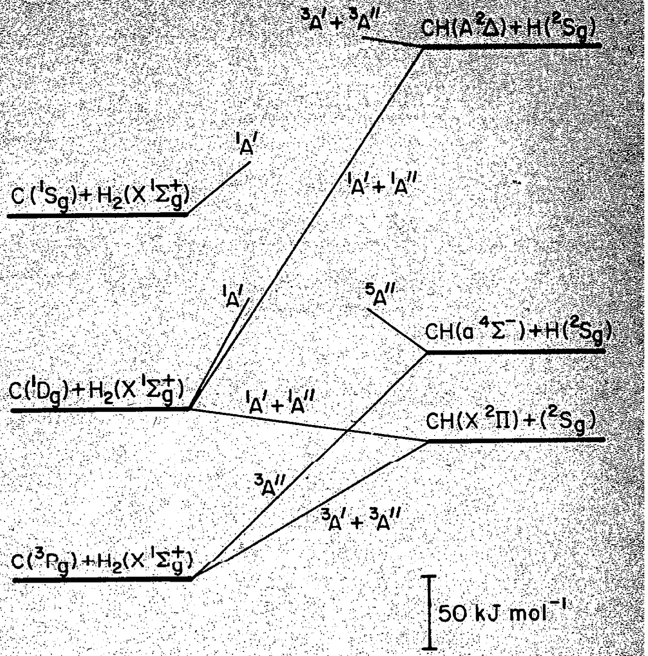

FIGURE 6. Correlation diagram connecting the states of C + H_2 and CH + H.

C($^1D_2$,$^1S_0$) + Inert Gases

Values have been reported by only one group of investigators and for C($^1D_2$) illustrate a more efficient quenching with the heavier atoms. The rate for Xe corresponds to about one third of the collision frequency. As a group, these values appear to be fundamentally similar to, for example, the corresponding interactions of O($^1D_2$) and S($^1D_2$).

The higher efficiencies of Kr and Xe have been explained in terms of favorable potential curve crossings between those correlating with the initial and the final states (Husain and Kirsch, 1971b.).

Similar curve crossings for corresponding C($^1S_0$) interactions to lower states of carbon are not expected and nonadiabatic transitions leading to relaxation should be slow, as already indicated for He and presumably also the case for Ar (Braun et al., 1969).

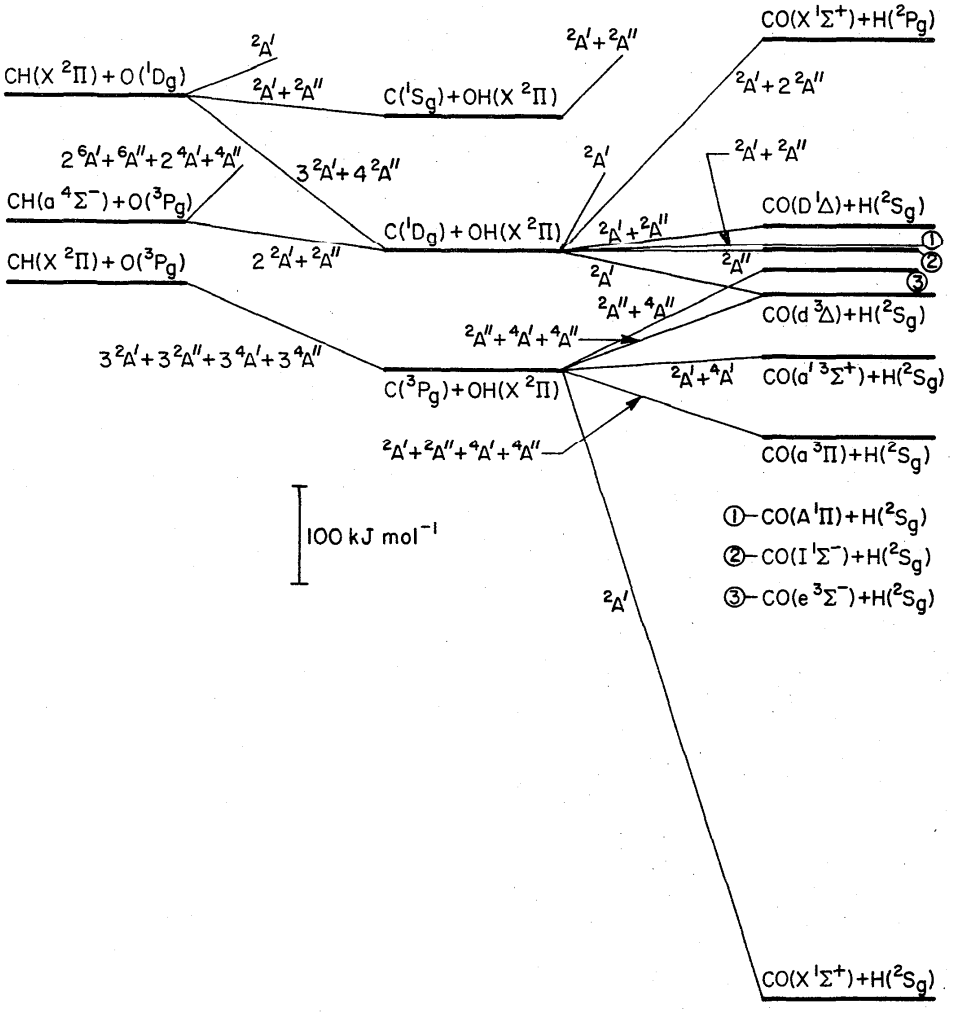

FIGURE 7. Correlation diagram connecting the states of C + OH with those of either CH + O or CO + H.

5.1.3. References

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5.2. Carbon Monoxide, CO($a\,^3\Pi$, $a'\,^3\Sigma^+$, $d\,^3\Delta$, $e\,^3\Sigma^-$, $A\,^1\Pi$)

These low lying states of CO all correlate to ground state atoms. $I\,^1\Sigma^-$ and $a\,^3\Pi$ are metastable. $A\,^1\Pi$ radiates to the ground state and the remaining triplet states all have allowed optical transitions to $a\,^3\Pi$. The importance of the mixing of certain levels in $A\,^1\Pi$, $e\,^3\Sigma^-$, $d\,^3\Delta$, and $a'\,^3\Sigma^+$ is evident and leads to a high probability of cross relaxation or energy transfer between these states.

These electronic systems are the most complex yet studied kinetically and indicate the many relaxation channels that become available in such a dense manifold of energy states.

No kinetic or lifetime data are available for $I\,^1\Sigma^-$. Kinetically the $a\,^3\Pi$ state is best characterized but limited data are available also for the $a'\,^3\Sigma^+$, $d\,^3\Delta$, $e\,^3\Sigma^-$ and $A\,^1\Pi$ states.

Table 4. Relative and dissociation energies of the low lying electronic states of CO.

	T_e	T_0	D_0''
		cm^{-1} [a]	
$A^1\Pi$	65,074.6	65,828.1	24,848
$I^1\Sigma^-$	65,085.4	65,627.9	25,049
$e^3\Sigma^-$	64,230.7	64,786.5	25,890
$d^3\Delta$	61,123.9[b]	61,705.6	28,971
$a'^3\Sigma^+$	55,826.1	56,437.4	34,239
$a^3\Pi$	48,687.4	49,555.6	41,121
$X^1\Sigma^+$	0.0	1,081.6	89,460

[a] Krupenie, 1966; Simmons & Tilford, 1971

[b] Herzberg et al., 1970

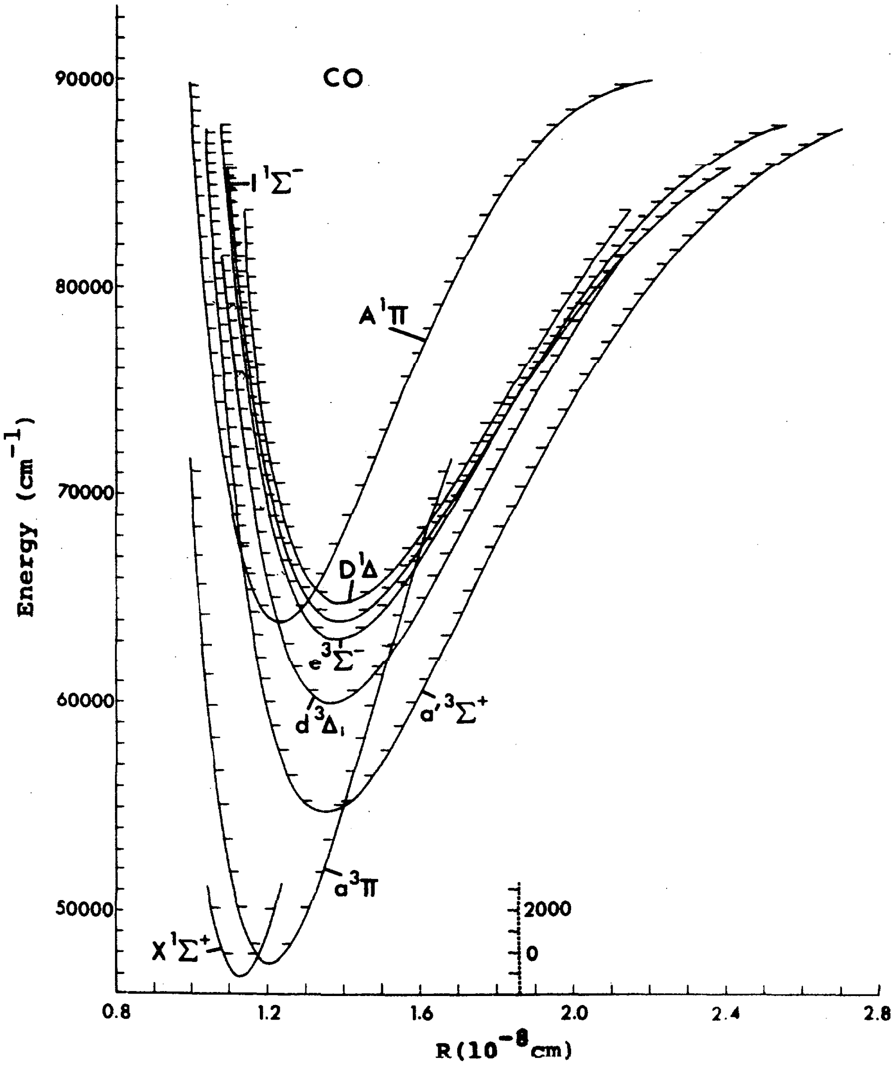

FIGURE 8. Potential energy curves of low-lying electronic states of CO (from Herzberg et al., 1970).

5.2.1. Radiative Lifetimes

CO($A\,^1\Pi$)

As indicated in table 5, lifetime measurements show no pronounced dependence on vibrational state and values approximate to 10(±1)ns. However, in regions of strong rotational perturbations, this lifetime can be significantly lengthened. Wallace et al. (1977) and Provorov et al. (1977) have measured the rotational dependence for $J=10$ to 28 in the $v=0$ state. Values range up to 20 ns and illustrate the perturbations at $J \sim 12$ and 16 arising from interactions with the $e\,^3\Sigma^-_{v=1}$ state and that at $J \sim 27$ due to $d\,^3\Delta_{v=4}$.

CO($I\,^1\Sigma^-$, $e\,^3\Sigma^-$)

Low lying vibrational levels of the singlet state are metastable and no lifetime data are yet reported. However, higher levels of $I\,^1\Sigma^-$ have the potential of coupling with low vibrational levels of $A\,^1\Pi$ and, as a result, may have much reduced lifetimes.

By studying the interactions between overlapping levels of $e\,^3\Sigma^-_{v=4}$ and $A\,^1\Pi_{v=2}$, Slanger and Black (1973b) have estimated a radiative lifetime of about 3 μs for the unperturbed levels of the $e\,^3\Sigma^-_{v=4}$ state and $\cong 5$ μs for $v=1$ (Slanger & Black, 1973c).

CO($d\,^3\Delta$)

Experimental values for the radiative lifetimes of the vibrational levels of CO($d\,^3\Delta$) are listed in table 6. There is substantial agreement between all three determinations which are based on monitoring the fluorescence decay following excitation of CO with either a 27 MHz RF discharge (Wentink et al., 1967), or a pulsed e-beam (Van Sprang et al., 1977), and the photodissociation of CO_2 with 92 nm radiation (Phillips et al., 1976). No vibrational dependence is apparent. However, within any one vibrational state a dependence on the particular rotational state will occur in regions of significant mixing with, for example, $A\,^1\Pi$. Slanger and Black (1973a) have illustrated this J dependence for the case of the interactive mixing of the $d\,^3\Delta_{v=5}$ and $A\,^1\Pi_{v=1}$ states.

CO($a'\,^3\Sigma^+$)

The measured radiative lifetimes of the CO($a'\,^3\Sigma^+$) state, corrected to zero pressure, also are listed in table 6. The values derived by Wentink et al. (1967) and by Van Sprang et al. (1977) are in close agreement and indicate a slight decrease to higher v'. Those of Hartfuss and Schmillen (1968) have been questioned and possibly refer rather to the CO^+($A\,^2\Pi$) $v=0-3$ levels. As discussed above for CO($d\,^3\Delta$), a dependence on rotational state is expected within a vibrational level for perturbed regions.

CO($a\,^3\Pi$)

This lowest lying metastable triplet state does not exhibit a single valued radiative lifetime but is a function of the particular rotational quantum number and electronic sublevel, $^3\Pi_{0,1,2}$, due to the varying extent of the spin-orbit mixing with $A\,^1\Pi$. James (1971b) and Johnson and Van Dyck (1972) have illustrated the magnitude of this variation for $v=0$ which can range from 3 to 450 ms. However, provided that rapid equilibration between these components can occur, as is normally the case in buffered gas experiments, an average lifetime can be measured and as seen from table 7 approximates to about 7.6 ms. Otherwise the experimental value derived will depend critically on the experimental conditions and the population distribution initially produced. Also, with the exception of $v=0-3$, all vibrational levels of CO($a\,^3\Pi$)

Table 5. Radiative lifetimes for CO($A\,^1\Pi$) states, ns.

v=0	1	2	3	4	5	6	Method	Reference
11.5	10.9	10.5	10.5	10.4	10.2		200 eV Modulated e-beam, phase shift	Hesser, 1968
		9.0					Hanle effect	Wells & Isler, 1970
15.9[a]	16.2	16.6	16.1	15.0	14.3		Pulsed discharge - emission decay	Chervenak & Anderson, 1971
10.69	10.37	9.35	8.97	9.67	9.75	10.45	Pulsed monoenergetic e-beam - decay	Imhof & Read, 1971
	10.4	8.5					Hanle effect	Burnham et al., 1972
10.8							Pulsed 154.6 nm source - decay	Lavollee & Tramer, 1977
10.9							vuv laser - fluorescence decay	Provorov et al., 1977
10.7	10.4	9.4	9.7	10.0	10.0	10.0	Suggested values	

[a] Data discarded

Table 6. Radiative lifetimes for CO($d^3\Delta$, $a'^3\Sigma^+$) states, μs.

v	CO($d^3\Delta$)			CO($a'^3\Sigma^+$)		
	Wentink et al., 1967	Phillips et al., 1976	Van Sprang et al., 1977	Wentink et al., 1967	Hartfuss & Schmillen, 1968	Van Sprang et al., 1977
1			7.30			
2			6.62			
3		4.7	5.75	10.12		
4			5.40	10.36		10.24
5			4.05	11.54	3.7[a]	9.12
6	5.03		4.90	7.82	3.6	8.82
7	4.18		4.18	7.12	3.1	8.15
8	4.36		5.23	5.98	2.9	7.11
9	4.45		4.56	6.67		6.82
10	4.57		4.46			
11			4.46			
12			4.65			
13			4.67			
14			4.54			
15			4.16			
16			2.94			

[a] These values probably refer to $CO^+(A^2\Pi)$ levels (Van Sprang et al., 1977)

Table 7. Radiative lifetime for CO($a^3\Pi$)$_{v=0}$, ms.

Average Lifetime v=0	Method	Reference
12[a]	Integrated band absorption measured	Donovan & Husain, 1967
6	Oscillator strength measured	Fairbairn, 1970, 1971
8.7	Oscillator strength measured	Hasson & Nicholls, 1971
1[a]	Electron excitation - TOF mass spectrometer	Borst & Zipf, 1971
7.5	Pulsed photodissociation CO_2 - emission decay	Lawrence, 1971
4.4	Optically pumped via higher triplets	Slanger & Black, 1971
9.5	Oscillator strength measured	James, 1971a
8.75	Theoretically calculated oscillator strength	James, 1971b
7	He/CO_2 discharge - emission decay	Wauchop & Broida, 1972
6.5-9.8	Electron impact CO_2 TOF mass spectrometer	Johnson, 1972
7.6	Suggested average value	

[a] Discarded data

are perturbed at low J values by one or more of the neighboring electronic states (Field et al., 1972a,b).

The spontaneous vibrational transition probabilities for the lower vibrational levels within the $a\,^3\Pi$ state have been calculated by Wicke and Klemperer (1975) and measured by Marcoux et al. (1977). These imply radiative lifetimes, relating only to this vibrational relaxation, of 17.5(19.0), 7.8(13.1), 4.7(5.6), 3.3 and 2.3 ms for $v=1-5$, respectively, the experimental values being indicated by parentheses. These are comparable to electronic radiative transitions to the ground state and provide an additional decay process for levels above v=0. Wicke and Klemperer (1975) also noted that levels at or above $v=5$ have allowed optical transitions to those of $a'\,^3\Sigma^+$ which lie at lower energies. The fact that the latter also couple efficiently via optical transitions to low vibrational levels of $a\,^3\Pi$ implies that high vibrational levels of $a\,^3\Pi$ have an alternate mechanism for redistribution to lower levels within the same state by means other than direct collisional or radiative vibrational relaxation, both of which processes appear to be slow.

5.2.2. Recommended Rate Constant Values, 300 K

CO($a\,^3\Pi$), k_{elect}

CH_4	3.5×10^{-10}	SF_6	$<10^{-12}$
C_2H_6	$\cong 4.9\times10^{-10}$	OCS	3.4×10^{-10}
C_2F_6	1×10^{-12}	CO_2	1.7×10^{-11}
C_2H_4	6.8×10^{-10}	H_2	1.8×10^{-10}
C_2H_2	7.4×10^{-10}	D_2	1.8×10^{-10}
C_2N_2	$\cong 3.3\times10^{-10}$	O	2×10^{-10}
N_2O	$\cong 2.6\times10^{-10}$	He	$<10^{-14}$
NH_3	$\cong 3.1\times10^{-10}$	Ar	$<10^{-14}$
SO_2	$\cong 1.9\times10^{-10}$		
CS_2	$3.3\times(v=0)$, $3.6\times(v=1)$, $3.8\times10^{-10}(v=2)$		
CO	$1.1\times(v=0)$, $2.0\times(v=1)$, $2.3\times10^{-10}(v=2)$; via E-V energy transfer		
NO	2.0×10^{-10}; channels to NO($A\,^2\Sigma^+$, $B\,^2\Pi$ and possibly $a\,^4\Pi$, $b\,^4\Sigma^-$ or $X\,^2\Pi$). Efficiency of NO($A\,^2\Sigma^+$) channel $\cong 8-23\%$, that for ($B\,^2\Pi$)$\cong 2-9\%$.		
N_2	$0.9\times(v=0)$, $1.8\times(v=1)$, $2.0\times10^{-11}(v=2)$; $\cong 25\%$ efficient channel to $N_2(A\,^3\Sigma^+)$.		
O_2	1.7×10^{-10}; potential chemical channel.		

Independent of v unless indicated.

$T^{1/2}$ dependence found with CH_4, C_2H_4, C_2H_2, CO, O_2, H_2 D_2, and probably the general case.

CO($a\,^3\Pi$), k_{vib}

He $\leq 6\times10^{-17}$.
Appears insignificant with possible exception of SF_6.

CO($a'\,^3\Sigma^+$), $k_{\text{elect(+vib)}}$

CO $\cong 2.8\times10^{-10}$, limited data.

CO($d\,^3\Delta$), $k_{^3\Delta_1\rightarrow{}^3\Delta_{2,3}}$, spin-multiplet relaxation

He$\geq 4\times10^{-11}$, Ar$\geq 1.4\times10^{-10}$.

$k_{\text{elect+vib}}$

$k_{\text{CO,NO}} > k_{N_2,\,H_2,\,\text{Ar}} > k_{\text{He}}$.
Relax to ground state vibration with CO(62% efficiency) and N_2 (96% efficiency).

$k_{d\,^3\Delta_{v=7}\rightarrow e\,^3\Sigma^-_{v=4}}$, cross relaxation

CO, N_2, H_2, Ar$\cong(2-6)\times10^{-12}$,
He$\cong 2\times10^{-13}$.

k_{vib}

No specific values.
Limited data are available for all these interactions.

CO($e\,^3\Sigma^-$), $k_{\text{elect+vib}}$

$k_{\text{CO}} > k_{H_2} > k_{N_2} > k_{\text{Ar,Kr}} > {}_{\text{He,Ne}}$, limited data.

$k_{e\,^3\Sigma^-\rightarrow A\,^1\Pi}$, cross relaxation

$k_{e\,^3\Sigma^-_{v=4}\rightarrow A\,^1\Pi_{v=2}}$, $k_{e\,^3\Sigma^-_{v=1}\rightarrow A\,^1\Pi_{v=0}}$,
$k_{e\,^3\Sigma^-_{v=4}\rightarrow d\,^3\Delta_{v=3,4}}$
Limited data but these processes appear to be efficient.

CO($A\,^1\Pi$), k_{elect}, limited data $v=0-14$

CO, N_2, O_2, H_2, D_2, Kr, Xe efficient quenchants.
He, Ne$\cong$ 1% collision efficiency.
Ar intermediate in nature.
Slight dependence on v.

k_{vib}, limited data $v=1-14$
$k_{\text{vib}}\cong k_{\text{elect}}$ for rare gases.
Slight decrease with increasing v.
N_2, H_2, D_2 rates an order of magnitude lower than k_{elect}.
$\Delta v=2$ and 3 transitions reported.

5.2.3. Discussion

The kinetics of electronically excited CO are of particular interest owing to the richness of its energy states 50,000-65,000 cm^{-1} above the ground state. Rotational perturbations are extensive for all the low lying states and have been studied in detail particularly for the $a\,^3\Pi$ and $A\,^1\Pi$ configurations (Field et al., 1972a,b; Hall et al., 1973). For example, with the exception of $a\,^3\Pi(v=0-3,6)$, all its vibrational levels exhibit perturbations at low J values as a result of interactions with various of the adjacent electronic states. The same is true for all levels of $A\,^1\Pi$ ($v=0-18$). Mixing of levels in $d\,^3\Delta$ and $e\,^3\Sigma^-$ states also has been noted.

The mixed nature of these states permits optical pumping of "forbidden" transitions from $X\,^1\Sigma^+$. Monitoring of the subsequent fluorescence is a very sensitive probe to locate perturbed levels (Slanger & Black, 1970).

a. Carbon Monoxide, CO($a\,^3\Pi$)

A significant amount of data, listed in table 8, now accumulating concerning the electronic quenching of CO($a\,^3\Pi$). Although studied by a variety of techniques, CO($a\,^3\Pi$) concentrations are generally monitored in emission via the $a\,^3\Pi$–$X\,^1\Sigma^+$ Cameron bands. It has also been measured from the intensities of the NO β and γ bands that result from energy exchange with a trace of NO (Slanger & Black, 1971).

The most notable feature of the rate coefficients, illustrated in figures 9 and 10, is their generally large values which begin to approximate to gas kinetic collision frequencies. Quenching is inefficient only with C_2F_6, SF_6, He and Ar, which may be the only observed interactions that reflect a conventional low-probability curve crossing mechanism. The very fast rates are surprising owing to the large amount of energy (579.9 kJ mol^{-1}, 138.6 kcal mol^{-1}) associated with CO($a\,^3\Pi$).

A $T^{1/2}$ dependence has been noted for several of the species (Clark & Setser, 1975) and, with the exception of CO and N_2, values are independent of the vibrational state of $a\,^3\Pi$.

Data for CH_4, C_2H_6, C_2F_6, C_2H_4, C_2H_2, C_2N_2, N_2O, NH_3, SO_2, SF_6, CS_2, OCS, and D_2 have been obtained only by Setser's group. Values from their original work (Taylor & Setser, 1971b) appear too low by a factor of about 1.75, possibly as a result of insufficiently rapid mixing. Their later work using He instead of Ar carrier gas is preferred. The recommended values for C_2H_6, C_2N_2, N_2O, NH_3 and SO_2 measured only in their original study reflect this adjustment. Of all these species, only CS_2 shows a slight dependence on vibrational state, reported values being 3.3 × ($v=0$), 3.6 × ($v=1$), and 3.8 × 10^{-10}($v=2$). Although no product analyses have yet been undertaken, collision induced physical relaxation to vibrationally excited ground state CO presumably is the predominant mechanism for these species.

The importance of collisional relaxation of vibrational energy within the $a\,^3\Pi$ state has not been specifically studied to any extent. Quenching rate constants derived from measurements of the a–$X(1,v'')$ or $(0,v'')$ bands will depend on the relative magnitudes of electronic (a–X) and vibrational cascading. Taylor and Setser (1973) state that such vibrational relaxation should produce a curvature in plots of the a–X intensities as a function of quenchant pressure. Its absence in their data, with the possible exception of SF_6, suggests that vibrational relaxation may be insignificant in general for CO($a\,^3\Pi$). The only quantitative measure that has been reported is for He, $k_{vib} \leq 6 \times 10^{-17}$ cm^3 molecule^{-1}s^{-1} (Marcoux et al., 1977).

CO($a\,^3\Pi$) + CO, CO_2

The recommended value for CO_2, 1.7×10^{-11}, is based on a mean of the results of Lawrence (1971), Slanger and Black (1971), and Taylor and Setser (1973). Values of Wauchop & Broida (1972) appear consistently high. Other than for the polyfluorides this interaction is the least efficient of the polyatomics. It is even slower than with CO for which data are in reasonable accord and suggest a value of 1.1×10^{-10} for $v=0$. There does appear to be an unexplained dependence

Table 8. Rate constants for interactions of CO($a^3\Pi$)

M	k_M, 10^{-11} cm^{3}molecule^{-1}s^{-1}		
CO_2	1.7		1.2
CO	7.6	12($v=0$), 28($v=1$)	
NO	23	31($v=0$), 70($v=1$)	
O_2	14		
H_2	16		
He		$<10^{-3}$	
Ar		$<10^{-3}$	
Exp. Temp. K	300	300	300
Method	Pulsed microwave discharge CO-source pumps $d^3\Delta_{v=5} \to X^1\Sigma^+$ which populates $a^3\Pi$. Flow system, CO 0.16, NO 0.13, M≤2.4, Ar 800 Pa. $a^3\Pi$ monitored either via emission >215 nm, or by NO γ bands 256 nm.	Weak pulsed Tesla type discharge 5×10^3 cm^3 bulb, CO 0.03-0.3, Ar carrier 0.2-0.8 kPa, flowing system. $a^3\Pi$-$X^1\Sigma^+$ (0,0), 206.1 nm & (1,0) 198.9 nm resolved emission.	Pulsed 104.8 nm Ar photolysis of CO_2<4 Pa, He <2.7 kPa in cell. $a^3\Pi$-$X^1\Sigma^+$ emission.
Comments	CO(a)+NO=CO+NO($A^2\Sigma$). Population of CO($a^3\Pi$) 53%, 21%, 18% in v=0, 1, 2, respectively.	He & Ar carrier gas data same.	v=0,1 equally populated.
Reference	Slanger & Black, 1971	Young & Van Volkenburgh, 1971	Lawrence, 1971

Table 8. Rate constants for interactions of $CO(a^3\Pi)$ -- continued

M	k_M, 10^{-11} $cm^3 molecule^{-1} s^{-1}$		
CH_4	24		
C_2H_6	28		
C_2F_6	0.18		
C_2H_4	39		
C_2N_2	19		
N_2O	15		
NH_3	18		
SO_2	11		
OCS	13*		
CO_2	1.4	4.1	
CO	14		
NO	18	32	
N_2	1.0	7.3, 3.8(v=0)	
O_2	11		12(v=0), 14(v=1)
H_2	14		
D_2	10		
O			19(v=0), 21(v=1)
He		$<10^{-3}$	
Exp. Temp. K	300	300	300
Method	Hollow cathode discharge in Ar, CO_2 added to produce $a^3\Pi(v=0)$. Flow velocity 20 m s^{-1}, total pressure 230 or 430 Pa. a-X emission resolved.	Microwave discharge in 27-800 Pa He, CO_2 added. $CO(a^3\Pi) \approx 10^9$ cm^{-3} formed from $CO_2^+ + e$. a-X resolved emission monitored.	Weak pulsed Tesla type discharge, slow flow, 5×10^3 cm^3 bulb. CO 0.04, He, Ar 530-800 Pa. O from microwave discharge in O_2/He, Ar & measured by NO_2 titration. a-X(0,0) 206.1 nm, (1,0) 198.9 nm emission resolved.
Comments	v=0 Lower limit values, efficient mixing not obtained sufficiently rapidly, up to a factor of 2 low. *Taylor & Setser, 1973	v=0-4	
Reference	Taylor & Setser, 1971b	Wauchop & Broida, 1972	Felder et al., 1972

Table 8. Rate constants for interactions of $CO(a^3\Pi)$ -- continued

M	k_M, 10^{-11} $cm^3 molecule^{-1} s^{-1}$			
CH_4	34(v=0,1 or 2)		18	36
C_2F_6	0.1			
C_2H_4	70		27	67
C_2H_2	74		68*	180*
SF_6	<0.1			
CS_2	33(v=0), 36(v=1), 38(v=2)			
OCS	34			
CO_2	2.0			
CO	11(v=0), 20(v=1), 23(v=2)		7.5	13
NO	18			
N_2	0.9(v=0), 1.8(v=1), 2.0(v=2)	0.1(v=0)		
O_2	20		16	23
H_2	20		10	20
D_2			12	18
Exp. Temp. K	300	300	77	300
Method	DC hollow cathode discharge in He, CO_2 added, flow velocity 20 m s^{-1}, M<0.08 Pa total pressure 130-400 Pa. $[a^3\Pi] \approx 10^8-10^9$ cm^{-3}, a-X resolved emission	Microwave discharge <13 Pa N_2, 0.8 kPa Ar flows through $5x10^3$ cm^3 bulb. 0.4-0.8 Pa CO, ≤90 Pa N_2 added. $CO(a^3\Pi)$ excited by energy transfer, monitored by a-X emission	DC hollow cathode discharge in He, CO_2 added, flowing afterglow, total pressure 0.67 kPa. a-X 200-320 nm emission unresolved.	
Comments	Planar velocity profile assumed in flow tube. Values should be increased by factor between 1 & 1.6. Unless indicated, values for v=0, 1, 2 identical. No evidence for vib. relaxation within $a^3\Pi$ except for SF_6.	Based on k_{CO} $1.2x10^{-10}$; $k_{N_2} \propto k_{CO}$ value.	Mainly v=0. $T^{½}$ dependence. *Absolute value too large, ratio at the two temperatures alright. $k_{vib}(He) \lesssim 6x10^{-17}$ (Marcoux et al., 1977).	
Reference	Taylor & Setser, 1973	Young & Morrow, 1975	Clark & Setser, 1975	

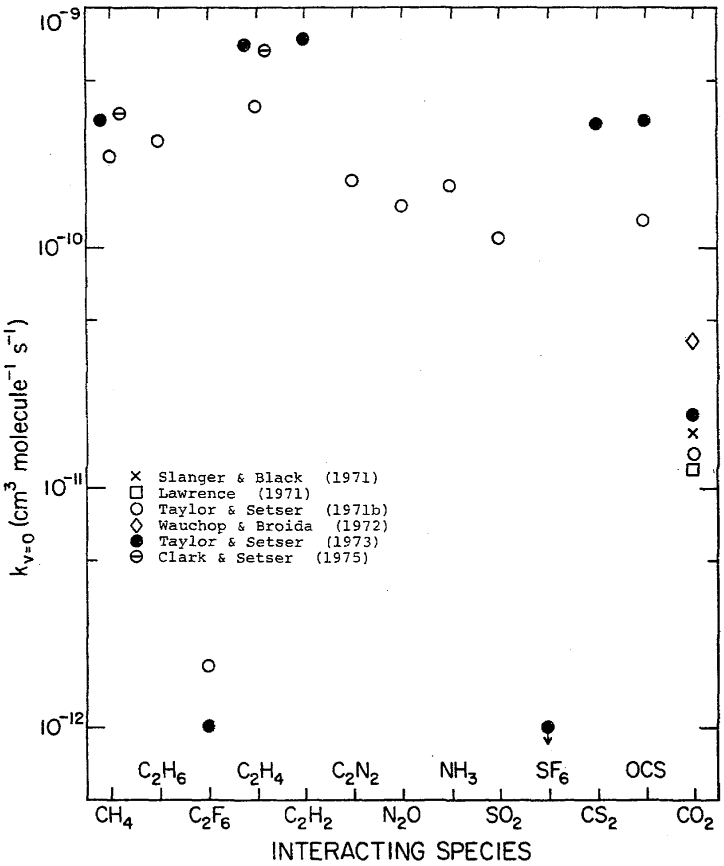

FIGURE 9. Rate constants for the interactions of $CO(a\,^3\Pi)_{v=0}$ with various polyatomic species. 300 K.

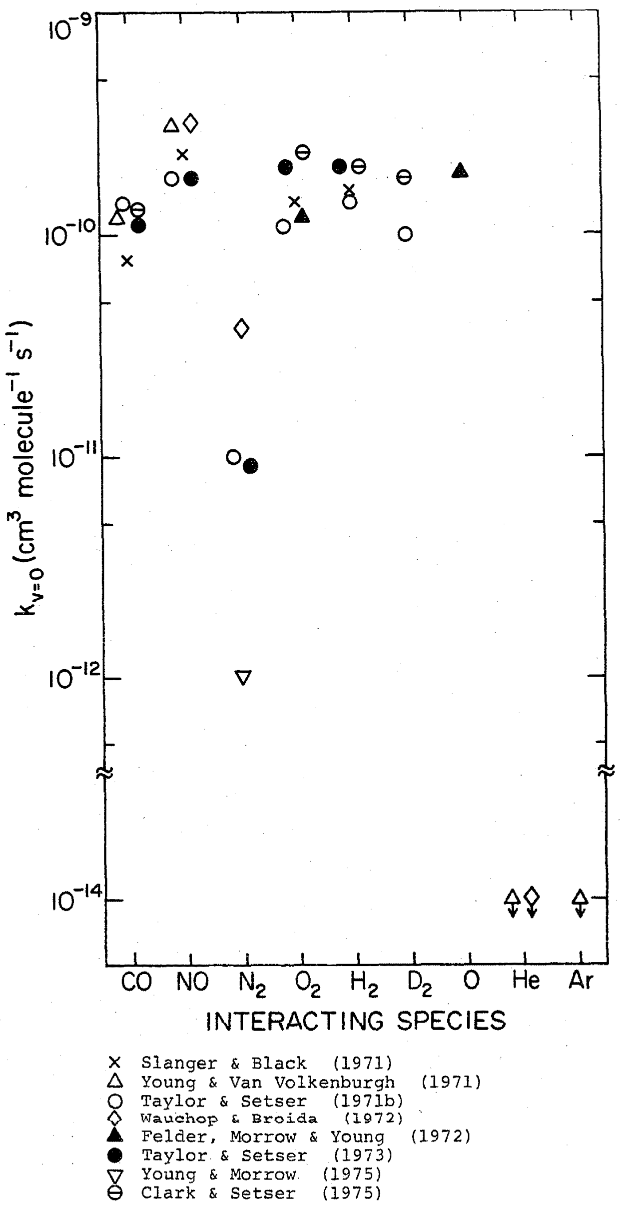

FIGURE 10. Rate constants for the interactions of $CO(a\,^3\Pi)_{v=0}$ with various atomic and diatomic species, 300 K.

on vibrational state in this case, values for $v = 1(2.0 \times 10^{-10})$ and $2(2.3 \times 10^{-10})$ being significantly larger.

The allowed reaction

$$CO(a\,^3\Pi) + CO = CO_2 + C \quad \Delta H^\circ_{298\,K} = -37.4 \text{ kJ mol}^{-1} \quad (-8.93 \text{ kcal mol}^{-1})$$

has been suggested as a possible mechanism. However, Dunn et al. (1973) concluded that only 1.6% of $CO(a\,^3\Pi)$ decays via this channel. An alternative (Willis & Devillers, 1968) is too energy deficient for the $(a\,^3\Pi)$ state

$$CO(a\,^3\Pi) + CO = C_2O + O \quad \Delta H^\circ_{298\,K} = +177.0 \text{ kJ mol}^{-1} \quad (+42.3 \text{ kcal mol}^{-1})$$

Slanger et al. (1975) have measured the efficiency of the electronic-vibration energy transfer as 89%,

$$CO(a\,^3\Pi) + CO = CO^\dagger + CO^\dagger$$

confirming the observation of Donovan and Husain (1967) that, although spin forbidden, it is very efficient and the predominant channel. Also, the electronic energy appears to be vibrationally shared between the two product molecules, being no more than 18 vibrational quanta in either. An equal distribution would produce a mean level of about $v = 12$. There is sufficient energy to excite up to $v = 26$ if it had channeled into one CO alone.

$CO(a\,^3\Pi) + NO$

The recommended value of 2.0×10^{-10} is based on the measurements of Taylor and Setser (1973) and Slanger and Black (1971). Whereas Young and Van Volkenburgh (1971) reported a strong vibrational effect this was not the case in the studies of Taylor and Setser (1973). Energy transfer reactions to produce NO γ and β radiation are evident.

$$CO(a\,^3\Pi) + NO = CO + NO(A\,^2\Sigma^+) \quad \Delta H^\circ_{v=(0-0)} = -51.1 \text{ kJ mol}^{-1} \quad (-12.2 \text{ kcal mol}^{-1})$$

$$= CO + NO(B\,^2\Pi) \qquad = -35.6 \text{ kJ mol}^{-1} \quad (-8.50 \text{ kcal mol}^{-1})$$

However, these are not the predominant pathways, accounting for only 10 to 33% of the total quenching (Slanger & Black, 1971; Wauchop & Broida, 1972; Taylor & Setser, 1973). Additional exothermic channels to $NO(a\,^4\Pi$, $b\,^4\Sigma^-$ or even the ground $X\,^2\Pi$ state) may also occur. Preliminary experiments in a low pressure crossed-beam experiment have observed radiation from only $NO(A\,^2\Sigma^+)$, indicating that the $B\,^2\Pi$ may result from secondary processes (Setser, 1978). The measured ratio of the branching to $NO(A\,^2\Sigma^+)$ or $(B\,^2\Pi)$ varies from 1.5 (Taylor & Setser, 1973) and 2.5 (Slanger & Black, 1971) to 4.6 (Wauchop & Broida, 1972). There is no general support for Young and Van Volkenburgh's contention that there is a conservation of vibrational quanta in the transfer. It does appear that $NO(A\,^2\Sigma^+)$ $v = 0$ is populated predominantly, with about 12–20% in $v = 1$ (Wauchop & Broida, 1972; Taylor & Setser, 1973). The distribution does not appear to be sensitive to that of $CO(a\,^3\Pi)$.

$CO(a\,^3\Pi) + N_2$

Of all the data for $CO(a\,^3\Pi)$, the scatter for N_2 is the greatest, a factor of 38 spread. Because Wauchop & Broida's other values are consistently high and those of Taylor and Setser (1973) reliable, the latter's value of 0.9×10^{-11} is recommended for $v = 0$. There is evidence for a factor of two increase for the rate constants with $v = 1$ and 2 (Wauchop & Broida, 1972; Taylor and Setser, 1973), which values are about 1.8 × and 2.0×10^{-11}, respectively. Energy exchange to $N_2(A\,^3\Sigma^+)$

$$\mathrm{CO}(a\,^3\Pi) + \mathrm{N_2} = \mathrm{CO} + \mathrm{N_2}(A\,^3\Sigma^+) \quad \Delta H^\circ_{v=(0-0)} = +15.3\ \mathrm{kJ\ mol^{-1}}\ (+3.66\ \mathrm{kcal\ mol^{-1}})$$

is apparent, however, the slight endothermicity for the $v=(0\rightarrow 0)$ transition should strongly affect the rate constant for $v=0$ and 1 by much more than a factor of 2 at room temperature. In fact, this channel has been reported as only 25% efficient (Taylor & Setser, 1973) and presumably decay is mainly to either ground state $\mathrm{CO}^{\dagger}$ or $\mathrm{N_2}^{\dagger}$.

$\mathrm{CO}(a\,^3\Pi) + \mathrm{O_2}$

The small data spread suggests a mean value of 1.7×10^{-10} at 300 K with no pronounced dependence on vibrational energy. No suggestions for the quenching mechanism have been presented but reaction is possible.

$$\mathrm{CO}(a\,^3\Pi) + \mathrm{O_2} = \mathrm{CO_2} + \mathrm{O} \quad \Delta H^\circ_{298\,\mathrm{K}} = -613.7\ \mathrm{kJ\ mol^{-1}}\ (-146.7\ \mathrm{kcal\ mol^{-1}})$$

As indicated in the correlation diagram, figure 11, allowed surfaces are available to either $\mathrm{O}(^3\mathrm{P})$ or $\mathrm{O}(^1\mathrm{D})$ products.

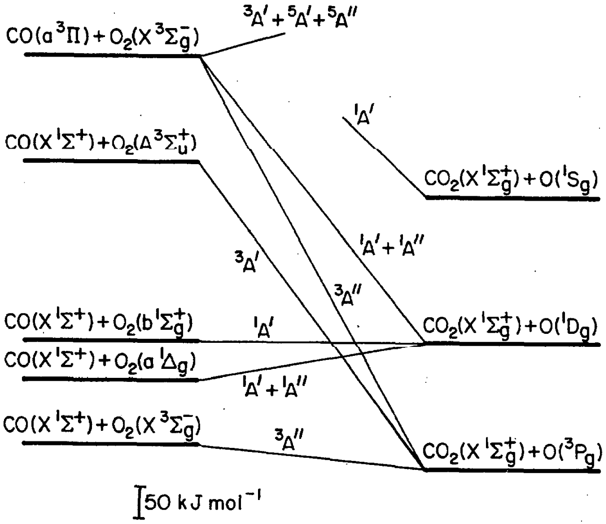

FIGURE 11. Correlation diagram connecting the states of $\mathrm{CO} + \mathrm{O_2}$ and $\mathrm{CO_2} + \mathrm{O}$.

$\mathrm{CO}(a\,^3\Pi) + \mathrm{O}$

Only a single measure of k_0 is available, of unknown reliability (Felder et al., 1972). However, their value for $k_{\mathrm{O_2}}$, also reported, lends some support for its acceptance. It indicates a surprisingly fast relaxation with only a slight dependence, if any, on vibrational state. This must reflect the catalyzed conversion of $\mathrm{CO}(a\,^3\Pi)$ to CO ground electronic state vibrational energy, sufficient to populate up to $v=26$ unless some also channels into electronic or translational excitation of atomic oxygen.

$\mathrm{CO}(a\,^3\Pi) + \mathrm{H_2}, \mathrm{D_2}$

The lack of any noticeable isotope effect implies that chemical reaction is unlikely and that relaxation is to the CO ground electronic state. A suggested value of 1.8×10^{-10} is indicated for both $k_{\mathrm{H_2}}$ and $k_{\mathrm{D_2}}$.

$\mathrm{CO}(a\,^3\Pi) + \mathrm{Hg}$

The very interesting case of electronic energy transfer from CO $(a\,^3\Pi)$ to Hg results in 253.7 nm radiation from the $\mathrm{Hg}(6^3\mathrm{P}_1)$ state (Dugan, 1969; Taylor & Setser, 1971a). Single collision beam conditions indicate that the $6^3\mathrm{P}_1$ state is produced directly (Van Itallie & Martin, 1972; Lee and Martin, 1976).

$$\mathrm{CO}(a\,^3\Pi) + \mathrm{Hg} = \mathrm{CO} + \mathrm{Hg}(6^3\mathrm{P}_1) \quad \Delta H^\circ_{298\,\mathrm{K}} = -108.4\ \mathrm{kJ\ mol^{-1}}\ (-25.9\ \mathrm{kcal\ mol^{-1}})$$

Absolute rate coefficients have not been measured.

There is also some evidence for the reverse "spin forbidden" reaction with $\mathrm{Hg}(6^1\mathrm{P}_1)$, which lies at about 540 $\mathrm{cm^{-1}}$ above $\mathrm{CO}(a\,^3\Pi)_{v=3}$ (Luiti et al., 1966; Gover & Bryant, 1966; Granzow et al., 1968).

$\mathrm{CO}(a\,^3\Pi) + \mathrm{He, Ar}$

Data are available only for these two of the inert gases and indicate their inefficient quenching, $k_{\mathrm{He,Ar}} < 10^{-14}$.

b. Carbon Monoxide, $\mathrm{CO}(a'\,^3\Sigma^+)$

Data are available only for collisional quenching by CO and are listed in table 9. The earlier study of Hartfuss and Schmillen (1968) is questionable, their emission measurements probably referring instead to bands of the $\mathrm{CO^+}(A\,^2\Pi\text{-}X\,^2\Sigma^+)$ comet tail system which lie in the same spectral range. A single value, reported recently by Van Sprang et al. (1977), may be more reliable and indicates an efficient interaction that corresponds to a unit gas kinetic collision frequency. As with $\mathrm{CO}(a\,^3\Pi)$, an efficient $E\rightarrow V$ mechanism may be responsible.

c. Carbon Monoxide, $\mathrm{CO}(d\,^3\Delta, e\,^3\Sigma^-)$

In recent years, Slanger, Black and co-workers have characterized the kinetic nature of the electronically excited states of CO undoubtedly better than any other molecule. This has illustrated the multitude of mechanisms that become possible in a system of mixed electronic states. Such perturbations, particularly between the $d\,^3\Delta$ and $e\,^3\Sigma^-$ triplets and the neighboring $(A\,^1\Pi)$ state, results in a breakdown of the forbidden nature of some of their transitions making it possible, for example, to optically pump the $d\,^3\Delta_{v=5}$ and $e\,^3\Sigma^-{}_{v=4}$ states directly from $X\,^1\Sigma^+$. Because radiative lifetimes differ significantly for perturbed and unperturbed states, great care is required in unravelling the relative importance of the radiative, vibrational or rotational relaxation, and electronic interstate relaxation processes.

$d\,^3\Delta$

Numerous channels are available for the decay of the $\mathrm{CO}(d\,^3\Delta)$ state. Firstly spin-multiplet relaxation within the

$^3\Delta_{3,2,1}$ sublevels is rapid. For example, with Ar, at least one half of the collisions induce such transitions. This can be important since only the $d\,^3\Delta_1(v=5)$ substate is perturbed by $A\,^1\Pi(v=1)$ resulting in its reduced radiative lifetime and differing probabilities of $d\,^3\Delta$–$a\,^3\Pi$ emission for each subband (Slanger & Black, 1973a).

Quenching of the unperturbed $d\,^3\Delta(v=7)$ level (based on its total rate of disappearance) is very efficient with CO and NO, requires about 10 to 40 collisions for Ar, N$_2$ and H$_2$ and is least effective with He, as indicated in table 10. Furthermore, Slanger et al. (1975) have shown that a large fraction of this electronic energy is relaxed to ground state vibrational energy with CO (62% efficiency) and N$_2$ (96% efficiency). It has been reported that whereas $d\,^3\Delta$ $v=7$ and 4 levels are quenched by CO with a rate of about 1.2×10^{-10} that for $v=3$ is about twice as fast and close to gas kinetic collision fre-

Table 9. Rate constants for interactions of CO($a'\,^3\Sigma^+$)

M	k_M, cm^3 molecule^{-1} s^{-1}	
CO	1.31×10^{-11} (v=5) 1.18 (v=6) 1.89 (v=7) 1.48 (v=8)	2.82×10^{-10} (v=4-9)
Exp. Temp. K	300	300
Method	Pulsed RF discharge in 1.3-130 Pa CO. Decay of a'-a emission, 699-792 nm.	Pulsed e-beam (10 eV) excitation, 0.07-1.3 Pa CO. a'-a emission, 587-859 nm, 0.5-2.5 nm monochromator bandpass.
Comments	Data probably refers to CO$^+$($A^2\Pi$) emission (Van Sprang et al., 1977)	
Reference	Hartfuss & Schmillen, 1968	Van Sprang et al., 1977

Table 10. Rate constants for interactions of CO($d^3\Delta$), cm^3 molecule^{-1} s^{-1}

M	Spin-Multiplet Relaxation	Quenching Interactions			Cross Relaxation
	$k_{^3\Delta_1 \to ^3\Delta_{2,3}}$		$k_{\text{elect+vib}}$		$k_{d^3\Delta_{v=7} \to e^3\Sigma^-_{v=4}}$
He	$\geq 4.2 \times 10^{-11}$			1.5×10^{-12}	1.6×10^{-13}
Ar	$\geq 1.4 \times 10^{-10}$	3.5×10^{-12}		6.6×10^{-12}	2.6×10^{-12}
N$_2$		1.3×10^{-11}		3.6×10^{-11}	2.9×10^{-12}
H$_2$				3.8×10^{-11}	6.2×10^{-12}
CO			2.76×10^{-10}	1.2×10^{-10}	3×10^{-12}
NO				$\approx 5 \times 10^{-10}$	
Exp. Temp. K	300	300	300	300	
Method	Microwave discharge 1% CO$_2$/Ar pumps $d^3\Delta_1$(v=5) in 10^3 cm^3 bulb, residence time 1 s. 0.04-13 Pa CO/$\leq$2.1 kPa He, Ar. d→a(5,0) emission via narrow filter, $^3\Delta_1$ subband 562.5 nm, $^3\Delta_{2,3}$ 569 nm.	Flow system, microwave discharge N$_2$/Ar. Total pressure 0.2-1 kPa, 5% CO. d→a (10,1) 476.7 nm band spectrally resolved.	Pulsed e-beam, 13 eV, excitation, 0.14-1.3 Pa CO, d-a emission, 693 nm. 0.5-2.5 nm monochromator bandpass.	Cooled 147 nm Xe lamp pumps unperturbed $d^3\Delta_{v=7}$, 1.5×10^3 cm^3 bulb, residence time 1.5 s. 2-13 Pa CO/Ar$\leq$2.8 kPa. d→a(7,0) & e→a(4,0) emissions, narrow filters centered at 505.3 and 514.7 nm, respectively.	
Comments	$d^3\Delta$(v=5)	$d^3\Delta$(v=10), total rate of disappearance. Based on τ 4.5 μs, values are ∝ τ^{-1}.	$d^3\Delta$(v=2), total rate of disappearance.	$d^3\Delta$(v=7), total rate of disappearance. Relaxes to ground state CO with CO (62% efficiency) and N$_2$ (96% efficiency) (Slanger et al., 1975)	Collision induced cross-relaxation
Reference	Slanger & Black, 1973a	Golde & Thrush, 1972a	Van Sprang et al., 1977	Slanger, 1968; Slanger & Black, 1978	

quency (Slanger & Black, 1973c). Van Sprang et al. (1977) also indicate such a higher rate for $v=2$.

Slightly less efficient but also of importance is collision induced interstate relaxation for example from $d\,^3\Delta_{v=7}$ to $e\,^3\Sigma^-_{v=4}$which, with the exception of He, is effective in about one collision in ninety and appears not to be facilitated by the extra degrees of freedom of a diatomic (table 10).

Separate data for vibrational relaxation within the $d\,^3\Delta$ state are not available. However, it has been found that $d\,^3\Delta(v=5)$ is a less important source of $d\,^3\Delta(v=4)$ than $e\,^3\Sigma^-(v=4)$ (Slanger & Black, 1973c).

$e\,^3\Sigma^-$

Less data are available for $e\,^3\Sigma^-$. This might change as a result of the recently noted alternate means for optically pumping the $v=4$ level selectively, using the 148.3 nm line of atomic S (Slanger & Black, 1975). Values that reflect a measure of vibrational and electronic quenching appear similar to those for $d(^3\Delta)$. Cross relaxation processes are particularly important and it would appear that a rapid equilibration occurs between the perturbed states of $e\,^3\Sigma^-{}_{v=4}$ and $A\,^1\Pi_{v=2}$, and $e\,^3\Sigma^-{}_{v=1}$ and $A\,^1\Pi_{v=0}$. The CO($e\,^3\Sigma^-{}_{v=4}$) level appears to be relaxed by ground state CO to $A\,^1\Pi_{v=2}$ or $d\,^3\Delta_{v=3,4}$ with a cross section greater than the normal gas kinetic value and will occur faster than rotational relaxation processes. Also, it has been shown that the $d\,^3\Delta_{v=3,4}$ levels are populated largely through this relaxation of $e\,^3\Sigma^-{}_{v=4}$ rather than by relaxation of $d\,^3\Delta_{v=5}$.

d. Carbon Monoxide, CO($A\,^1\Pi$)

Several studies have reported data, up to $v'=14$, for vibrational and electronic relaxation and are listed in tables 12 and 13. Generally, values are large and only He, Ne and Ar have somewhat reduced efficiencies. Their variations as a function of CO($A\,^1\Pi$) vibrational level are more clearly illustrated in figures 12 and 13. Finer detail would undoubtedly show some dependence also on rotational state (Provorov et al., 1977). For He, Ne and Ar there is substantial disagreement for $v'=0$ between the recent measurements of Lavollee and Tramer (1977) with those of Fink and Comes (1974). However, the former's values do appear unreasonably large, for example, with He which usually quenches electronic states inefficiently.

The rate constants for vibrational and electronic relaxation with the inert gases are of the same magnitude, as illustrated in figure 12. Comes and Fink (1972; Fink & Comes, 1974) note a significantly increased value for k_{elect} with $v'=1$ as compared to $v'=0$ for He, Ne and Ar but not so for Kr. Values decrease slightly, to various extents, with increasing vibrational number with no pronounced discontinuities, indicating equally efficient mechanisms for unperturbed states. Data for Xe, only available at $v'=9$ and 14, indicate a unit collision removal efficiency.

More limited data are available with other species. Measurements of k_{elect} with CO indicate a unit collision efficiency. The larger values for $v'=9$ and 14 ($k_{\text{elect+vib}}$) may reflect an equally efficient vibrational relaxation. Using C^{16}O

Table 11. Rate constants for interactions of CO$(e\,^3\Sigma^-)_{v=1,4}$, cm^3 molecule^{-1} s^{-1}.

	Quenching Interactions		Cross Relaxation		Cross Relaxation
M	$k_{\text{elect+vib}}$		$k_{e^3\Sigma^-_{v=1}\to A^1\Pi_{v=0}}$	$k_{e^3\Sigma^-_{v=4}\to A^1\Pi_{v=2}}$	$k_{e^3\Sigma^-_{v=4}\to d^3\Delta_{v=3,4}}$
He	1.4×10^{-12}	6×10^{-13}	4.5×10^{-11}		
Ne		6×10^{-13}	4.5×10^{-11}		
Ar	6.7×10^{-12}	6×10^{-12}	6.2×10^{-11}	$\approx 1 \times 10^{-10}$	
Kr		7.5×10^{-12}	$1.0_5 \times 10^{-10}$		
N_2	2.1×10^{-11}				
H_2	7.3×10^{-11}				
CO	1.2×10^{-10}			4×10^{-9}	$>3 \times 10^{-12}$
Exp. Temp. K	300		300	300	300
Method	Microwave discharge 1% CO$_2$/Ar, pumps $e^3\Sigma^-(v=4)$. 1.5x10^3 cm^3 bulb, residence time 1.5 s. 2-13 Pa CO. e→a(4,0) emission via filter centered 514.7 nm.	Pulsed narrow band (0.1 nm) excitation of $A^1\Pi(v=0)$ perturbed rotational levels, 154.6 nm synchroton light source. 2.7-26.7 Pa CO in 0 27 kPa inert gas. Unresolved $A^1\Pi$ fluorescence monitored with solar blind PM tube. Decay curves fit to kinetic model.		140.3 nm S line from 1% H$_2$S/Ar pumps $e^3\Sigma^-(v=4, J=27)$. 13 Pa CO/270 Pa Ar. e→a emission monitored.	Microwave discharge 1% CO$_2$/Ar source pumps $e^3\Sigma^-(v=4)$. 10^3 cm^3 bulb, residence time 1s. 13 Pa. CO. d→a(3,0; 4,0), e→a (1,1) bands isolated with filters.
Comments	Assumes τ 3.3 μs for CO $e^3\Sigma^-(v=4)$.	$e^3\Sigma^-(v=1)\leftrightarrow A^1\Pi(v=0)$, reversible process. Data for He, Ne and Ar are in doubt because their values for $A^1\Pi$ quenching are too large.			
Reference	Slanger & Black, 1973b	Lavollee & Tramer, 1977		Slanger & Black, 1975	Slanger & Black, 1973c

Table 12. Rate constants for interactions of CO($A^1\Pi$)

M	k_{elect}	$k_{elect + vib}$	k_{elect}	$k_{elect}(k_{elect + vib})$								
	$v'=0-2$	$v'=0-2$	$v'=0$	$v'=0$	1	2	3	4	5	6	7	
CO	$2x10^{-9}$											
N_2		$2.5x10^{-10}$	$2.9x10^{-10}$									
H_2			$3.4x10^{-10}$									
D_2			$3.7x10^{-10}$									
He			$4.6x10^{-13}$	1.0	8.7(15)	1.8(6.6)	–(4.5)	1.8(5.6)	3.7(5.9)	2.1(4.3)	2.6(5.6)	$x10^{-12}$
Ne			$9.7x10^{-13}$	0.9	4.0(8.9)	2.7(5.6)	2.4(4.8)	–(2.5)	2.3(4.3)	0.74(2.0)	0.61(3.7)	$x10^{-12}$
Ar			$2x10^{-11}$	1.8	8.2(16)	5.9(13)	1.2(13)	2.2(11)	4.0(7.7)	2.5(5.3)	10(12)	$x10^{-11}$
Kr			$1.5x10^{-10}$	1.6	1.5(3.0)	3.1(4.9)	2.2(4.8)	0.85(2.8)	2.9(3.7)	3.4(4.2)	–(–)	$x10^{-10}$
Exp. Temp. K	300	300	295	298								
Method	Xe lamp, CO impurity pumps $v'=0-2$. CO 7-670 Pa, Ar≤ 1.3 kPa. Spectrally resolved fluorescence.	Xe lamp, CO impurity pumps $v'=0-2$. Spectrally resolved fluorescence.	Microwave discharge CO_2/He source of A-X(0,0) band. 3 nm bandwidth excites fluorescence, (0,1) monitored. CO<13 Pa, M≤93 kPa	Microwave discharge CO_2/He source of A-X emission. Specific (v',0) band isolated, 3 nm bandwidth, excites fluorescence which was spectrally resolved. CO<7 Pa, M≤20 kPa.								
Comments	CO data approximate; does indicate an efficient process.	$v'=0:1:2:3$ populations 1:4:2.6: 0.15	Quenching for $v'=1 \simeq v'=0$. $k \propto \tau^{-1}$.	k_{elect} calculated from k(total relaxation)-k_{vib}. Data calculated assuming lifetimes in table 5, $k \propto \tau^{-1}$.								
Reference	Becker & Welge, 1965	Slanger & Black 1969	Comes & Fink, 1972	Fink & Comes, 1974								

Table 12. Rate constants for interactions of CO($A^1\Pi$) -- continued

M	k_{elect}	$k_{elect + vib}$		$k_{elect + vib}$	$k(A^1\Pi \rightarrow triplets)$	k_{elect}
	v'=0	v'=9	$C^{18}O$,v'=9	v'=14	v'=0	v'=0
SF_6		$1.6x10^{-10}$	$1.6x10^{-10}$			
CO	$5.2x10^{-10}$	$9.6x10^{-10}$	$7.5x10^{-10}$	$1.37x10^{-9}$		$3x10^{-10}$(J=24), $4.5x10^{-10}$(J=14)
$C^{18}O$		$9.6x10^{-10}$	$14\ \ x10^{-10}$			
N_2	$2.8x10^{-10}$					
O_2				$9.1x10^{-10}$		
H_2		$2.2x10^{-10}$	$2.9x10^{-10}$	$2.6x10^{-10}$		
D_2		$1.8x10^{-10}$	$1.8x10^{-10}$	$1.4x10^{-10}$		
He		$7.8x10^{-12}$	$4.0x10^{-12}$	$<2.1x10^{-13}$	$7.7x10^{-11}$	
Ne		$2.2x10^{-12}$	$8.7x10^{-13}$	$<5.7x10^{-13}$	$7.7x10^{-11}$	
Ar		$2.6x10^{-11}$	$2.2x10^{-11}$	$1.2x10^{-11}$	$1.7x10^{-10}$	
Kr		$1.4x10^{-10}$	$2.5x10^{-10}$	$1.2x10^{-10}$	$2.45x10^{-10}$	
Xe		$5.3x10^{-10}$	$6.0x10^{-10}$	$8.9x10^{-10}$		
Exp. Temp. K	297	298		298	300	300
Method	Microwave discharge 1% CO_2/Ar source. A-X fluorescence monitored with various CO/N_2 mixtures at relatively high pressures.	130.6 nm O line (microwave discharge in CO free O_2/He) excites $C^{16}O$ to v'=9, J'=22 and $C^{18}O$ to J'=6. Measure extent of absorption and resolve (9,19) fluorescence, 245-248 nm (CO), 242-245 nm ($C^{18}O$). CO≃100 Pa, M≤29 kPa.		121.6 nm H Lyman α, microwave discharge in purified H_2/He, excites (14,0). Fluorescence of (14,22) band resolved. CO 250 Pa, M≤ 100 kPa.	Pulsed narrow band (0.1 nm) excitation of $A^1\Pi$ (v=0) perturbed rotational levels, 154.6 nm synchrotron light source. 2.7-26.7 Pa CO in 0-27 kPa inert gas. Unresolved $A^1\Pi$ fluorescence, solar blind PM tube. Decay curves fit to kinetic model.	Tunable pulsed VUV laser excitation ($\leq 7x10^{-4}$ nm) of selected rotational levels in v'=0. Unresolved fluorescence 168-180 nm. CO 53-530 Pa.
Comments		Recalculated assuming $\tau(v'=9)=10$ ns. Values are $\propto\tau^{-1}$. Probably k_{vib} with SF_6.		Based on $\tau(v'=14)$ 11.8 ns.	Fast reversible process $A^1\Pi(v=0) \leftrightarrow e^3\Sigma^-(v=1)$. Values for He, Ne & Ar seem unreasonably large.	J(24) mixing with $d^3\Delta$(v=4). J(14) mixing with $e^3\Sigma^-$(v=1).
Reference	Slanger & Black, 1974	Melton & Yiin, 1975		Melton & Yao, 1976	Lavollee & Tramer, 1977	Provorov et al., 1977

Table 13. Vibrational relaxation rate constants for CO($A^1\Pi$).

			Δv=1									Δv=2		Δv=3
M	v'=1,2	v'=1	v'=1	2	3	4	5	6	7	8	v'=2	3	4	v'=3
CO	2×10^{-9}													
N_2		4.0×10^{-11}												
H_2		3.4×10^{-11}												
D_2		$2\ \times10^{-11}$												
He		4.9×10^{-12}	6.1	4.5	3.1	2.2	2.2	2.3	2.9	1.4×10^{-12}	0.35	1.5	1.5×10^{-12}	1×10^{-13}
Ne		4.3×10^{-12}	4.9	2.7	1.9	1.9	2.0	1.3	3.1	$0.7_7\times10^{-12}$	1.7	4.5	4.6×10^{-13}	3×10^{-14}
Ar	2×10^{-11}	6.9×10^{-11}	7.8	5.3	5.9	6.4	3.7	2.7	2.3	1.4×10^{-11}	1.9	3.9	2.0×10^{-11}	2×10^{-11}
Kr		1.2×10^{-10}	1.5	1.3	1.3	1.3	0.7_7	0.7_4	0.6_2	$-\ \times10^{-10}$	5.2	8.9	6.6×10^{-11}	3.7×10^{-11}
Exp. Temp. K	300	295	298											
Method	Xe lamp, CO impurity pumps v'= 0-2. CO 7-670 Pa, Ar ≤1.3 kPa. Spectrally resolved fluorescence.	Microwave discharge CO_2/He source of A-X (1,0) band. 3 nm bandwidth excites fluorescence. Intensities of (1,1) and (0,1) monitored. CO<13 Pa. M≤93 kPa.	Microwave discharge CO_2/He source of A-X emission. Specific (v',0) band isolated, 3 nm bandwidth, excites fluorescence which was spectrally resolved. CO<7 Pa, M≤20 kPa.											
Comments	CO data may be questionable.		Data recalculated assuming lifetimes in table 5, $k^{v}_{\Delta v=n} \propto \tau^{-1}_{v-n}$											
Reference	Becker & Welge, 1965	Comes & Fink, 1972	Fink & Comes, 1974											

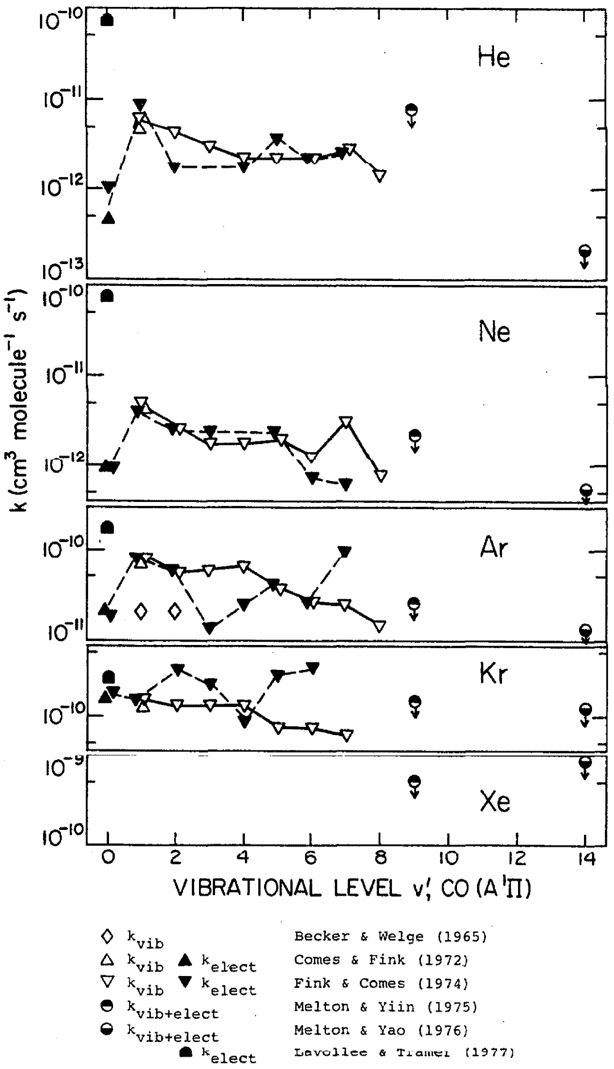

FIGURE 12. Rate constants for electronic quenching and vibrational relaxation of CO($A\,^1\Pi$), at 300 K, with the inert gases, as a function of vibrational state.

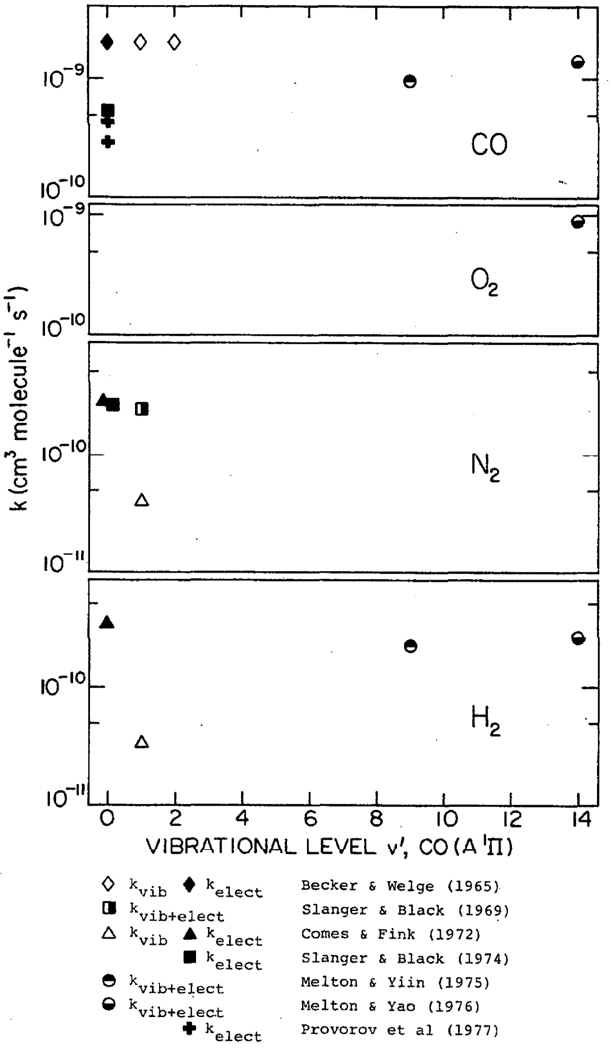

FIGURE 13. Rate constants for electronic quenching and vibrational relaxation of CO($A\,^1\Pi$), at 300 K, as a function of vibrational state.

and $C^{18}O$, Melton and Yiin (1975) noted slight differences with some quenchants. The largest values measured, $k_{\mathrm{elect+vib}} = 1.4 \times 10^{-9}$ are for the CO/CO($A\,^1\Pi$) and $C^{18}O/C^{18}O(A\,^1\Pi)$ combinations. Although chemical reaction is possible

$$\mathrm{CO}(A\,^1\Pi) + \mathrm{CO} = \mathrm{C_2O} + \mathrm{O} \quad \Delta H^\circ_{298\ \mathrm{K}} = -17.7\ \mathrm{kJ\ mol^{-1}}\ (-4.2\ \mathrm{kcal\ mol^{-1}})$$

quantum yield measurements indicate only small amounts, 0.5–4%, of C_3O_2 and CO_2 products with Kr and Xe sources (Rommel, 1967).

For N_2, H_2 and D_2, whereas electronic quenching occurs at unit collision frequency, the vibrational relaxation of $v'=1$ is about an order of magnitude slower. The report by Golde and Thrush (1972b) that quenching with N_2 occurs at considerably less than the collision rate does not appear to be the case. Replacement of D_2 for H_2 only modifies the quenching slightly. Generally, SF_6 is a very inefficient quencher of electronic energy. The value of 1.6×10^{-10} for CO$(A\,^1\Pi)_{v=9}$ probably refers to k_{vib}.

Data are available with O_2 only at $v'=14$ but indicate efficient removal. As with CO ($a\,^3\Pi$) there is the possibility of chemical reaction

$$\mathrm{CO}(A\,^1\Pi) + \mathrm{O_2} = \mathrm{CO_2} + \mathrm{O} \quad \Delta H^\circ_{298\ \mathrm{K}} = -808.5\ \mathrm{kJ\ mol^{-1}}\ (-193.2\ \mathrm{kcal\ mol^{-1}}).$$

The available energy is considerable and highly excited products must result.

Fink and Comes (1974) have noted that vibrational relaxation via $\Delta v=2$ transitions also can occur to a significant degree. As expected, the probability for $\Delta v=3$ relaxation is much reduced but surprisingly still significant, for example, with Ar or Kr.

Electronic quenching appears to occur via collision induced crossing to the adjacent $d\,^3\Delta$, $e\,^3\Sigma^-$ and probably $a'\,^3\Sigma^+$ states. A lack of specific perturbations does not appear to reduce the efficiency. However, Slanger and Black (1973c) have noted that in the presence of Ar a large part of the $d\,^3\Delta_{v=4}$ and $e\,^3\Sigma^-_{v=4}$ population originates from cross over from $A\,^1\Pi(v=0)$ and $(v=2)$ respectively. The energy transfer, in this case, populates only the closest and thus most perturbed levels. Such transitions that have been noted connect $A\,^1\Pi_{v=0} - d\,^3\Delta_{v=4} - e\,^3\Sigma^-{}_{v=1}$, $A\,^1\Pi_{v=1} - d\,^3\Delta_{v=5}$ and $A\,^1\Pi_{v=2} - d\,^3\Delta_{v=7} - e\,^3\Sigma^-{}_{v=4}$ levels.

There is no explanation for the efficiency of vibrational relaxation within the $A\,^1\Pi$ state.

5.2.4. References

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5.3. Carbon Monosulfide, CS ($a\,^3\Pi$, $A\,^1\Pi$)

The spectroscopic features of CS are not yet well characterized but the similarity to CO is quite evident with the exception that corresponding states lie at much lower energies (figure 14). Only $a\,^3\Pi$ is metastable since the other triplets each have an allowed radiative transition to $a\,^3\Pi$, and $A\,^1\Pi$ radiates to the ground state. As with CO, interactive mixing of these states appears to be important (Robbe & Schamps, 1976; Cossart et al., 1977).

Collision-free radiative lifetime data are available only for the $A\,^1\Pi$ and $a\,^3\Pi$ states and are listed in table 14. Low lying vibrational levels of $A\,^1\Pi$ have a value of about 200 ns. Due to the mixing with neighboring triplet states, weak perturbations are apparent for low lying vibrational levels of $A\,^1\Pi$ but radiative lifetimes are not expected to be a strong function of v' or J'.

There has been a considerable uncertainty concerning the magnitude of the lifetime of CS($a\,^3\Pi$). Piper et al. (1972) estimated experimentally a value of ≅0.3 ms and considered this accurate to within a factor of four. However, by comparing the emission intensities of CS($a\,^3\Pi$) from CS_2 and S(^1S) from OCS in their 145 nm photolyses, and using the known quantum yields, Black et al. (1977) suggest a lifetime of 16 ms. Although still somewhat uncertain this has to be regarded as the most reliable estimate at present. As with CO($a\,^3\Pi$) the value represents a weighted average summed over the three closely spaced sublevels. Its value is supported by an unpublished estimate by Bergeman of 7.5 ms for the $^3\Pi_1$ state (Black et al., 1977). Piper et al. (1972) did note that a value as large as 40 ms would be incompatible with their observations.

Very little quantitative kinetic data have been reported for electronically excited CS and relates solely to the $a\,^3\Pi$ state.

5.3.1. Suggested Rate Constant Values

CS($A\,^1\Pi$)

No quantitative data are available.

CS($a\,^3\Pi$)

Rate coefficients follow the order

CS_2, OCS, $CSCl_2$ > CO, NO, O_2 > H_2 > CO_2, N_2, He, Ar.

$k_{CO_2,\,N_2,He,Ar} \leq 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

5.3.2. Discussion

a. Carbon Monosulfide, CS($A\,^1\Pi$)

Although vacuum ultraviolet photolysis of CS_2 appears to induce the spin-forbidden transition to CS($A\,^1\Pi$), the threshold of which lies at 133.7 nm (Okabe, 1972), its efficiency is estimated at no more than 7% in this spectral region. In fact Black et al. (1977) note that the predominant channel is to CS($a\,^3\Pi$) with near unit efficiency in the 125 to 140 nm range. Likewise, OCS and $CSCl_2$ have been shown to photodissociate to an unknown extent to CS($A\,^1\Pi$) at wavelengths shorter than 102.4 and 127 nm, respectively (Lee & Judge, 1975; Okabe, 1975). However, no quenching or vibrational relaxation data are yet reported.

The period between gas kinetic collisions becomes comparable to the radiative lifetime at pressures of about 70 Pa. The fact that strong A–X radiation is seen from microwave discharged CS_2 at about 100 Pa (Bell et al., 1972) and from higher temperature diffusion flames diluted with Ar at about 1.3 kPa (Tewarson & Palmer, 1968) indicates that collisional quenching rates occur with less than unit efficiency, at least 20-fold so lower for Ar. Similarly, spectral observations indicate no pronounced vibrational relaxation within the $A\,^1\Pi$ state.

b. Carbon Monosulfide, CS($a\,^3\Pi$)

Energy transfer from Ar($^3P_{0,2}$) or He($^3S_1$) metastables to such molecules as CS_2, OCS or $CSCl_2$ (Taylor et al., 1972; Piper et al., 1972; Taylor, 1973) and 125–140 nm photolysis of CS_2 (Black et al., 1977) provide sources of CS($a\,^3\Pi$) suitable for kinetic studies. Even so, quenching data are still quite limited (table 15).

Although Tewarson and Palmer (1968) and Palmer (1971) noted the absence of extensive vibrational relaxation within the state in diffusion flames diluted with Ar at 1100 K and pressures of about 1.3 kPa, it is evident to a slight extent in room temperature discharge flow systems with Ar at about 0.3–0.7 kPa (Piper et al., 1972; Taylor, 1973). Other than this noted inefficiency with Ar, no data are available for k_{vib}.

The one main set of collisional electronic quenching data indicate that efficiencies are either about the same or much

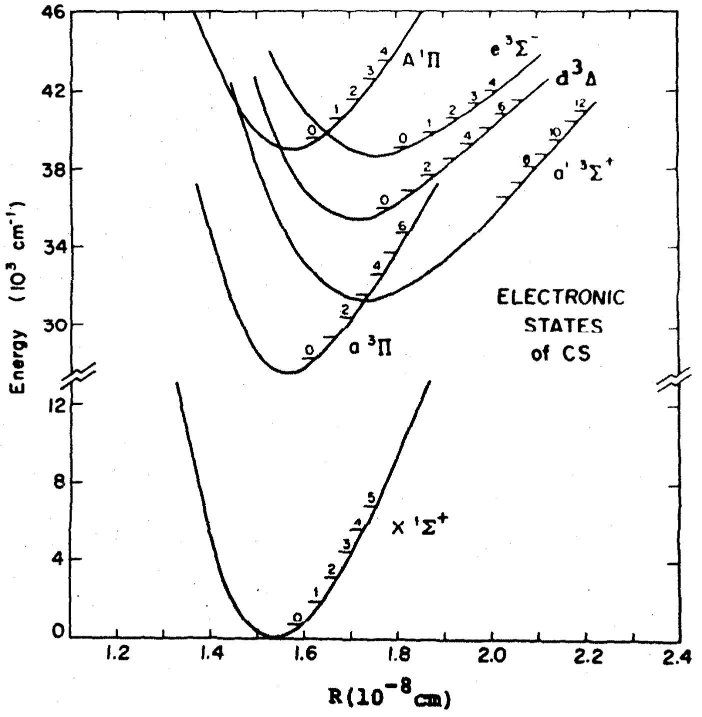

FIGURE 14. Potential energy curves for electronic states of CS (from Field and Bergeman, 1971).

Table 14. Energies and radiative lifetimes of the low-lying electronic states of CS.

	T_e	T_0 cm^{-1} ^{a}	D_0^0	τ s	Reference
$A^1\Pi$	38,905	38,798	≈21,200	≈0.2×10^{-6}	Smith, *1969*; Silvers et al., 1970, & Chiu, 1972
$e^3\Sigma^-$	38,683	38,419	≈21,500	Allowed transitions to $a^3\Pi$	
$d^3\Delta$	35,621	35,406	≈24,600		
$a'{}^3\Sigma^+$	≈31,380	31,149	≈28,800		
$a^3\Pi$	27,658	27,584	≈32,380	≈16×10^{-3}	Black et al., 1977
$X^1\Sigma^+$	0	641	59,320	-	

[a] Tewarson & Palmer, 1968; Rosen, 1970; Field & Bergeman, 1971; Bell et al., 1972; Robbe & Schamps, 1972; Taylor et al., 1972; Bruna et al., 1975

Table 15. Quenching and relaxation rate constants, CS($a^3\Pi$), 300 K.

M	k_{vib}	k_M, $cm^3 molecule^{-1} s^{-1}$	
CS_2		$\geq 6.9 \times 10^{-11}$	5×10^{-10}
OCS		$\geq 8.5 \times 10^{-11}$	
$CSCl_2$		$\geq 3.5 \times 10^{-11}$	
CO_2			$\leq 10^{-15}$
CO			3.2×10^{-11}
NO			1.0×10^{-10}
N_2			$\leq 10^{-15}$
O_2			2.6×10^{-11}
H_2			7.2×10^{-13}
He			$\leq 10^{-15}$
Ar	$<(0.4-2) \times 10^{-14}$		$\leq 10^{-15}$
Exp. Temp. K	300	300	296
Method	Flow system, hollow cathode Ar discharge. CS($a^3\Pi$) emission, v'=0-3 from Ar($^3P_2$)+ 0.01 Pa CS_2. 0.73 kPa Ar carrier	Fast flow system, hollow cathode Ar discharge. CS ($a^3\pi$) emission from Ar($^3P_2$)+ slight excess $CSCl_2$. Fixed point observation.	Photolysis of 0.07-5.9 Pa CS_2 in 0.26-0.67 kPa Ar buffer. Wavelengths used in 125-145 nm range. Emission monitored via filters for either 320-390 or ≥310 nm.
Comments	Based on τ 3×10^{-4} s. The longer τ now reported will reduce this k_{vib} value.	Reliable only to within a factor of 5	v'=0-3
Reference	Piper et al., 1972	(Taylor, unpublished data) Taylor, 1973	Black et al., 1977

reduced from those of the more energetic CO($a\,^3\Pi$). Quenching particularly with CO, O_2, H_2, CO_2, and N_2 is significantly slower, and is very inefficient for H_2, CO_2 and N_2. Although an *E–V* process for the CS($a\,^3\Pi$)/CO interaction may occur, this mechanism appears very inefficient with H_2, CO_2 and N_2. Chemical channels are plausible with O_2 and NO and electronic energy transfer processes with CS_2 and O_2, however, the actual relaxation mechanisms occurring remain unknown.

5.3.3. References

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5.4. Atomic Nitrogen, $N(2^2D_{3/2,5/2}, 2^2P_{1/2,3/2})$

As indicated by the long lifetimes in table 16, these low lying atomic states are metastable. Spin orbit splitting is small and rate constants refer to the unresolved levels ^2P_J or ^2D_J. A considerable body of chemical kinetic data now is available for their chemical and physical interactions with a large number of molecules and atoms.

5.4.1. Recommended Rate Constant Values

$N(^2D_{3/2,5/2})$

Chemical Interaction, 300 K

$N(^2D)+H_2O = NH+OH?$	$2.5(\pm0.5)\times10^{-10}$
$N(^2D)+CH_4 =$ products	$\cong1.5\times10^{-12}$, limited data
$N(^2D)+C_2H_4 =$ products	$\cong6\times10^{-11}$, limited data
$N(^2D)+N_2O = N_2+NO$	$1.8(^{+0.7}_{-0.4})\times10^{-12}$
	$1.2(\pm0.3)\times10^{-11}\exp(-570\mp70/T)$, 200-400 K
$N(^2D)+NH_3 = NH+NH_2?$	$\cong5\times10^{-11}$, limited data
$N(^2D)+CO_2 = NO+CO$	$2.5(^{+2.0}_{-1.0})\times10^{-13}$, positive activation energy
$N(^2D)+NO = N_2+O(^3P,^1D,^1S)$	$6.3(\pm2.0)\times10^{-11}$, predominant channel unknown
$N(^2D)+O_2 = NO+O(^3P,^1D)$	$6.0(^{+1.5}_{-1.0})\times10^{-12}$, predominant channel unknown
	$3.5\times10^{-13}T^{1/2}$, 200-400 K, zero activation energy
$N(^2D)+O_2^+ = N^++O_2?$ $= NO^++O(^3P,^1D,^1S)?$ $= NO^+(A^3\Sigma^+)+O?$	No available data. First channel requires an activation energy ≥7.6 kJ mol^{-1} (1.8 kcal mol^{-1})
$N(^2D)+H_2 = NH+H?$	$2.2(\pm0.8)\times10^{-12}$, exact channel unknown
$N(^2D)+H_2^+ = NH(a^1\Delta)+H^+?$ $= NH^+(A^2\Sigma^-,B^2\Delta)+H?$	No available data
$N(^2D)+OH = NH+O?$	No available data

Physical Relaxation, 300 K

$N(^2D)+CO$	$2.5(\pm1.0)\times10^{-12}$
$+N_2$	$1.7(\pm0.3)\times10^{-14}$
	$9.4(^{+6.9}_{-4.2})\times10^{-14}\exp(-510\mp155/T)$, 200-400 K
$+O$	$2(^{+2}_{-1})\times10^{-12}$, activation energy $4(\pm2)$ kJ mol^{-1}
$+N$	No available data
$+He$	$\leq1.5\times10^{-16}$
$+Ar$	$1(\pm0.6)\times10^{-1}$[illegible]

$N(^2P_{1/2,3/2})$

Chemical Interaction, 300 K

$N(^2P)+H_2O = NH(a^1\Delta)+OH?$	No data, chemical channel probable.
$N(^2P)+N_2O = N_2+NO$	$4(^{+3}_{-2})\times10^{-14}$, product either $NO(B^2\Pi, C^2\Pi)$ or $N_2(A^3\Sigma_u^+)$
$N(^2P)+O_2 = NO+O(^1D,^1S)$ $= NO(a^4\Pi)+O$	$2(\pm1)\times10^{-12}$, predominant channel unknown
$N(^2P)+O_2^+ = NO^+(B^3\Pi)+O?$	No available data
$N(^2P)+OH = NH+O(^1D)?$	No available data

Physical Relaxation, 300 K

$N(^2P)+CO_2$	$1.25(\pm0.25)\times10^{-15}$
$+CO$	$\cong8\times10^{-14(+1)}$, conflicting data, chemical channel?
$+NO$	$3.0(\pm0.5)\times10^{-11}$, chemical channel?
$+N_2$	$2\times10^{-18(+0.5)}$
$+H_2$	$1.5(\pm1)\times10^{-15}$, chemical channel?
$+O$	$\cong1\times10^{-11}$, limited data, may refer to $N(^2P)+O = NO^++e^-$
$+N$	$1\times10^{-12(+0.3)}$, exact mechanism unknown
$+Ar$	$\cong7\times10^{-16}$, 400 K, limited data

5.4.2. Discussion

A considerable body of data is beginning to accumulate for the chemical and relaxation processes of the $N(^2P, ^2D)$ metastable states. Techniques for production and monitoring of these are well developed. However, nearly all the data refer to room temperature measurements and none are yet available above 400 K. Discrepancies can arise from a potential interference resulting from the formation of products that are efficient quenchers and precautions must be taken to minimize the effect. Cascading from ^2P to ^2D does not appear to be a problem in these studies.

In many cases the question as to whether the interaction is chemical or physical in nature has been resolved. However, additional studies are required in most instances to specify the exact channel.

a. $N(^2D,^2P) + H_2O$

Although only measured in one recent study, the interaction of $N(^2D)$ with H_2O has the largest rate constant

Table 16. Energies and radiative lifetimes of low-lying electronic states of atomic nitrogen.

Electronic State	Energy[a] Level (cm^{-1})	Radiative[b] Lifetime (s)
$^2P_{3/2}$	28,839.31	11.7
$^2P_{1/2}$	28,838.92	12.5
$^2D_{3/2}$	19,233.18	6.1×10^4
$^2D_{5/2}$	19,224.46	1.4×10^5
$^4S_{3/2}$	0.00	-

[a] Moore, 1975

[b] Wiese et al., 1966

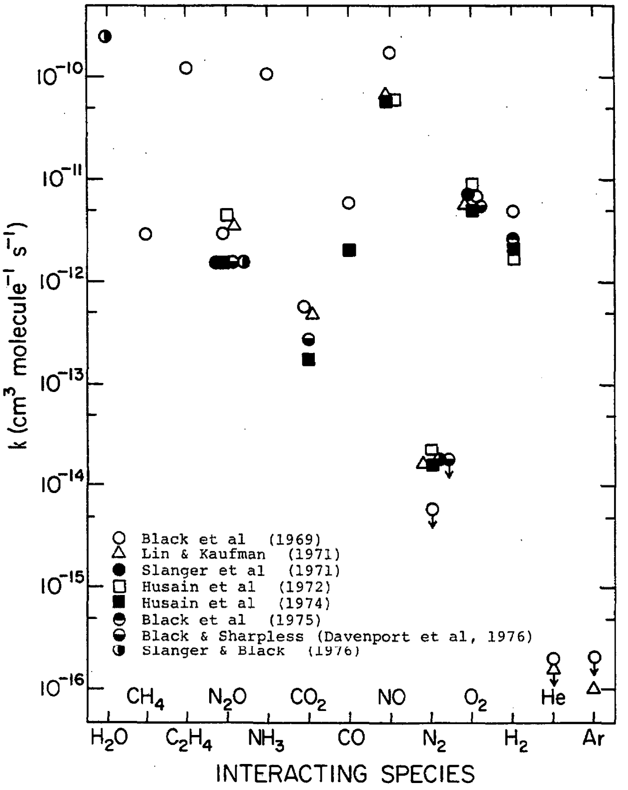

FIGURE 15. Rate constants characterizing the various interactions of N($^2D_{3/2,5/2}$), 300 K.

reported for any interaction of N(^{2}D) or N(^{2}P). No data are available for N(^{2}P). The correlation diagram supports chemical reaction

$$N(^2D) + H_2O = NH + OH \quad \Delta H^\circ_{298\,K} = -43.87\ \mathrm{kJ\ mol^{-1}}\ (-10.49\ \mathrm{kcal\ mol^{-1}}).$$

It also appears probable, unless kinetic constraints prevail, that a similar chemical interaction will occur for N(^{2}P) but producing NH($a\,^1\Delta$) and OH.

Consequently, if such H_2O quenching is to be avoided in studies of N(^{2}D, ^{2}P) chemistry, dry gases appear to be a prerequisite.

b. N(^{2}D, ^{2}P) + CH_4, C_2H_4

The single measurements with N(^{2}D), figure 15, indicate a 40-fold larger rate constant for N(^{2}D) with C_2H_4 than with CH_4. Evidence indicates that chemical reactions occur with the formation of HCN as a major product and that the reactions of hot or thermal N atoms with hydrocarbons are similar (Dubrin et al., 1966). The exact mechanism is uncertain (Wright and Winkler, 1968), however, it is unlikely on kinetic grounds to proceed in the one stage reaction that is often indicated as

$$N(^2D) + C_2H_4 = HCN + CH_3 \quad \Delta H^\circ_{298\,K} = -474.3\ \mathrm{kJ\ mol^{-1}}\ (-113.4\ \mathrm{kcal\ mol^{-1}})$$

An overall examination of the available data for N(^{2}D) indicates that the values of Black et al. (1969) generally are about a factor of 2 high. Consequently, at 300 K, k_{CH_4} and $k_{C_2H_4}$ are more probably $\cong 1.5 \times 10^{-12}$ and 6×10^{-11}, respectively.

No data are available for the corresponding reactions with N(^{2}P).

c. N(^{2}D, ^{2}P) + N_2O

That the interaction of N_2O with N(^{2}D) is chemical in nature is well established (Lin & Kaufman, 1971; Dodge & Heicklen, 1971; Black et al., 1969, 1975). The predominant reaction pathway appears to be to ground state products with a small contribution (0.3%) in the channel producing NO($B\,^2\Pi$) (Slanger et al., 1971; Herbelin & Cohen, 1973). The latter is formed in preference to NO($A\,^2\Sigma^+$) (Welge, 1966). There is no evidence for formation of $N_2(A\,^3\Sigma^+)$ although the reaction has sufficient exothermicity.

$$N(^2D) + N_2O = N_2 + NO \quad \Delta H^\circ_{298\,K} = -694.4\ \mathrm{kJ\ mol^{-1}}\ (-166.0\ \mathrm{kcal\ mol^{-1}})$$

$$= N_2 + NO(A^2\Sigma^+) \quad = -165.7\ \mathrm{kJ\ mol^{-1}}\ (-39.60\ \mathrm{kcal\ mol^{-1}})$$

$$= N_2 + NO(B^2\Pi) \quad = -150.1\ \mathrm{kJ\ mol^{-1}}\ (-35.87\ \mathrm{kcal\ mol^{-1}})$$

$$= N_2(A^3\Sigma_u^+) + NO \quad = -99.2\ \mathrm{kJ\ mol^{-1}}\ (-23.71\ \mathrm{kcal\ mol^{-1}})$$

The stoichiometry of the reaction was verified by Lin and Kaufman (1971) who monitored the oxygen atoms produced by the subsequent reaction between N and the NO product. The nine measures of k_{N_2O} vary by a factor of three. Of the two values obtained by Husain et al. (1972, 1974), which differ by a similar factor, they state a preference for the lower value since it is less likely affected by the interference of products resulting from the photolysis pulse. Their assumption of negligible cascading from N(^{2}P) appears to be valid. The lower values are preferred and a rate constant at 300 K of 1.8 $(^{+0.7}_{-0.4}) \times 10^{-12}$ is recommended with an activation energy of 4.7 ± 0.6 kJ mol^{-1} (1.1 ± 0.15 kcal mol^{-1}). This is relatively slow in view of the available exothermic surfaces to either NO($X\,^2\Pi$, $A\,^2\Sigma^+$, $B\,^2\Pi$) or $N_2(A\,^3\Sigma_u^+)$ products.

Of the three datum points for N(^{2}P), the two values obtained most recently are in reasonable accord, 2.5 and 5 × 10^{-14}. A value of $4(\pm^{3}_{2}) \times 10^{-14}$ is suggested. The earlier work of Husain et al. (1972) was clearly affected by the additional quenching resulting from products of the N_2O photolysis. That this arises was shown by Young and Dunn (1975) who measured the rate constant as a function of discharge energy and found an order of magnitude variation. Available surfaces constructed on a basis of C_s symmetry correlate either to the excited products NO($B\,^2\Pi$, $C\,^2\Pi$) or to $N_2(A\,^3\Sigma_u^+)$. The reduced collision efficiency must reflect the effect of energy barriers leading to these states.

Table 17. Rate constants for interactions of $N(^2D_{3/2,5/2})$

M		k_M, $cm^3 molecule^{-1} s^{-1}$	
CH_4		$3x10^{-12}$	
C_2H_4		$1.2x10^{-10}$	
N_2O	$k_{N_2O}:k_{NO} \approx 0.04$	$3x10^{-12}$	$3.5(\pm 1.2)x10^{-12}$
NH_3		$1.1x10^{-10}$	
CO_2		$6x10^{-13}$	$5(\pm 2)x10^{-13}$
CO		$6x10^{-12}$	
NO	$k_{NO}:k_{N_2O} \approx 25$	$1.8x10^{-10}$	$7(\pm 2.5)x10^{-11}$
N_2		$\leq 6x10^{-15}$	$1.6(\pm 0.7)x10^{-14}$
O_2		$7x10^{-12}$	$6(\pm 2)x10^{-12}$
H_2	$k_{H_2} \approx k_{N_2O}$	$5x10^{-12}$	
He		$\leq 2x10^{-16}$	$\leq 1.6x10^{-16}$
Ar		$\leq 2x10^{-16}$	$1(\pm 0.6)x10^{-16}$
Exp. Temp. K	300	300	300
Method	147 nm Xe photolysis N_2O/Ar, He, N_2, NO mixtures. $N_2O \leq$ 0.9 kPa, total pressure ≤ 2.8 kPa. $1.5x10^3$ cm^3 cell, residence time 1.5 s. NO(0,11) β band emission monitored at 380 nm as measure of $N(^2D)$.	Vacuum uv photolysis cell, slow flow, 1 s residence time, 147 Xe, 116.5+123.6 Kr RF resonance lamps. N_2O 0.8-2.1 Pa, He or Ar background gas, total pressure 0.4-0.7 kPa. $[N^2D]$ from NO(0,10) β band intensity at 358 nm.	Microwave discharge flow, velocity ≈ 50 m s^{-1}, N_2 2-90 Pa, He/Ar carrier gas 0.45-2.1 kPa. $[N(^2D)]$ $2.4x10^{12}$ cm^{-3}. Atomic absorption at 149.3 nm using microwave discharge N line source.
Comments		Accuracy of 25% quoted. Confirmed that $NO(B^2\pi)$ emission mirrors $[N^2D]$ via $N(^2D)+N_2O = N_2+NO(B^2\pi)$.	Also monitored [O] at 130.2 nm. Established that $N(^2D)+N_2O$, CO_2 and O_2 are chemical interactions.
Reference	Young et al., 1968	Black et al., 1969	Lin & Kaufman, 1971

Table 17. Rate constants for interactions of $N(^2D_{3/2,5/2})$ -- continued

M		k_M, $cm^3 molecule^{-1} s^{-1}$	
N_2O	$3.6x10^{-13}T^{1/2}exp(-400/T)$ $1.6x10^{-12}$(300 K)	$4.8(\pm 0.9)x10^{-12}$	$1.6(\pm 0.1)x10^{-12}$
CO_2			$1.8(\pm 0.2)x10^{-13}$
CO			$2.1(\pm 0.2)x10^{-12}$
NO		$6.1(\pm 3.7)x10^{-11}$	$5.9(\pm 0.4)x10^{-11}$
N_2		$2.3(\pm 1.1)x10^{-14}$	$1.5(\pm 0.1)x10^{-14}$
O_2	8.2, 7.4, $8.6x10^{-12}$ (237, 295, 365 K)	$9.3(\pm 2.2)x10^{-12}$	$5.2(\pm 0.4)x10^{-12}$
H_2		$1.7(\pm 0.5)x10^{-12}$	$2.1(\pm 0.3)x10^{-12}$
Exp. Temp. K	237, 295, 365	300	300
Method	147 nm Xe photolysis, 0.4-8 Pa N_2O, 800 Pa Ar background gas, $O_2 \leq 1.6$ Pa, NO β band emission monitored as a measure of $N(^2D)$.	N_2O flash photolysis, static system, $\lambda > 105$ nm, E=550-810 J Kr lamp. $[N^2D] \approx 2x10^{12}$ cm^{-3}. N_2O 6.7, He 6700, M<13, $N_2 < 1000$ Pa. $[N^2D]$ by 149.3 nm atomic absorption using a microwave discharge N line source.	Repetitive 0.1 Hz pulsed photolysis of N_2O, $\lambda > 105$ nm, E=80 J N_2 lamp, slow flow, ≈ 1.5 s residence time. N_2O 6.35, He 2700, M<21, N_2, $CO_2 < 1500$ Pa. $[N^2D]$ by 149.3 nm atomic absorption using a microwave discharge N line source.
Comments	For O_2, the data suggests a zero activation energy with a possible $T^{1/2}$ preexponent dependence. N_2O shows an activation energy of 3.3 ± 0.8 kJ mol^{-1} (0.8 ± 0.2 kcal mol^{-1}).		
Reference	Slanger et al., 1971	Husain et al., 1972	Husain et al., 1974

Table 17. Rate constants for interactions of $N(^2D_{3/2,5/2})$ -- continued

M	k_M, cm^3 $molecule^{-1}$ s^{-1}			
H_2O				$2.5(\pm0.5)x10^{-10}$(300 K)
N_2O	$*2.6(\pm0.3)x10^{-12}$	$k_{N_2O} = k_{H_2}$	$1.6(\pm0.2)x10^{-12}$	$1.15(\pm0.3)x10^{-11}exp(-570\mp70/T)$ $1.7(\pm0.1)x10^{-12}$(300 K)
CO_2			$2.8(\pm0.2)x10^{-13}$	
N_2	$<1.8x10^{-14}$			$1.0(^{+0.83}_{-0.46})x10^{-13}exp(-510\mp155/T)$ $1.85(\pm0.15)x10^{-14}$(300 K)
O_2			$5.8(\pm0.5)x10^{-12}$	
H_2	$2.7(\pm0.2)x10^{-12}$	$k_{H_2} = k_{N_2O}$		
O		$k_{O_2}:k_O = 3.0(\pm1.0):1$		
Exp. Temp. K	300	315	300	198-372
Method	Pulsed H_2 110-150 nm vacuum uv photolysis of N_2O ≤20 Pa in 270 Pa N_2. Flow cell. Use NO β emission as monitor of $N(^2D)$.	Microwave discharge flow system, velocity 29 m s^{-1}, 0.2% N_2 in 2-3.3 kPa Ar. O from second such discharge by partially titrating with NO. $N(^2D)$ from atomic absorption at 149.3 nm using microwave discharge N line source.	-	Pulsed 121.6 nm photolysis of 93 Pa 10% N_2O/Ar, 1.3 kPa He mixture, N_2 0-0.7 kPa or 0.93 kPa 1% N_2O/Ar, 1.3 kPa He mixture, H_2O 0-0.13 Pa. 300 cm^3 cell, residence time 0.15 s. NO β decay followed as a measure of $N(^2D)$.
Comments	$N(^2D)$ established as the precursor for NO β bands throughout this N_2O photolysis range. *Value discarded--too large owing to N_2O impurities (Slanger & Black, 1976)	$k_{O_2}:k_O$=1.9(355 K), 1.95 (390 K), 1.85(400 K). k_O activation energy 4.2±2.1 kJ mol^{-1}. k_{CO_2} has a positive activation energy.	Unpublished data of Black and Sharpless (1975).	
Reference	Black et al., 1975	Davenport et al., 1976	Davenport et al., 1976	Slanger & Black, 1976

$$N(^2P) + N_2O = N_2 + NO(B\,^2\Pi) \quad \Delta H^\circ_{298\,K} = -265.1\ kJ\ mol^{-1}\ (-63.36\ kcal\ mol^{-1})$$

$$= N_2 + NO(C\,^2\Pi) \quad = -182.9\ kJ\ mol^{-1}\ (-43.72\ kcal\ mol^{-1})$$

$$= N_2(A\,^3\Sigma^+) + NO \quad = -214.2\ kJ\ mol^{-1}\ (-51.20\ kcal\ mol^{-1})$$

d. $N(^2D) + NH_3$

An overall assessment of the available data for $N(^2D)$ indicates that the single value of Black et al. (1969) for NH_3 may be about a factor of two high, suggesting $k \cong 5 \times 10^{-11}$ at 300 K. The interaction is probably the fast exothermic chemical reaction

$$N(^2D) + NH_3 = NH + NH_2 \quad \Delta H^\circ_{298\,K} = -150.2\ kJ\ mol^{-1}\ (-35.90\ kcal\ mol^{-1})$$

which is not observed with low temperature ground state N atoms owing to its endothermicity.

e. $N(^2D, ^2P) + CO, CO_2$

For $N(^2D)$ the measured values of k_{CO_2} (4 datum points) and k_{CO} (2 datum points) each have about a factor of three spread. With CO_2, Lin and Kaufman (1971) monitored, in absorption, the oxygen atoms produced by subsequent reaction of N with the NO product and reported the expected stoichiometry assuming the predominance of the reaction

$$N(^2D) + CO_2 = NO + CO \quad \Delta H^\circ_{298\,K} = -329.4\ kJ\ mol^{-1}\ (-78.72\ kcal\ mol^{-1})$$

These reactants correlate with ground state products and the rate constant indicates an energy barrier in the reactive surface. Giving more weight to the lowest values suggests $k_{CO_2} = 2.5(^{+2.0}_{-1.0}) \times 10^{-13}$ at 300 K and is probably temperature dependent.

For CO, thermochemical considerations rule out reaction with $N(^2D)$ and indicate a physical quenching mechanism involving a crossing from a doublet to a quartet surface. $N(^2D)$ and CO correlate with $NCO(X\,^2\Pi)$ causing this low lying doublet surface to cross that of the quartet associated with

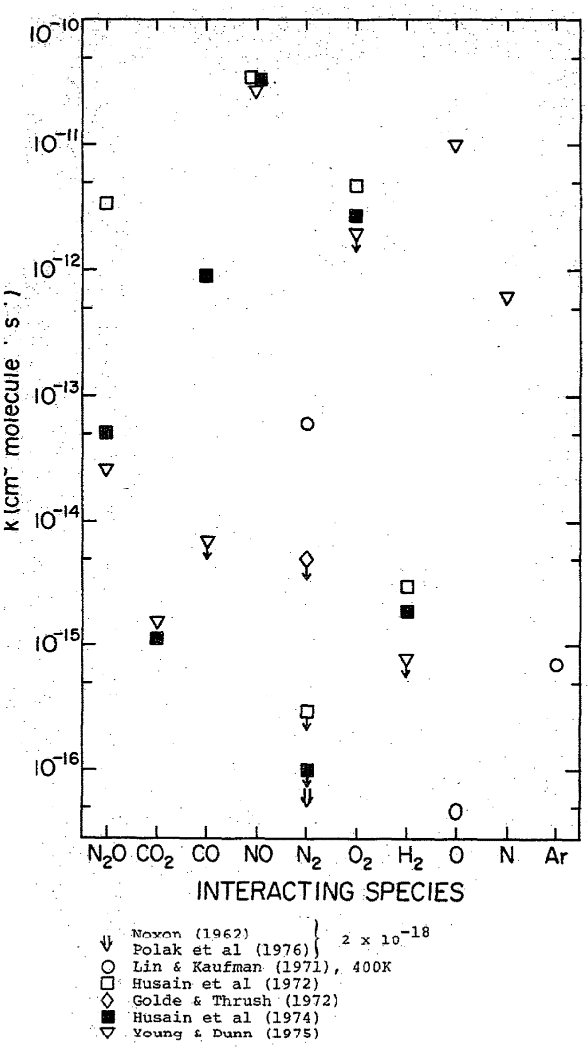

FIGURE 16. Rate constants characterizing the various interactions of $N(^2P_{1/2,3/2})$, 300 K.

$N(^4S)$ so facilitating relaxation (Dixon, 1960). Weighting preferentially the lower value gives $k_{CO} = 2.5\,(\pm 1.0) \times 10^{-12}$ at 300 K.

Although the two results for $N(^2P)$ with CO_2 are in close agreement, those for CO by the same investigators are completely at odds. With CO_2, there are no available surfaces to ground state products or to any other states for which reaction would still be exothermic. This is in accord with the measured slow rate and a value of $1.25\,(\pm 0.25) \times 10^{-15}$ is suggested at room temperature for a physical quenching mechanism.

Reaction of $N(^2P)$ with CO to form C + NO is endothermic but that to CN + O is exothermic by 22.8 kJ mol⁻¹ (5.45 kcal mol⁻¹). However, there is no available adiabatic route (Dixon, 1960) and a slow surface crossing mechanism is evident. Whether quenched reactants or reactive products result remains uncertain. The reasonable agreement between values for the collisional decay of $N(^2P)$ with other gases makes the disagreement between the two measured values with CO difficult to explain, 9.0×10^{-13} and $<7 \times 10^{-15}$. A mean value of about 8×10^{-14} with an order of magnitude uncertainty will have to be assumed until this discrepancy is resolved.

f. $N(^2D, {}^2P)$ + NO

Three of the four experimental datum points for the interaction of $N(^2D)$ with NO are in excellent agreement, 5.9, 6.1 and 7×10^{-11} cm³ molecule⁻¹ s⁻¹. The value obtained by Black et al. (1969) is too high by about a factor of three. The earliest relative value of Young et al. (1968), $k_{NO}: k_{N_2O} \cong 25$, implies $k_{NO} \cong 4.5 \times 10^{-11}$ based on k_{N_2O} recommended above, additionally supporting the lower measures. Consequently, a value of $6.3(\pm 2.0) \times 10^{-11}$ is suggested for 300 K and indicates a rapid chemical reaction with a collision efficiency of about 1 in 5. The correlation diagram, figure 17, illustrates reactive surfaces leading to either $O(^3P_J$, $^1D_2$ or $^1S_0)$

$$N(^2D) + NO = N_2 + O(^3P_J) \quad \Delta H^\circ_{298\,K} = -543.7 \text{ kJ mol}^{-1} \; (-130.0 \text{ kcal mol}^{-1})$$

$$= N_2 + O(^1D_2) \quad = -353.9 \text{ kJ mol}^{-1} \; (-84.6 \text{ kcal mol}^{-1})$$

$$= N_2 + O(^1S_0) \quad = -139.5 \text{ kJ mol}^{-1} \; (-33.3 \text{ kcal mol}^{-1})$$

the exact channel favored is not yet known.

The data for $N(^2P)$ also are in remarkedly good agreement, in fact this is the most accurately specified interaction for this electronic state. A value of $3.0(\pm 0.5) \times 10^{-11}$ is recommended at 300 K, only a factor of two slower than that for $N(^2D)$. However, the correlation diagram rules out chemical reaction via an adiabatic surface, figure 17, and the true nature of the interaction remains uncertain. Moreover, the involvement of an atom exchange mechanism likewise is not known.

g. $N(^2D, {}^2P) + N_2$

Relaxation of the nitrogen metastable states by molecular nitrogen clearly arises via nonadiabatic transitions involving the crossing of doublet and quartet surfaces. The rate constants are small as expected.

For $N(^2D)$ the early value of Black et al. (1969) is too low. Of the other measurements 1.5 ×, 1.6 × and 1.85×10^{-14} (Husain et al., 1974; Lin & Kaufman, 1971; Slanger & Black, 1976) a recommended value of $1.7(\pm 0.3) \times 10^{-14}$ is favored at room temperature. Coupled with Slanger and Black's (1976) measured activation energy of 4.3 ± 1.3 kJ mol⁻¹ (1.0 ± 0.3 kcal mol⁻¹) this suggests the expression $9.4\,(^{+6.9}_{-4.2}) \times 10^{-14} \exp(-510 \mp 155/T)$ in the 200 to 400 K range.

The interaction of $N(^2P)$ with N_2 is clearly very inefficient and Lin and Kaufman's (1971) estimate erroneous. Other than upper limit estimates, the only quantitative measure, $2(\pm 1) \times 10^{-18}$, results from a reanalysis by Polak et al. (1976) of Noxon's (1962) data and is probably reasonably accurate. It is supported by the fact that their estimate also of $k(N^2P + N)$ in the same analysis is only a factor of three different from the measurements of Young and Dunn (1975). Consequently, at present the most reliable value for $k(N^2P + N_2)$ is $2 \times 10^{-18(\pm 0.5)}$.

Table 18. Rate constants for interactions of N($^2P_{1/2,3/2}$)

M		k_M, cm^3 molecule^{-1} s^{-1}	
N_2O			3.4(±1.5) x 10^{-12}
NO			3.4(±1.1) x 10^{-11}
N_2	2(±1) x 10^{-18}	≈6 x 10^{-14}	≤3 x 10^{-16}
O_2			4.6(±2.5) x 10^{-12}
H_2			3.0(±1.1) x 10^{-15}
N	1.8(±0.9) x 10^{-12}		
Ar		7 x 10^{-16}	
Exp. Temp. K	≈300	400	300
Method	HV ozonizer discharge in pure N_2, 2.7-100 kPa. Closed loop flow system ≤100 cm s^{-1}. N(^{2}P) 346.6 nm emission monitored by photograph/densitometer. Exposures include time intervals of 0.5-1.7 to 1.5-5.1 s from the discharge.	Microwave discharge flow system, velocity 50 m s^{-1}, 20 Pa N_2O in 0.44-2 kPa Ar carrier gas. N(^{2}P) <4x10^{11} cm^{-3}. Atomic absorption at 174.4 nm using microwave discharge N line source.	Flash photolysis of N_2O, static system, λ>105 nm, E=550-810 J Kr lamp. N(^{2}P)≈7x10^{11} cm^{-3}. N_2O 6.7, He 6700, M<4, H_2, N_2<6000 Pa. Atomic absorption at 174.4 nm using microwave discharge N line source.
Comments	Reanalysis of Noxon's data assuming N(^{2}P) formed via N+N_2($A^3\Sigma^+$) and removed via N and N_2 quenching and 3 body recombination. The latter shown to be negligible.		
Reference	Noxon, 1962; Polak et al., 1976	Lin and Kaufman, 1971	Husain et al., 1972

Table 18. Rate constants for interactions of N($^2P_{1/2,3/2}$) -- continued

M		k_M, cm^3 molecule^{-1} s^{-1}	
N_2O		5(±2) x 10^{-14}	2.5 x 10^{-14}
CO_2		1.1 x 10^{-15}	1.4 x 10^{-15}
CO		9.0(±0.4) x 10^{-13}	<7 x 10^{-15}
NO		3.2(±0.1) x 10^{-11}	2.8 x 10^{-11}
N_2	< 5 x 10^{-15}	≤1 x 10^{-16}	
O_2		2.6(±0.2) x 10^{-12}	≤2 x 10^{-12}
H_2		1.9(±0.2) x 10^{-15}	<8 x 10^{-16}
O	k_O:k_N = 7(±2)		1.0 x 10^{-11}
N			6.2 x 10^{-13}
Exp. Temp. K	300	300	300
Method	Discharge flow system, N_2 270-800 Pa. N(^{2}P) from 346.6 nm emission. [N] from N_2 1st positive band emission (∝[N]^2) and [O] from NO δ emission (∝[N][O]). [N] ≈0.1%, [O]≈0.01%.	Repetitive 0.1 Hz pulsed photolysis of N_2O, λ>105 nm, E=80 J N_2 lamp, slow flow ≈1.5 s residence time. N_2O 41.9, He 2700, CO, NO, O_2<26, H_2, N_2, CO_2, N_2O <3000 Pa. N(^{2}P) 174.4 nm atomic absorption using microwave discharge N line source.	Pulsed Tesla discharge in 5x10^3 cm^3 bulb, slow flow, 1 s residence time. 1-70 N_2, 300-400 Pa Ar. Emission decay of N(^{2}P) and (0,6)N_2($A^3\Sigma^+$) at 346.6 and 276.0 nm, respectively. N produced by additional microwave discharge and O by partial titration of N by NO.
Comments	N(^{2}P) from N+N_2($A^3\Sigma^+$). Absolute values of k_O=7x10^{-11}, k_N=1x10^{-11} discarded. These were based on Husain et al's (1972) incorrect values for k_{N_2O} and k_{O_2}.		±20% error stated. N(^{2}P) from reaction N+N_2($A^3\Sigma^+$)=N(^{2}P)+N_2. N_2O data extrapolated to zero Tesla discharge pulse energy.
Reference	Golde and Thrush, 1972	Husain et al., 1974	Young and Dunn, 1975

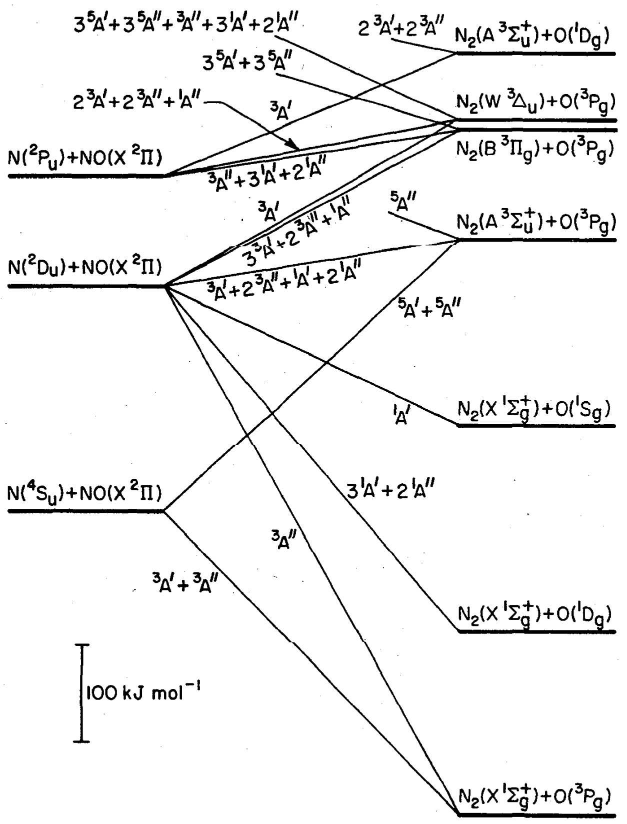

FIGURE 17. Correlation diagram connecting the states of N + NO and O + N_2.

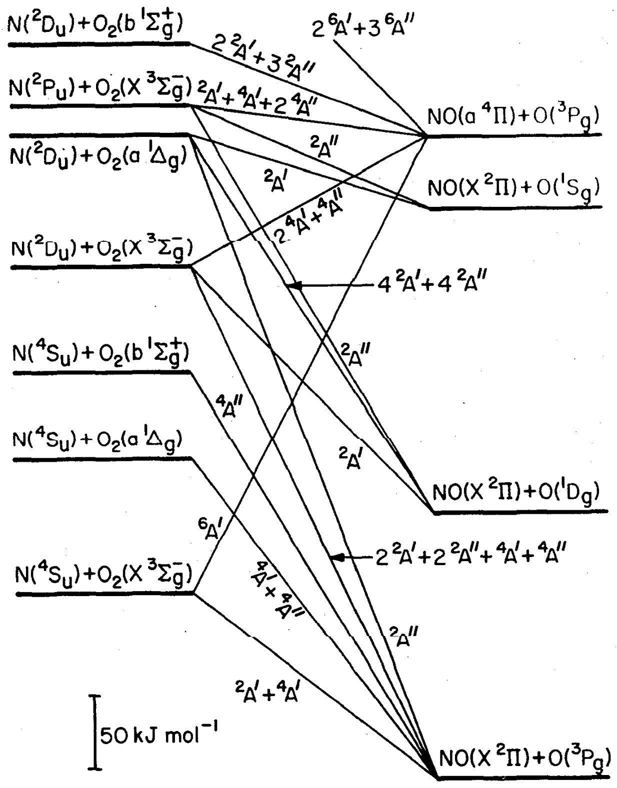

FIGURE 18. Correlation diagram connecting the states N + O_2 and NO + O.

h. $N(^2D, {}^2P) + O_2$

Lin and Kaufman (1971) established the chemical nature of this interaction for $N(^2D)$ by monitoring the oxygen atoms produced from either

$$N(^2D) + O_2 = NO + O(^3P_J) \quad \Delta H^\circ_{298\,K} = -363.2 \text{ kJ mol}^{-1} \; (-86.80 \text{ kcal mol}^{-1})$$

$$= NO + O(^1D_2) \quad = -173.3 \text{ kJ mol}^{-1} \; (-41.43 \text{ kcal mol}^{-1})$$

The six values for k_{O_2} are within a factor of two. By discarding the two high measures of 7.4 × and 9.3 × 10^{-12} (Slanger et al., 1971; Husain et al., 1972), favoring their later studies, the value $6.0(^{+1.5}_{-1.0}) \times 10^{-12}$ is recommended at room temperature. The reaction has been reported to have zero activation energy and the expected $T^{1/2}$ preexponential dependence (Slanger et al., 1971). Its reduced efficiency is somewhat unexpected since, as noted in figure 18, reactive exothermic surfaces are available for both these channels. As with carbon, a linear collision complex N-O-O is probably favored over one resulting from symmetrical insertion.

This reaction is of prime importance for aeronomy. Although previous models for 520 nm dayglow data resulted in estimates for k_{O_2} that were too low (Wallace & McElroy, 1966; Rusch et al., 1975, 1976) more recent work (Frederick & Rusch, 1977) is now compatible with the laboratory measure- The correlation diagram also indicates that the reactions

$$N(^2D) + O_2(a^1\Delta_g) = NO + O(^3P_J, {}^1D_2, {}^1S_0)$$

have available exothermic surfaces and may be efficient if energy barriers are small. The similar isoelectronic reaction

$$N(^2D) + NF(a^1\Delta) = N_2(B^3\Pi_g) + F \quad \Delta H^\circ_{298\,K} = -300.0 \text{ kJ mol}^{-1} \; (-71.71 \text{ kcal mol}^{-1})$$

has been suggested to explain the 1st. positive emission from a NF_3/Ar discharge system (Herbelin and Cohen, 1973). Although the correlation of states is completely different, this reaction can proceed adiabatically on three surfaces ($2^2A'$ + $^2A''$) and may also produce $N_2(W\,^3\Delta_u, B'\,^3\Sigma_u^-)$.

The reaction with $N(^2P)$ is less well characterized but proceeds with a rate constant only nominally smaller. A value of $2(\pm 1) \times 10^{-12}$ is tentatively suggested for 300 K. Exothermic surfaces are available either to $O(^1D_2, {}^1S_0)$ or $NO(a\,^4\Pi)$ states (figure 18). Chemical reaction is probable.

$$N(^2P) + O_2 = NO + O(^1D_2) \quad \Delta H^\circ_{298\,K} \quad 288.3 \text{ kJ mol}^{-1} \; (\; 68.91 \text{ kcal mol}^{-1})$$

$$= NO + O(^1S_0) \quad 73.91 \text{ kJ mol}^{-1} \; (-17.67 \text{ kcal mol}^{-1})$$

$$= NO(a\,^4\Pi) + O \quad \cong -14 \text{ kJ mol}^{-1} \; (-3.3 \text{ kcal mol}^{-1})$$

i. N(^{2}D, ^{2}P) + O_2^+

These reactions have not yet been studied and no data are available, however, Dalgarno (1970) pointed out the near resonance of the charge exchange

$$N(^2D) + O_2^+ = N^+ + O_2 \quad \Delta H^\circ_{298\,K} = +7.6\ \text{kJ mol}^{-1}\ (+1.8\ \text{kcal mol}^{-1})$$

and suggested it as an additional source of N$^+$ ions in the F region of the atmosphere (Bailey & Moffett, 1972; Roble & Rees, 1977). Correlating reactive surfaces are available. The corresponding reaction with N(^{2}P) correlates only endothermically with allowed products.

However, alternate reactive channels are available for this interaction and can proceed adiabatically, viz

$$\begin{aligned}
N(^2D) + O_2^+ &= NO^+ + O(^3P) \quad \Delta H^\circ_{298\,K} = -628.0\ \text{kJ mol}^{-1}\ (-150.1\ \text{kcal mol}^{-1})\\
&= NO^+ + O(^1D) \quad = -438.2\ \text{kJ mol}^{-1}\ (-104.7\ \text{kcal mol}^{-1})\\
&= NO^+ + O(^1S) \quad = -223.8\ \text{kJ mol}^{-1}\ (-53.5\ \text{kcal mol}^{-1})\\
&= NO^+(A\,^3\Sigma^+) + O \quad \cong -29\ \text{kJ mol}^{-1}\ (-7\ \text{kcal mol}^{-1})\\
&= NO + O^+(^2D) \quad = +106.9\ \text{kJ mol}^{-1}\ (+25.5\ \text{kcal mol}^{-1})
\end{aligned}$$

A correlation diagram describing these transitions has been presented by Tully et al. (1971) and by Krauss et al. (1975). The corresponding reactions with N(^{2}P) are

$$\begin{aligned}
N(^2P) + O_2^+ &= NO^+(B\,^3\Pi) + O \quad \Delta H^\circ_{298\,K} \cong -25\ \text{kJ mol}^{-1}\ (-6\ \text{kcal mol}^{-1})\\
&= NO(a\,^4\Pi) + O^+ \quad = +135\ \text{kJ mol}^{-1}\ (+32.4\ \text{kcal mol}^{-1})\\
&= NO + O^+(^2P) \quad = +155\ \text{kJ mol}^{-1}\ (+37.1\ \text{kcal mol}^{-1})
\end{aligned}$$

The electronically excited energy states of NO$^+$ are not yet accurately fixed. They have been assumed to be somewhat similar to those for isoelectronic N$_2$. Clearly, some of these exothermic pathways to NO or NO$^+$ are alternatives to that forming N$^+$.

j. N(^{2}D, ^{2}P) + H$_2$, H_2^+

Other than the result of Black et al. (1969) which appears too high, the other three measures indicate for N(^{2}D) a value of 2.2($\pm$0.8) $\times$ 10^{-12} at 300 K. This is consistent with the reported result that $k_{H_2} \cong k_{N_2O}$ (Young et al., 1968; Davenport et al., 1976). To an unknown extent, chemical reaction probably occurs.

$$N(^2D) + H_2 = NH + H \quad \Delta H^\circ_{298\,K} = -107.4\ \text{kJ mol}^{-1}\ (-25.67\ \text{kcal mol}^{-1})$$

Data for N(^{2}P) are somewhat conflicting but indicate a much slower interaction with a rate constant 1.5($\pm$1) $\times$ 10^{-15} at room temperature. This is in full accord with the correlation diagram, figure 19, and reflects a curve crossing process leading either to quenched reactants or chemical products. Nonadiabatic transition to N(^{2}D) followed by reaction as above also is possible.

Electronic state correlation diagrams for the interaction of N(^{2}D) with H_2^+ suggest available exothermic surfaces to either NH($a\,^1\Delta$) + H$^+$ or NH$^+$ ($A\,^2\Sigma^-$, $B\,^2\Delta$) + H according as to whether an insertion or collinear intermediate is formed, respectively (McClure et al., 1977). Kinetic data are not available.

k. N(^{2}D, ^{2}P) + OH

Although no kinetic data are available for these interactions, correlation diagrams, figure 20, indicate the availability of surfaces for the following reactions

$$\begin{aligned}
N(^2D) + OH &= NO + H \quad \Delta H^\circ_{298\,K} = -434.1\ \text{kJ mol}^{-1}\ (-103.7\ \text{kcal mol}^{-1})\\
&= NO\,(a\,^4\Pi) + H \quad \cong +30\ \text{kJ mol}^{-1}\ (+7\ \text{kcal mol}^{-1})
\end{aligned}$$

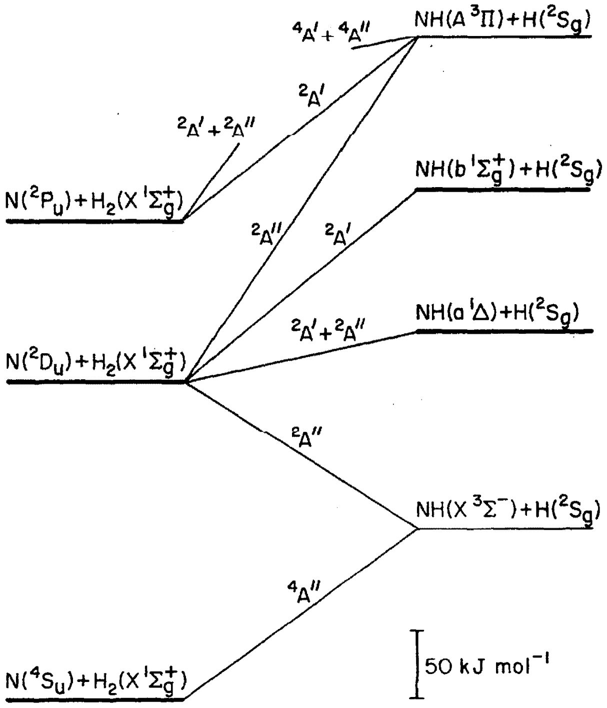

FIGURE 19. Correlation diagram connecting the states of N + H$_2$ and NH + H (from Donovan & Husain, 1970).

$$N(^2D) + OH = NH + O \qquad = -116.0 \text{ kJ mol}^{-1} \; (-27.7 \text{ kcal mol}^{-1})$$

$$= NH\,(a^1\Delta) + O \qquad \cong +28 \text{ kJ mol}^{-1} \; (+7 \text{ kcal mol}^{-1})$$

$$N(^2P) + OH = NH + O(^1D) \qquad = -41.1 \text{ kJ mol}^{-1} \; (-9.8 \text{ kcal mol}^{-1})$$

$$= NH\,(b^1\Sigma^+) + O \qquad \cong +14 \text{ kJ mol}^{-1} \; (+3 \text{ kcal mol}^{-1})$$

As to whether the two exothermic channels with the lowest enthalpy changes occur must remain to be examined experimentally.

l. $N(^2D, {}^2P) + O$

Although important to aeronomy at higher altitudes, the rate constant with $N(^2D)$ has only been measured recently and is reported as being a factor of three smaller than k_{O_2}. Accepting the reliability of the measure, a value $2(^{+2}_{-1}) \times 10^{-12}$ is recommended with an activation energy of 4.2(±2.1) kJ mol^{-1} (300 to 400 K range). Values deduced from modeling 520 nm day and nightglow satellite data generally have been significantly lower (Rusch et al., 1975, 1976; Torr et al., 1976; Frederick & Rush, 1977; Ogawa & Kondo, 1977) but are contingent upon various uncertainties in the $N(^2D)$ formation processes and the requirement of rate data pertinent to higher temperatures. One such model (Strobel et al., 1976) is consistent with a value of 1×10^{-12}, significantly closer to the laboratory value but still in disagreement considering its associated temperature of 800 to 950 K.

The correlation diagrams for this quenching are simply the potential energy curves of NO and involve a nonadiabatic curve crossing with an efficiency of about 1% of the collision frequency. Preliminary calculations by Olson and Smith (Davenport et al., 1976) indicate that production of ground state atoms might be favored over the less exothermic energy exchange mechanism to $O(^1D)$ but this remains uncertain.

$$N(^2D) + O = N + O \quad \Delta H^\circ_{298\,K} = -230 \text{ kJ mol}^{-1} \; (-54.97 \text{ kcal mol}^{-1})$$

$$= N + O(^1D) \qquad = -40.2 \text{ kJ mol}^{-1} \; (-9.60 \text{ kcal mol}^{-1})$$

The identity of the relevant curves and the mechanism await more detailed publications.

In a study of the chemiionization processes in $NH_3/O_2/N_2$ and $C_2N_2/H_2/O_2/N_2$ flames, NO^+ was found to be the predominant ion and shown to be a primary flame ion (Bertrand & Van Tiggelen, 1974; Bredo et al., 1974). The proposed mechanism

$$N(^2D) + O = NO^+ + e^- \quad \Delta H^\circ_{298\,K} = +38.3 \text{ kJ mol}^{-1} \; (+9.16 \text{ kcal mol}^{-1})$$

is highly speculative, especially considering the fast quenching rate of $N(^2D)$ by H_2O which is a major flame species.

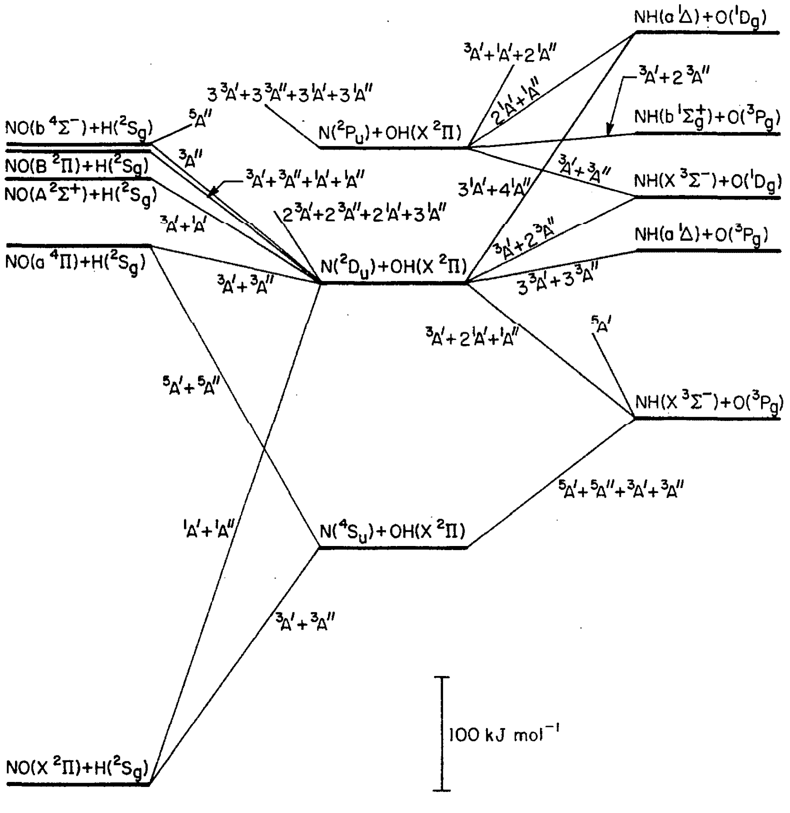

FIGURE 20. Correlation diagram connecting the states of N + OH with those of NO + H or NH + O.

Owing to its endothermicity this alternate channel can only contribute in systems at higher temperatures or collision energies.

Values for the interaction of O with N(^{2}P) have been reported in two independent studies. Golde and Thrush (1972) measured k_O relative to k_{N_2O} and k_{O_2} converting it to an absolute value using the data of Husain et al. (1972). However, the latter results now are known to be too high, k_{N_2O} by a factor of about 85 and k_{O_2} by about 2.3, leaving in some doubt the correct magnitude for k_O. Originally quoted as 7 × 10^{-11} it now requires correcting downward to an unknown extent. It is, however, somewhat supporting of the 1×10^{-11} value derived by Young and Dunn (1975) which is tentatively recommended for present use at 300 K. This is a very efficient atom-atom reaction and might be explained by the exothermic ionization mechanism (Golde & Thrush, 1972; Bertrand & Van Tiggelen, 1974; Bredo et al., 1974)

$$N(^2P) + O = NO^+ + e^- \quad \Delta H^\circ_{298\,K} = -76.6 \text{ kJ mol}^{-1} \; (-18.32 \text{ kcal mol}^{-1})$$

or must involve an efficient curve crossing to other atomic electronic states.

m. N(^{2}D, ^{2}P) + N

No measurements have been reported yet for N(^{2}D).

Of the studies involving N(^{2}P), the preliminary data of Golde and Thrush (1972) gave $k_O/k_N = 7 \pm 2$ compared to 16 ± 6 by Young and Dunn (1975) whose absolute value is 6.2 × 10^{-13}. More recently, Polak et al. (1976) have reanalyzed Noxon's (1962) data and obtained an estimate of 1.8 (±0.9) × 10^{-12}, which is closer to the 1.4 × 10^{-12} value implied by Golde and Thrush's ratio. Until further resolved, a value 1 × $10^{-12(\pm 0.3)}$ is suggested for 300 K.

Polak et al. (1976) also noted that the three-body recombination of N(^{2}P) + N + N_2 is negligible at atmospheric pressure as compared to the two-body process. They also note that the previous approximate estimate by Meyer et al. (1970) which derived a much lower figure for k_N ($\leq 1.7 \times 10^{-15}$) resulted from underestimating the efficiency of N(^{2}P) wall quenching. Otherwise, it becomes compatible with their measurements.

n. N(^{2}D, ^{2}P) + Inert Gases

Limited data are available for N(^{2}D) with He and Ar. The interactions are clearly inefficient, $k_{He} \leq 1.5 \times 10^{-16}$, $k_{Ar} = 1(\pm 0.6) \times 10^{-16}$ at room temperature. Similarly only one value has been reported for N(^{2}P) with Ar and is correspondingly slow, 7 × 10^{-16} (400 K).

5.4.3. References

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5.5. Hydroxyl Radical, OH, OD ($A\,^2\Sigma^+$)

The $A\,^2\Sigma^+$ state is the most important and best characterized of the electronically excited states of OH and gives rise to the strong $A\,^2\Sigma^+ \leftrightarrow X\,^2\Pi_i$ allowed transitions. The ground state is an inverted doublet, low N levels of $^2\Pi_{3/2}$ being at about 130 cm^{-1} lower energy than their corresponding levels in the $^2\Pi_{1/2}$ state (Herzberg, 1950).

The specific energies of the various rotational and vibrational levels of these $A\,^2\Sigma^+$ and $X\,^2\Pi_{3/2,1/2}$ states have been tabulated for OH (Dieke & Crosswhite, 1962) and for OD (Clyne et al., 1973).

As a result of curve crossing by the $a\,^4\Sigma^-$ dissociative state (Michels & Harris, 1969; Gaydon & Kopp, 1971; Sutherland & Anderson, 1973; Smith et al., 1974), predissociation occurs for those $OH(A\,^2\Sigma^+)$ levels above $N'=29$ in $v'=0$, $N'=21$ in $v'=1$ and for all levels of $v'=2$ (Sutherland & Anderson, 1973). Corresponding levels for OD are those above $N'=43$ for $v'=0$, $N'\cong 34$ $v'=1$, and $N'\cong 27$ for $v'=2$ (Palmer & Naegeli, 1968; Wilcox et al., 1975).

Consequently, interest centers mainly on the $v'=0$ and 1 levels. Chemical kinetic rate coefficients are available not only for collisional electronic quenching of $A\,^2\Sigma^+$ but also for the rates of vibrational and rotational relaxation within this electronic state. At present there is no indication that quenching involves specific chemical reactions although the possibility cannot be completely ruled out.

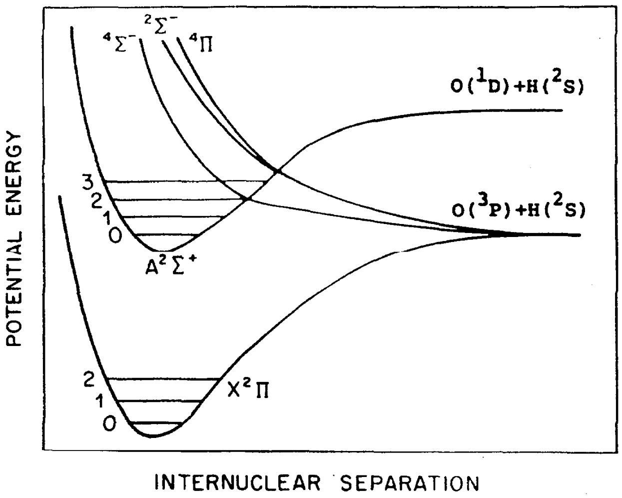

FIGURE 21. Potential energy curves for the low-lying electronic states of OH (from German, 1975b).

5.5.1. Radiation Lifetimes

Although extensively studied, the radiative lifetime of the low rotational levels in $v'=0,1$ and 2 still are uncertain to about 10%. The various data have been discussed by German (1975a) and are listed in table 20. An explanation for the discrepancies is not readily apparent. Values appear to be the same for $v'=0$ and 1. Lifetimes decrease rapidly at higher N levels in the regions of onset of predissociation (Elmergreen & Smith, 1972; Sutherland & Anderson, 1973). However, they are reasonably constant over the first 25 or so rotational states.

The suggested values have been assessed from the distribution of the data and are average values with the exception of one discarded datum point.

Table 19. Relative and dissociation energies of the low-lying electronic states of OH and OD.

		T_e	T_0 cm^{-1}	D_0^0	Reference
OH	$A^2\Sigma^+$	32,720	34,287	18,850	Dieke & Crosswhite, 1962
	$X^2\Pi_{3/2}$	0	1,847	35,420	Carlone & Dalby, 1969 Rosen, 1970
OD	$A^2\Sigma^+$	32,681	33,826	19,260	Carlone & Dalby, 1969
	$X^2\Pi_{3/2}$	0	1,349	35,870	Clyne et al., 1973 Coxon, 1975 Coxon & Hammersley, 1975

Table 20. Radiative lifetimes for OH($A^2\Sigma^+$) states, μs.

OH			OD				
v'=0	1	2[b]	v'=0	1	2	Method	Reference
0.770						Hanle effect	German & Zare, 1969
0.850	0.750	0.550				Phase shift	Smith, 1970
0.660			0.598			Hanle effect	DeZafra et al., 1971
0.753			0.751			Phase shift	Elmergreen & Smith, 1972
0.775	0.775					RF Excitation-decay	Sutherland & Anderson, 1973
0.83			0.82			Pulsed photolysis-decay	Becker & Haaks, 1973
0.58[a]			0.65			Hanle effect	German et al., 1973
0.82						Laser fluor.-decay	Becker et al., 1974
0.788			0.754			Laser fluor.-decay	Brophy et al., 1974
0.720	0.765					Laser fluor.-decay	Hogan & Davis, 1974
0.688			0.692			Laser fluor.-decay	German, 1975a
0.693	0.736	0.270	0.691	0.712	0.736	Laser fluor.-decay	German, 1975b
			0.800	0.77		RF Excitation-decay	Wilcox et al., 1975
0.76±0.07	0.76±0.04	-	0.72±0.06	0.74±0.04	0.74±0.04	Suggested values	

[a] Inconsistent with other values

[b] Strongly predissociated

5.5.2. Recommended Rate Constant Values

OH($A\,^2\Sigma^+$)

Electronic Quenching:	$k_{v'=1}$ slightly larger than $k_{v'=0}$, independent or very slight decrease with increasing N'.
Vibrational Relaxation:	Decreases significantly to higher N' values. Limited data, accuracy not established.
Rotational Relaxation:	Only limited data available, no pronounced N' dependence.

OD($A\,^2\Sigma^+$)

Electronic Quenching:	Values for $v'=1$ appear slightly larger than for $v'=0$, however only limited data are yet available.
Vibrational Relaxation:	$v'=2$ relaxes at approximately similar rates to $v'=1$ with N_2 and O_2. Only limited data.
Rotational Relaxation:	No data available.

Table 21. Summary of recommended rate constant values for OH($A^2\Sigma^+$), 300 K.

M	k_{elect}[a]	$k_{vib}(N'=0,1)$[b]	k_{rot}[c]
H_2O	$5.0(\pm 2.0)\times 10^{-10}$	fast	$\approx 2\times 10^{-10}$?
CO	$\approx 3\times 10^{-10}$	-	$\approx 5\times 10^{-11}$?
N_2	$2.2(^{+1.8}_{-1.2})\times 10^{-11}$	$\approx 1.7\times 10^{-10}$	$\approx 4\times 10^{-10}$
O_2	$\approx 1.0\times 10^{-10}$	$\approx 1.5\times 10^{-11}$	-
H_2	$9.2(\pm 3.5)\times 10^{-11}$	$\approx 1.7\times 10^{-10}$	$\approx 3\times 10^{-10}$
D_2	$7.0(\pm 5.0)\times 10^{-11}$	$\approx 2.1\times 10^{-10}$	$\approx 1.2\times 10^{-10}$?
He	$\leq 1\times 10^{-14}$	$\approx 1\times 10^{-12}$	$\approx 1\times 10^{-11}$?
Ar	$\leq 4\times 10^{-14}$	$\approx 3\times 10^{-12}$	$\approx 1.5\times 10^{-10}$

[a] Additional values of k_{elect} ($k_{CH_3OH} \approx 1.4\ k_{H_2O}$; $k_{CO_2} \approx 1.3\times 10^{-10}$; $k_{NO_2} \approx 3k_{H_2}$; $k_H \approx 5\times 10^{-10}$; $k_{air} \approx 4\times 10^{-11}$)

[b] A function of N'

[c] No pronounced N' dependence

Table 22. Summary of recommended rate constant values for $OD(A^2\Sigma^+)$, 295 K.

M	k_{elect}	$k_{vib}(N'=0,1)^a$
D_2O	$\simeq 4\times10^{-10}$	fast?
N_2	$\simeq 3.0\times10^{-11}$	$\simeq 1.2\times10^{-10}$
O_2	$\simeq 9\times10^{-11}$	$\simeq 3\times10^{-11}$
H_2	$\simeq 1.3\times10^{-10}$	$\simeq 1.7\times10^{-10}$
D_2	$\simeq 7\times10^{-11}$	$\simeq k_{H_2}$?

[a] A function of N'

5.5.3. Discussion

The collisional quenching of $OH(A\,^2\Sigma^+)$ is complicated by the fact that rotational and vibrational relaxation within the state compete with the electronic $A\,^2\Sigma^+ \rightarrow X\,^2\Pi$ radiationless transitions. The experimental technique determines as to which rates are measured. For example, monitoring radiation from a single rotational level in $v'=0$, other than $N'=0$, defines a rate constant which includes both the electronic and rotational relaxation effects ($k_{elect\ +\ rot}$). However, if the emission from adjacent rotational levels is included within the detector bandpass, only k_{elect} results, and the rotational relaxation does not affect the analysis. Consequently, to derive k_{elect} from $v'=1$ data requires an integral measure of radiation from both $v'=1$ and 0, otherwise $k_{elect\ +\ vib}$ will be measured ($v'=1$ radiation only) or $k_{elect\ +\ vib\ +\ rot}$ ($v'=1$, single N' radiation monitored).

As seen from table 23, various experimental techniques have been used for these measurements. Dye lasers or Bi line induced optical pumping specifically selects a particular vibronic state. However, less selective are exciting methods based on using OH discharge sources, short wavelength photolyses, Kr or Ar photosensitization, or e-beam dissociation of H_2O. These produce rotational distributions that peak at various N' values dependent on the available pumping energies or method used. Generally, the distributions can be described over various N' ranges by several high Boltzmann temperatures (Kaneko et al., 1969; Sokabe et al., 1971; Sokabe, 1972; Becker & Haaks, 1973; Mohlmann et al., 1976; Vinogradov & Vilesov, 1976; Masanet & Vermeil, 1977; Akamatsu & O-ohata, 1977; Lee & Judge, 1977). Whereas electronic and rotational relaxation rates are reasonably insensitive to N', vibrational relaxation shows a strong dependence.

a. Electronic Quenching, $OH(A\,^2\Sigma^+)$

Table 23 and figure 22 indicate the extensive studies made of the electronic collisional relaxation of $A\,^2\Sigma^+$. Data are available for quenching by 12 species, however, nearly all the reported studies are in the vicinity of room temperature. Of the two sets of higher temperature flame results Carrington's data involves a rather questionable and involved analysis (Hooymayers & Alkemade, 1967) and give values for H_2O, CO_2 and O_2 that are consistently low. The measurements of Hooymayers and Alkemade (1967) must be regarded as being approximate and a wide temperature average.

The earliest results by Neuimin and Terenin (1936) are not consistent with present day results.

There is insufficient data for $v'=1$ to indicate its general reactivity relative to $v'=0$. Slightly increased rates have been noted with N_2, H_2 and O_2 but a reduced rate with H_2O. Values initially reported by Hogan and Davis (1975) for $v'=1$ have since been shown to be invalid and refer rather to $v'=0$ (Lengel & Crosley, 1976; Hogan & Davis, 1976; German, 1976).

Room temperature data show about the least scatter for quenching by H_2O, values differing by a factor of three. Low and high N' data do not vary significantly. A mean value of $5.0(\pm2.0)\times10^{-10}$ cm^3 molecule^{-1} s^{-1} is suggested at room temperature. The flame result (Hooymayers & Alkemade, 1967) suggests a possible $T^{1/2}$ dependence.

The data for H_2 show a three and a half fold spread in values. High N' data appear to lie slightly below those for small N'. More recent findings confirm this very slight decrease between $N'=1$ and 5 (German, 1976). The data of Brophy et al. (1974) appear too large and may include effects due to the NO_2 present. Disregarding this measure a mean value of $k_{H_2} = 9.2(\pm3.5)\times10^{-11}$ is suggested. Only two independent values are reported for D_2, the high N' value having the smaller rate constant if valid; $k_{D_2} \cong 7.0(\pm5.0)\times10^{-11}$. Allowing for reduced mass differences these infer similar collision probabilities for H_2 and D_2.

Values with N_2 have an 8-fold scatter and are significantly lower than for other di- and triatomics. Wang and Davis' (1975) value for the ratio $k_{H_2O}:k_{N_2}$ is compatible with the other data. There is no significant difference between low and high N' values. An average value for $v'=0$ of $k_{N_2} = 2.2\,(^{+1.8}_{-1.2})\times10^{-11}$ is recommended. Hooymayers and Alkemade's (1967) flame N_2 value is too high for a $T^{1/2}$ dependence. Measurements for $v'=1$ with N_2 indicate a slightly increased rate (German, 1976).

Measurements with Ar are not well defined. However, the two upper limit estimates indicate $k_{Ar} < 7\times10^{-14}$ and $\leq 4\times10^{-14}$ (Kley & Welge, 1968; Black, 1976). Data for He are rather inconclusive with three orders of magnitude spread. The quenching is inefficient and susceptible to impurities.

Table 23. Rate constants for $OH(A^2\Sigma^+)v'=0,1$ electronic quenching (10^{-11} cm^3 $molecule^{-1}$ s^{-1})

Relaxing State	Quenchant						Exp. Temp. K	Method and Comments	Reference
	H_2O	N_2	H_2	He	Ar	Other			
v'=0		0.05	0.6		0.02	1.0(CO)	295	Photolysis H_2O, OH emission, total pressure 0.3-5.3 kPa. Not consistent with present values.	Neuimin & Terenin, 1936
v'=0,N' low	46				<2	18(CO_2) 8(O_2)	850-1500	C_2H_2/O_2 low pressures flames, 0.4-0.8 kPa, OH microwave discharge source induces fluorescence. Resolved fluorescence monitored. Corrected to τ 0.76 s. $k_{elect+rot}$. Questionable analysis.	Carrington, 1959
v'=0,N'≤25	61					85(CH_3OH)	315	Static system, 200 eV pulsed e-beam. OH emission via 315 nm filter, 20 nm FWHM. Total pressure H_2O or CH_3OH 0.7 Pa.	Bennett & Dalby, 1964
v'=0,N'=10,11	95	18				30(O_2)	1500-1790	$H_2/O_2/N_2$/Ar atm. pressure flames. Bi line induced fluorescence, filter 310 nm (20 nm FWHM). Corrected to τ 0.76 s. Approximate values.	Hooymayers & Alkemade, 1967
v'=0,N'≤20	50	4.0	6.0	1.0		4.0(D_2) 30(CO)	300	Flow system, Kr 123.6 nm photolysis of H_2O, (0,0) integrated OH emission, H_2O carrier gas, total pressure ≤0.5 kPa. k_{elect}	Kaneko et al., 1968
v'=0,N'≤20	29	0.51		<0.014	<0.007		295	Flow cell, Kr 123.6 nm photolysis of H_2O, OH emission resolved. $H_2O \simeq 30$ Pa, M≃0.67 kPa, k_{elect}.	Kley & Welge, 1968
v'=0,N'≤20	45	1.0	6.5	<0.1	0.1	64(CH_3OH)	295	Static and flow systems, Kr 123.6 nm pulsed photolysis of H_2O or CH_3OH at 0.1-13 Pa. Unresolved OH emission, (0,0) with 30 nm filter, (1,0) 8 nm filter. *$k_{elect+vib}$	Becker & Haaks, 1973
v'=1,N'≤15	40*								
v'=0,N' low	35	1.6		<0.6	<0.6		298	Discharge flow system, OH from $H+NO_2$, OH source induced fluorescence, resolved. He carrier gas, total pressure ≃0.3 kPa. Based on τ 0.76 μs.	Clyne & Down, 1974
v'=0, N'=2			7.1		0.05	50(H)	295	Flow system, 0.3 Pa OH from H+NO_2, dye laser fluorescence, resolved. Ar carrier gas, total pressure ≃0.13 kPa.	Becker et al., 1974
v'=0,N'=1			20.8				295	Flow cell, OH from $H+NO_2$, dye laser fluorescence, unresolved. H_2 carrier gas, total pressure 2-13 Pa.	Brophy et al., 1974
v'=0,N' low	$k_{H_2O}:k_{N_2}=44:1$						296	Flow system, dye laser 2 photon dissociation of H_2O and OH fluorescence. Atm. pressure air.	Wang & Davis, 1975

Table 23. Rate constants for $OH(A^2\Sigma^+)v'=0,1$ electronic quenching (10^{-11} cm^3 $molecule^{-1}$ s^{-1}) -- continued

Relaxing State	Quenchant H_2O	N_2	H_2	He	Ar	Other	Exp. Temp. K	Method and Comments	Reference
v'=0,N'=1			12			4.0(Air) 35(NO_2)	300	Flow cell, OH from HNO_3, dye laser fluorescence, unresolved 240-400 nm filter. Total pressure ≈2-60 Pa.	German, 1975a
v'=0,N' low		4.3	8.3			10(D_2)	320	Flow system, OH from HNO_3, dye laser fluorescence, total pressure ≈130 Pa.	Lengel & Crosley, 1975
v'=0,N' low		2.3	12.6	0.005_6	0.034		300	Flow cell, OH from O_3/H_2 photolysis, dye laser fluorescence unresolved, total pressure not specified.	Hogan & Davis, 1975, 1976
v'=0,N'=1		2.6	13.8			10.4(O_2)	295	Flow system, OH from $H+NO_2$, dye laser fluorescence resolved, use integrated intensity of vibrational bands. Total pressure ≤130 Pa.	German, 1976
=4		2.7	12.8			8.8(O_2)			
=5		2.5	12.7			8.5(O_2)			
v'=1,N'=1		3.0	14.3			15.7(O_2)			
=4		3.8	10.6			11.9(O_2)			
v'=0,1,N' high	92						300	Narrow band photolysis (in range 110-128 nm) of 1.3-21 Pa H_2O vapor. Unresolved emission monitored. Independent of exciting wavelength. Corrected to τ 0.76 μs.	Vinogradov & Vilesov, 1976
v'=0,1,N' high	56			≤0.001	≤0.004		300	Flow cell, 121.5 nm pulsed photolysis 0.3-13 Pa H_2O/270 Pa Ar. Experiments also with 50 kPa He and 13 kPa Ar. Unresolved emission monitored via 240-400 nm filter.	Black, 1976
v'=0,N' low		1.6				13(CO_2)	300	Flow cell, OH from $H+NO_2$ in excess He. Optically pumped with OH(0,0) lamp. 313.5 nm fluorescence unresolved (filter 5.5 nm FWHM) 10-23 Pa CO_2 or N_2, total pressures several hundred Pa. Corrected to τ 0.76 μs. $k_{elect+rot}$?	Erler et al., 1977
v'=0,N' low		4.2	8.3			10(D_2)	320	Flow system, OH from $H+NO_2$ (0.8 Pa H_2O/1.5 Pa NO_2). Pulsed dye laser fluorescence resolved, (1,0) lines pumped, (1,1), (0,0) monitored. Band intensities integrated. Quenchant ≤150 Pa. Converted to τ 0.76 μs. $k \propto \tau^{-1}$. Derived from analysis of vibrational relaxation data.	Lengel & Crosley, 1978

Consequently, Black's (1976) value of ≤ 1 × 10^{-14} is preferred.

German (1975a) reports a single measure of 4.0 × 10^{-11} for quenching with air which suggests, using k_{N_2} above, a value of about 1.1 × 10^{-10} for k_{O_2}. His later work (1976) indicates an average value for $N'=1$ to 5 of 9.2 × 10^{-11}. Based on these, a value of k_{O_2} = 1.0 × 10^{-10} is suggested at room temperatures. This supports the Hooymayers and Alkemade (1967) flame value over that of Carrington (1959) and indicates that O_2 is about four and a half times more efficient than N_2.

Only limited data are available for the remaining species. Both measures for CH_3OH indicate it to be 1.4 times more effective than H_2O, a value indicating a unit collision efficiency. NO_2 is measured as 3 times more efficient than H_2. Only one room temperature datum point exists for CO_2, 1.3 × 10^{-10}, but appears reliable. The one result for CO of 3 × 10^{-10} is consistent with its measured efficiencies relative to H_2O, H_2 and N_2.

The single value for atomic H, 5 × 10^{-10}, is probably reasonably accurate and indicates one of the most efficient quenching interactions measured. With this exception, efficiencies are in the expected order of polyatomics > diatomics > atoms.

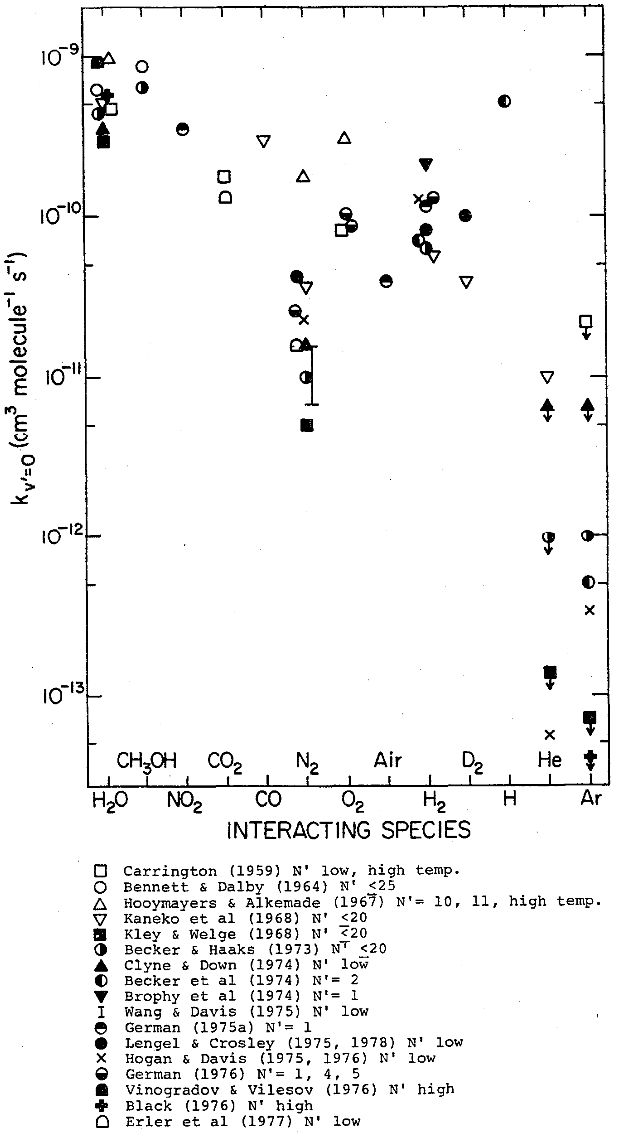

FIGURE 22. Rate constants for $OH(A\,^2\Sigma^+)_{v=0}$ electronic quenching with various interactants at 300 K.

b. Electronic Quenching, $OD(A\,^2\Sigma^+)$

There are only very limited data available for OD, table 24, but the values reflect those for the corresponding interactions of OH. As with k_{H_2}, the measure of k_{D_2} (Brophy et al., 1974) is probably a factor of two high due to additional quenching by NO_2. It may be better specified by a value $\cong 7 \times 10^{-11}$. Like $OH(A\,^2\Sigma^+)$, increased values for $v'=1$ have been reported for N_2, H_2 and O_2 but that for D_2O is slightly lower. The quenching mechanisms appear identical for $OH(A\,^2\Sigma^+)$ and $OD(A\,^2\Sigma^+)$.

c. Vibrational Relaxation, $OH(A\,^2\Sigma^+)$

Table 25 lists the more restricted numerical data for the vibrational relaxation of OH $A\,^2\Sigma^+$, some of which are also illustrated in figure 23. The results of Hogan and Davis (1975) are questionable and must be discarded (Lengel & Crosley, 1976; Hogan & Davis, 1976). Those of Lengel and Crosley (1975, 1978) and German (1976) are in substantial agreement for N_2 and H_2.

Values are available only with diatomics and atoms and show the latter's reduced efficiency for He and Ar. With the exception of O_2, vibrational relaxation proceeds at a significantly faster rate than electronic quenching.

Preliminary work concludes that vibrational relaxation by H_2O is of the order of or faster than electronic quenching (Wang et al., 1976; Killinger et al., 1976).

Lengel and Crosley (1977a, 1978) have studied these processes in considerable detail noting that the rates of vibrational relaxation are strongly dependent on the particular rotational state, N'. They have reported values for the levels $N'=0$-10 with H_2 and $N'=0$-13 with N_2. These decrease by factors of 2.7 and 8.0, respectively, over these rotational manifolds. However, there is no dependency on the particular electron spin component, values being the same for the levels $J = N \pm 1/2$.

Measurements have also been made using the much weaker $v'=2$ fluorescence (table 25). These indicate cross sections of a similar magnitude not only for the $\Delta v=1$ relaxation but also for the $\Delta v=2$ process. Relaxation by O_2 appears equally inefficient for $v'=2$ as for $v'=1$ but no quantitative data are available.

Vibrational relaxation with the diatomic species, with the exception of O_2, is essentially independent of the specific nature of the molecule. The relaxation produces a thermal but slightly hotter rotational distribution in the lower $OH(A\,^2\Sigma^+)$ vibrational state with no evidence of spin conservation propensity or rotational memory as was initially suggested (Lengel & Crosley, 1974). Consequently, a small fraction ($\sim 20-25\%$) of the vibrational energy decays to rotational quanta. Lengel and Crosley (1977a, 1978) find no evidence to support the possible isoenergetic transfer mechanisms some of which are essentially resonant to within a few wavenumbers, for example,

$$OH(A\,^2\Sigma^+, v'=1, N'=5) + M \rightarrow OH\,(A\,^2\Sigma^+, v'=0, N'=14) + M$$

$$(\qquad v'=1,\ N'=1) \qquad\qquad (\qquad v'=0,\ N'=13)$$

$$(\qquad v'=1,\ N'=15) \qquad\qquad (\qquad v'=0,\ N'=20)$$

Although such processes are expected to be quite plausible theoretically (Smith & Pack, 1972) and were inferred from earlier data (Welge et al., 1970) it now appears that they are not important.

The insignificance of direct resonant transfer mechanisms is further confirmed by the fact that although the D_2 vibrational energy spacing (2990 cm^{-1}) is almost coincident with that of $OH(A\,^2\Sigma^+$, 2989 cm^{-1}) it is no more effective than H_2 (vibrational quantum 4160 cm^{-1}). Atom exchange mechanisms such as

$$OH(A\,^2\Sigma^+, v'=1) + D_2 \rightarrow OD(A\,^2\Sigma^+, v'=0) + HD$$

$$OD(A\,^2\Sigma^+, v'=1) + H_2 \rightarrow OH(A\,^2\Sigma^+, v'=0) + HD$$

also are not evident (Lengel & Crosley, 1975, 1978).

Table 24. Rate constants for OD($A^2\Sigma^+$)v'=0,1 electronic quenching

(10^{-11} cm^3 $molecule^{-1}$ s^{-1})

Relaxing State	v'=0(N'≤26)	v'=1(N'≤26)	v'=0(N'=1)	v'=0(N'=1)	v'=0(N'=2)	v'=1(N'=1)	v'=0(N'=0-5)
D_2O	41	38*					
N_2				2.6		4.2	3.4
O_2				8.8	8.8	13.7	
H_2				15.4	13.9	20.4	12.0
D_2			14.1				
Exp. Temp. K	295		295	295			320
Method	Static and flow systems, Kr 123.6 nm pulsed photolysis of D_2O at 0.1-13 Pa. Unresolved OD emission, (0,0) with 30 nm filter, (1,0) 8 nm filter.		Flow cell, OD from $D+NO_2$, dye laser fluorescence, unresolved. D_2 carrier gas, total pressure 2-13 Pa.	Flow system, OD from $D+NO_2$, dye laser fluorescence resolved, use integrated intensity of vibrational bands. Total pressure ≤ 130 Pa.			Flow system, OD from $D+NO_2$ (0.8 Pa D_2O/ 1.5 Pa NO_2). Dye laser fluorescence resolved, (1,0) pumped (1,1)(0,0) monitored. Band intensities integrated. Quenchant ≤100 Pa.
Comments	$^*k_{elect}$ & vib		May include quenching by NO_2; too large.				Converted to τ=0.72 μs. $k \propto \tau^{-1}$.
Reference	Becker & Haaks, 1973		Brophy et al., 1974	German, 1976			Lengel & Crosley, 1978

Table 25. Rate constants for OH($A^2\Sigma^+$) v'=1,2 vibrational relaxation

(10^{-11} cm^3 $molecule^{-1}$ s^{-1})

Relaxing State	v'=1^a			v'=2(Δv=1)		v'=2(Δv=2)		v'=1$_*$	v'=1		v'=2(Δv=1)	v'=2(Δv=2)
	N'=0	3	5	N'=1	4	N'=1	4	N'=2*	N'=1	4	N'=1	N'=1
N_2	18.3	15.3	9.1	10.9	10.0	7.8	5.6	12	15	9.2	13	12
O_2									1.4	1.6		
H_2	17.4	14.4	10.9					28	18	12		
D_2	21.4	16.1	12.2									
He	.....	0.12	.....					≤0.005				
Ar	.....	0.29	.....					0.13				
Exp. Temp. K	320							300	295			
Method	Flow system, OH from $H+NO_2$ (0.8 Pa H_2O/ 1.5 Pa NO_2). Pulsed dye laser fluorescence resolved, (1,0), (2,1) pumped, integrated Δv=0 bands monitored. Quenchant ≤150 Pa. 5 G magnetic field to depolarize the fluorescence.							Flow cell, OH from O_3/H_2 photolysis. Dye laser fluorescence. Pressure unspecified.	Flow system, OH from $H+NO_2$. Dye laser resolved fluorescence, (3.5 nm bandpass) spectrometer. Total pressure ≤130 Pa.			
Comments	Converted to τ=0.76 μs, $k \propto \tau^{-1}$. Data for N'≤10(H_2) and N'≤13(N_2).							*Discard, questionable data (Lengel & Crosley, 1976; German, 1976)				
Reference	Lengel & Crosley, 1975, 1978							Hogan & Davis, 1975, 1976	German, 1976			

^{a}Additional values:

	N'=1,	2,	4,	6,	7,	8,	9,	10,	13
k_{N_2}	16.9	16.3	12.5	7.1	5.8	4.3	3.2	2.7	2.3
k_{H_2}	16.4	15.0	11.8	9.1	7.0	6.4	6.1	6.4	

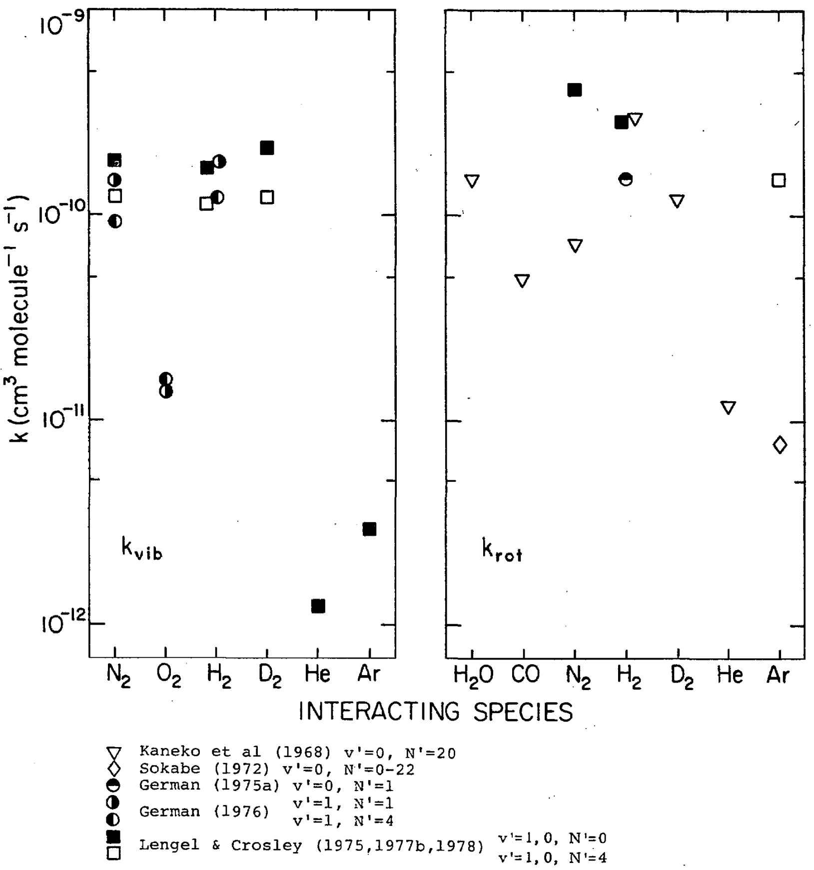

FIGURE 23. Rate constants for OH($A\,^2\Sigma^+$) vibrational and rotational relaxation, 300 K.

It is concluded that the vibrational relaxation mechanism involves a relatively long lived collision intermediate which provides for a redistribution of the available energy among the available internal degrees of freedom. It facilitates $\Delta v=2$ processes. The strong dependence on N' possibly derives from the formation dynamics being a function of orientation and consequently rotation of the species.

d. Vibrational Relaxation, OD($A\,^2\Sigma^+$)

Limited data are available for vibrational relaxation in OD($A\,^2\Sigma^+$) and are listed in table 26. Although only two independent studies have been reported, they are in substantial agreement. The values reflect those for OH($A\,^2\Sigma^+$) and vibrational relaxation occurs with an approximately equal probability per collision even though the vibrational spacings of OH($A\,^2\Sigma^+$) and OD($A\,^2\Sigma^+$) differ considerably. Data for $v'=2$ have been reported only by German (1976) and may be approximate owing to the more involved analysis. Consequently, their reported lower rate for $\Delta v=2$) may be suspect in the light of that for OH($A\,^2\Sigma^+$). It is very apparent that OH($A\,^2\Sigma^+$) and OD($A\,^2\Sigma^+$) relax by essentially identical mechanisms.

e. Rotational Relaxation, OH($A\,^2\Sigma^+$)

Until the recent and very extensive study of rotational relaxation within the $A\,^2\Sigma^+$ $v'=0$ state by Lengel and Crosley (1977b), available data were very limited and questionable, as is apparent from table 27 and figure 23. Nevertheless the rapid nature of the process with various species was noted. In the light of Lengel and Crosley's detailed study, previous measurements appear to be generally only qualitatively exact. For example, Sokabe's (1972) value for k_{Ar} is probably in error. Consequently these most recent values have to be regarded as the most reliable but unfortunately provide measures only with N_2, H_2 and Ar. The relative efficiencies of other species, particularly H_2O, CO and He remain in doubt.

By modeling the fluorescence intensities as a function of quenchant pressure, Lengel and Crosley (1977b) have been able in a very detailed and somewhat complex analysis to derive the specific transfer rates for all possible transitions with N_2, H_2 and Ar quenchants. Their data illustrating the rates of relaxation from a laser pumped rotational level to all others are listed in table 28. It shows various interesting features. Firstly, it is apparent that multiquantum transitions occur with a probability almost as large as single quantum changes, or in other words there are no strong propensity rules governing ΔN changes. Nevertheless, it may be added that $\Delta N=1$ transitions do still have a combined probability close to 50%, and rates to other N states decrease smoothly

Table 26. Rate constants for $OD(A^2\Sigma^+)v'=1,2$ vibrational relaxation (10^{-11} cm^3 $molecule^{-1}$ s^{-1})

Relaxing State	$v'=1(\Delta v=1)$ $N'=1$	$v'=2(\Delta v=1)$ $N'=1$	$v'=2(\Delta v=2)$ $N'=1$	$v'=1(\Delta v=1)$ $N'=0$	 3	 5
N_2	13	18	4.6	11.8	10.9	10.0
O_2	3.1	2.3	0.15			
H_2	10			16.5	14.3	12.4
Exp. Temp. K		295			320	
Method	Flow system, OD from $D+NO_2$, pulsed dye laser fluorescence resolved (3.5 nm band pass) spectrometer. Total pressure ≤ 130 Pa.			Flow system, OD from $D+NO_2$ (0.8 Pa D_2O/1.5 Pa NO_2). Pulsed dye laser fluorescence resolved, (1,0) pumped (1,1) (0,0) monitored. Quenchant ≤ 100 Pa.		
Comments	Analysis of $v'=2$ data more involved, values may be approximate.			Converted to $\tau=0.72$ μs.		
Reference	German, 1976			*Lengel & Crosley, 1978.*		

Table 27. Rate constants for $OH(A^2\Sigma^+)$ rotational relaxation (10^{-11} cm^3 $molecule^{-1}$ s^{-1})

Relaxing State	$v'=0$ $N'=20$	$v'=0$ $N'\leq 20$	$v'=0$ $N'=0-22$	$v'=0$ $N'=1$	$v'=0$ $N'=0$	 1	 3	 4	 6
H_2O	16								
CO	5.0								
N_2	7.5				41	45	47	41	41
H_2	31			16		29	28		
D_2	12								
He	1.2	$k_{He}=0.25\ k_{Ar}$							
Ar			0.79			15		13	
Exp. Temp. K	300	295	320	300			320		
Method	Flow system, Kr 123.6 nm photolysis of ≃150 Pa H_2O, OH emission resolved. Quenchant pressure ≤ 200 Pa.	Flow cell, Kr 123.6 nm photolysis of H_2O, OH emission. H_2O ≃30, M ≃670 Pa.	Flow system, microwave discharge, ≤ 1.3 kPa Ar sensitized decomposition of ≃5 Pa H_2O. OH emission resolved.	Flow cell, OH from $H+NO_2$, dye laser fluorescence total pressure ≃2-60 Pa.	Flow system, OH from $H+NO_2$ (0.8 Pa H_2O/1.5 Pa NO_2). Pulsed dye laser fluorescence resolved (0.07 nm bandpass). A specific low N' rotational level $N'=J-\frac{1}{2}$ in (0,0) pumped. $N'=0-6$. Quenchant ≤ 130 Pa.				
Comments	Difficult to measure k_{H_2O} and k_{CO} due to fast electronic quenching. Values increased by 25% to compensate for $N'=21\rightarrow 20$ relaxation.	$\Delta N=1$ most probable transition. $N'\sim 9-20$	Majority (~90%) in $v'=0$, rotational distribution has two maxima at $N'\sim 3$ and 10. Average value.	Approximate value.	Total rotational transfer rates out of the pumped level. Consists of many transitions (q.v. table 28).				
Reference	Kaneko et al., 1968	Kley & Welge, 1968	Sokabe, 1972	German, 1975a	Lengel & Crosley, 1975, 1977b				

Table 28. Specific rate constants k_{ij} for individual rotational transitions from the ith level to all other levels, j, in $OH(A^2\Sigma^+, v=0)$, (10^{-11} cm^3 $molecule^{-1}$ s^{-1}), from Lengel and Crosley (1977b)

M	i j	$F_1(0)$	$F_2(1)$	$F_1(1)$	$F_2(2)$	$F_1(2)$	$F_2(3)$	$F_1(3)$	$F_2(4)$	$F_1(4)$	$F_2(5)$	$F_1(5)$	$F_2(6)$	$F_1(6)$	$F_2(7)$	$F_1(7)$
N_2	$F_1(0)$	--	4.45	12.6	2.97	7.98	4.27	1.96	1.53	1.88	0.61	1.83	0.74	0.48	0.48	0.13
	$F_2(1)$	5.02	--	6.41	7.37	7.33	4.32	6.19	2.01	0.83	0.70	1.27	--	0.35	--	--
	$F_1(1)$	6.76	3.23	--	7.15	11.7	1.74	6.28	2.44	2.57	1.00	0.79	0.79	0.22	0.35	0.31
	$F_2(2)$	2.09	4.67	8.99	--	8.46	7.15	4.80	3.01	2.57	1.57	1.48	0.35	0.79	--	--
	$F_1(2)$	3.75	3.10	9.90	5.67	--	4.62	7.55	2.18	4.01	1.27	1.88	0.74	0.52	--	--
	$F_2(3)$	2.88	2.57	2.09	6.76	6.54	--	9.77	6.15	4.27	1.96	1.96	1.13	1.00	0.17	0.57
	$F_1(3)$	2.79	2.79	5.19	3.40	8.03	7.33	--	3.23	7.76	1.92	1.88	0.96	0.65	0.52	0.17
	$F_2(4)$	1.22	1.44	3.45	3.40	3.75	7.33	5.15	--	3.71	4.93	3.66	1.22	1.35	0.83	0.57
	$F_1(4)$	0.96	0.48	3.62	2.36	5.41	4.10	8.33	2.97	--	1.96	6.63	1.09	1.48	0.52	1.57
	$F_2(5)$	0.70	0.70	2.05	2.53	3.01	3.32	4.36	7.07	3.53	--	4.89	3.84	2.92	0.74	0.92
	$F_1(5)$	1.74	1.05	1.35	2.01	3.75	2.79	3.62	4.41	9.86	4.06	--	2.31	4.45	0.79	0.83
	$F_2(6)$	1.44	--	2.79	0.92	2.97	3.27	3.62	2.92	3.23	6.41	4.67	--	6.15	2.88	1.96
	$F_1(6)$	0.39	0.52	0.70	1.79	1.74	2.49	4.01	2.75	3.80	4.19	7.72	5.28	--	2.57	3.53
	$F_2(7)$	1.79	--	2.27	--	--	0.87	3.97	3.80	3.05	2.40	3.14	5.58	5.80	--	7.59
	$F_1(7)$	0.44	--	1.79	--	--	2.75	1.00	2.36	8.11	2.62	2.88	3.32	6.98	6.67	--
H_2	$F_1(1)$	4.54	3.14	--	3.45	6.76	1.44	3.75	1.74	1.92	0.57	0.39	0.35	0.35	0.24	0.17
	$F_1(3)$	2.22	0.48	3.45	2.18	5.54	3.45	--	1.70	4.06	1.05	1.92	0.96	0.48	0.13	0.87
Ar	$F_1(1)$	2.62	1.92	--	1.92	3.75	1.00	1.27	0.41	0.87	0.41	0.17	0.07	0.14	0.08	0.03
	$F_1(4)$	0.26	0.22	0.79	0.96	0.83	1.00	1.96	2.40	--	1.18	2.22	0.57	0.65	0.20	0.31

Levels in order of ascending energy $F_1(N')$, $J'=N'+\frac{1}{2}$; $F_2(N')$, $J'=N'-\frac{1}{2}$.
Based on $\tau(v'=0)=0.76$ μs, $k \propto \tau^{-1}$.

with increasing ΔN. Relaxation both up and down the rotational manifold occurs. A conservation of electron spin is noted and $\Delta N=\Delta J$ transitions are favored over $\Delta N \neq \Delta J$. This was also observed by Carrington (1960). Because the rotational spacing increases with N, being $\cong 33$ cm^{-1} for $N=0\text{-}1$, $\cong 320$ cm^{-1} for $N=9\text{-}10$ and $\cong 600$ cm^{-1} for $N=19\text{-}20$, some dependency on N might have been expected but is not at all pronounced. The earlier analysis of Kley and Welge (1968) indicating such a decreasing probability of relaxation with increasing N must be discounted.

With species such as H_2O, CO and O_2, rotational relaxation is of less importance and more difficult to measure owing to the fast electronic quenching. The latter also explains the apparent rotational population freezing and high rotational temperatures observed in some flames.

f. Mechanisms

For $OH(A\,^2\Sigma^+)$ the magnitude of the energies involved are $\cong 388$ kJ mol^{-1} (93 kcal mol^{-1}) for electronic quenching, 36 kJ mol^{-1} (8.6 kcal mol^{-1}) for vibrational relaxation, and $\cong 0.36\text{-}7.2$ kJ mol^{-1} (0.09-1.7 kcal mol^{-1}) for rotational relaxation.

In spite of possible chemical reaction pathways, the electronic interaction with the various molecules appears to induce physical quenching with relatively large cross sections and there is no indication at present of specific reactions although the possibility cannot be completely ruled out. With the exception of atomic H, the electronic quenching efficiencies follow the order polyatomic > diatomic > atoms. For a particular class of quenchant the cross sections do not vary by significantly large factors.

Whereas possible dissociative quenching is endothermic for $v'=0$

$$OH(A\,^2\Sigma^+, v'=0)+M \rightarrow O+H+M \quad \Delta H^\circ_{298\,K} = +35.6 \text{ kJ mol}^{-1} \; (+8.5 \text{ kcal mol}^{-1})$$

it is essentially resonant for $OH(A\,^2\Sigma^+, v'=1)$. However the very small difference noted between their respective cross sections negates its possible importance. Likewise, the endothermic reaction

$$OH(A\,^2\Sigma^+, v'=0)+H_2O=OH+OH+H \quad \Delta H^\circ_{298\,K} = +111 \text{ kJ mol}^{-1} \; (+26.6 \text{ kcal mol}^{-1})$$

has been reported as insignificant in flames (Hooymayers & Alkemade, 1967). Other possible mechanisms mentioned in the literature (Carrington, 1959; Kaneko et al., 1968; Becker et al., 1974) are:

$$\begin{aligned}
\mathrm{OH}(A\,{}^2\Sigma^+, v'=0)+\mathrm{H_2O} &= \mathrm{HO_2}+\mathrm{H_2} \quad \Delta H^\circ_{298\,\mathrm{K}} = -165\ \mathrm{kJ\ mol^{-1}}\\
&\qquad\qquad (-39.4\ \mathrm{kcal\ mol^{-1}})\\
\mathrm{O_2} &= \mathrm{HO_2}+\mathrm{O} \qquad\qquad = -157\ \mathrm{kJ\ mol^{-1}}\\
&\qquad\qquad (-37.6\ \mathrm{kcal\ mol^{-1}})\\
\mathrm{CO_2} &= \mathrm{HO_2}+\mathrm{CO} \qquad\qquad = -124\ \mathrm{kJ\ mol^{-1}}\\
&\qquad\qquad (-29.5\ \mathrm{kcal\ mol^{-1}})\\
\mathrm{NO_2} &= \mathrm{HO_2}+\mathrm{NO} \qquad\qquad = -349\ \mathrm{kJ\ mol^{-1}}\\
&\qquad\qquad (-83.5\ \mathrm{kcal\ mol^{-1}})\\
\mathrm{CO} &= \mathrm{CO_2}+\mathrm{H} \qquad\qquad = -493\ \mathrm{kJ\ mol^{-1}}\\
&\qquad\qquad (-118\ \mathrm{kcal\ mol^{-1}})\\
\mathrm{H_2} &= \mathrm{H_2O}+\mathrm{H} \qquad\qquad = -451\ \mathrm{kJ\ mol^{-1}}\\
&\qquad\qquad (-108\ \mathrm{kcal\ mol^{-1}})\\
\mathrm{H} &= \mathrm{O(^1D)}+\mathrm{H_2} \qquad\qquad = -206\ \mathrm{kJ\ mol^{-1}}\\
&\qquad\qquad (-49.3\ \mathrm{kcal\ mol^{-1}})
\end{aligned}$$

With the possible exception of the last one, which is allowed and has a $^1A'$ correlating surface (Donovan & Husain, 1970), these all appear unlikely.

Likewise vibrational relaxation seems to be controlled by physical processes. Lengel and Crosley (1977a, 1978) have ruled out the possible importance of isoenergetic V–V processes within $A\,{}^2\Sigma^+$ or possible atom exchange mechanisms with H_2 or D_2. The same also appears to be the case for rotational relaxation.

5.5.4. References

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5.6. Oxygen, $O_2(c\,^1\Sigma_u^-, C\,^3\Delta_u, A\,^3\Sigma_u^+, B\,^3\Sigma_u^-)$

5.6.1. Available Rate Data for $O_2(B\,^3\Sigma_u^-\, C\,^3\Delta_u, c\,^1\Sigma_u^-, b\,^1\Sigma_g^+, a\,^1\Delta_g)$

Evaluations of chemical kinetic rate data for some of the interactions of the $O_2(b\,^1\Sigma_g^+, a\,^1\Delta_g)$ states have been published previously by Wayne (1969), Kearns (1971), Hampson et al. (1973) and Davidson and Ogryzlo (1973). These will be updated by the author in the near future.

No kinetic data are available for the $C\,^3\Delta_u$, $c\,^1\Sigma_u^-$, or $B\,^3\Sigma_u^-$ states of oxygen. Consequently an evaluation of measured values is presented solely for $A\,^3\Sigma_u^+$.

The short radiative lifetime of about 40 ns for the $B^3\Sigma_u^-$ state (table 29) imples that collisional quenching or reaction will only be of importance at higher pressures. The time between gas kinetic collisions will be approximately comparable to this lifetime at pressures of about 350 Pa.

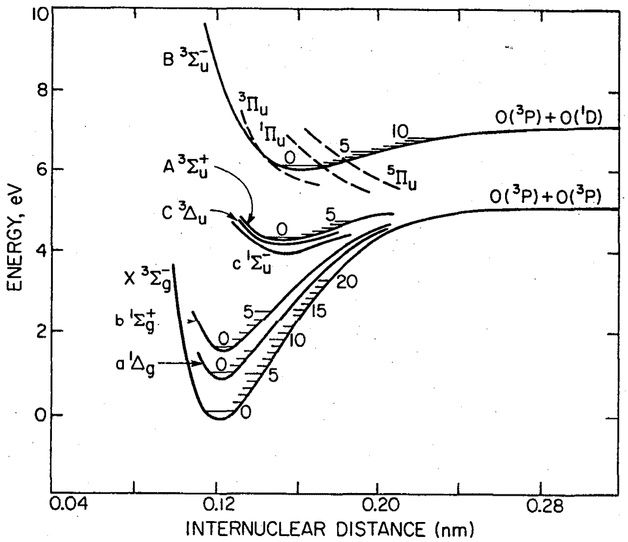

FIGURE 24. Potential energy curves for the low-lying states of molecular oxygen (from Krupenie, 1972 and Buenker et al., 1976).

5.6.2. Radiative Lifetimes

Other than the $B\,^3\Sigma_u^-$ - $X\,^3\Sigma_g^-$ Schumann-Runge system, all transitions between the low lying states of oxygen are forbidden as reflected by their long radiative lifetimes.

Vibrational levels of $B\,^3\Sigma_u^-$ above $v'=2$ are predissociated predominantly by crossing of the $^5\Pi_u$ repulsive state (Julienne & Krauss, 1975). Estimates for the $A\,^3\Sigma_u^+$ lifetime have varied over several orders of magnitude (Krupenie, 1972). However, the absolute absorption coefficient measurements of Hasson et al. (1970) imply a reasonably reliable value of about 0.2 s.

No specific lifetime measurements have been made for the $C\,^3\Delta_u$ or $c^1\Sigma_u^-$ states.

5.6.3. Oxygen, $O_2(A\,^3\Sigma_u^+)$

a. Suggested Rate Constant Values, 200–300 K

Experimental values (k_{obs}) refer to $k_1/(k_M\tau)$ where k_1 relates to the rate of formation of $O_2(A\,^3\Sigma_u^+)$ from the recombination reaction O + O + M, and τ and k_M describe the radiative and collisional quenching processes. k_M values cannot be extracted without assumptions concerning the magnitude of k_1.

$$k_{obs} \cong 2.5 \times 10^{-21}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ (N_2, O_2)$$
$$\cong 2.5 \times 10^{-20}\qquad (\text{He, Ar})$$

Values for k_M follow the order

$$k_{N_2O,\,CO_2,\,O} > k_{N_2,\,O_2} > k_{He,\,Ar}.$$

Table 29. Energies and radiative lifetimes of the low-lying electronic states of molecular oxygen.

	T_e	$T_0{}^a$ cm^{-1}	D_0^0	τ s	Reference
$B^3\Sigma_u^-$	49,794.33	50,145.53	7,770	$40x10^{-9}$	Nicholls, 1964
$A^3\Sigma_u^+$	35,398.70	35,794.53	6,253	≈0.2	Hasson et al., 1970; Degen, 1977
$C^3\Delta_u$	34,735	35,106	6,941	$>10^5$?	Krassovsky et al., 1962
$c^1\Sigma_u^-$	33,058.4	33,451.5	8,596	$\approx 10^4$?	
$b^1\Sigma_g^+$	13,195.31	13,908.29	28,139	11	Krupenie, 1972
$a^1\Delta_g$	7,918.11	8,669.77	33,378	2700	Badger et al., 1965
$X^3\Sigma_g^-$	0	787.38	41,260	-	

[a] Krupenie, 1972

b. Discussion, $O_2(A\,^3\Sigma_u^+)$

This state is monitored invariably via its forbidden and consequently weak Herzberg I band emission in the 250 to 500 nm region (Degen et al., 1968; Degen, 1977). The system is a major contributor to the atmospheric ultraviolet nightglow for which bands up to about $v'=10$ are observed (Krassovsky et al., 1962; Hennes, 1966; Degen, 1969). This indicates that vibrational relaxation within the state is less important in air than electronic quenching or radiation.

The available kinetic rate data for collisional quenching are listed in table 30 and are in a somewhat unsatisfactory

Table 30. Measured Herzberg $(A^3\Sigma_u^+ - X^3\Sigma_g^-)$ chemiluminescent reaction rate coefficient, $I_{Herzberg} = k_{obs}\,[O]^2$, and deduced values for $O_2(A^3\Sigma_u^+)$ collisional quenching constants, k_M.

M	k_{obs}	$k_M{}^a$ $cm^3 molecule^{-1} s^{-1}$	Exp. Temp. K	Method	Reference
N_2	-	Quenching effects observed for CO_2, N_2O and O_2.	300	Microwave discharge N_2 flow system. O from addition 1% excess NO. 310-380 nm unresolved emission. 130-1600 Pa N_2 pressure.	Young & Sharpless, 1963
N_2	$2.3x10^{-21}$	$3.3x10^{-13}$	300	Microwave discharge flow system in N_2 and 1% N_2/Ar or He mixtures. $72x10^3$ cm^3 bulb, residence time ≈1 s. O from N+NO titration. 310-380 nm unresolved emission. ≤1070 Pa total pressure.	Young & Black, 1966
N_2O	-	$4.7x10^{-12}$			
		$k_{N_2}/k_{N_2O}=0.07$			
N_2	$3x10^{-21}$	$8.3x10^{-13}$	200	Combination of rocket data for intensity of atmospheric Herzberg bands and mean [O] in 90-100 km region.	Vlasov, 1969
O	-	$\approx 5x10^{-12}$			
N_2		$\approx 1.5x10^{-12}$	200	Value required to reproduce profiles of 85-120 km rocket nightglow data for 557.7 nm and Herzberg emissions. $k_M\tau \approx 3x10^{-13}$.	Gadsden & Marovich, 1969
O_2	$2.5x10^{-21}$	$3x10^{-13}$	300	Microwave discharge flow system with O_2 and O_2/He or Ar mixtures. [O] by NO_2 titration. Resolved emission 260-420 nm, includes bands with v'=1-9. 130-1330 Pa pressure. Reduced quenching in He and Ar mixtures makes k_{obs} pressure dependent. No pronounced vibrational relaxation.	McNeal & Durana, 1969
N_2	-	$<6x10^{-14}$			
		$k_{N_2}<0.2k_{O_2}$			
CO_2		$k_{CO_2}>k_{O_2}$			
He, Ar	$\approx 2.5x10^{-20}$[b]				

[a] k_M refers to $O_2(A^3\Sigma_u^+)+M=O_2+M$.

Values calculated based on Barth's mechanism, $k_M=k_1/(k_{obs}\tau)$ taking $\tau=0.2$ s and assuming $k_1 \approx 5x10^{-34}$ (200 K) and $1.5x10^{-34}$ (300 K) $cm^6 molecule^{-2} s^{-1}$ for $M=O_2$, N_2, He, Ar (see discussion).

[b] Pressure dependent, quenching not dominant.

state since their absolute values depend on several factors. The rate constant, k_{obs}, is the value generally measured and describes the overall chemiluminescent reaction that relates the intensity of the Herzberg bands to the oxygen atom concentration

$$I_{\mathrm{Herzberg}} = k_{\mathrm{obs}}[\mathrm{O}]^2.$$

It represents a measure of the excitation and deactivation processes operative in the system. The detailed mechanism suggested by Barth (1964) now is accepted as satisfactorily modeling the detailed kinetics:

$$\begin{aligned}
\mathrm{O} + \mathrm{O} + \mathrm{M} &\overset{k_1}{=} \mathrm{O}_2\,(A\,^3\Sigma_u^+) + \mathrm{M}\\
\mathrm{O}_2(A\,^3\Sigma_u^+) + \mathrm{M} &\overset{k_{\mathrm{M}}}{-} \mathrm{O}_2 + \mathrm{M}\\
\mathrm{O}_2(A\,^3\Sigma_u^+) + \mathrm{O} &\overset{k_{\mathrm{O}}}{=} \mathrm{O}_2 + \mathrm{O}\\
\mathrm{O}_2(A\,^3\Sigma_u^+) &\overset{1/\tau}{=} \mathrm{O}_2 + h\nu\\
\mathrm{O}_2(A\,^3\Sigma_u^+) + \mathrm{wall} &\overset{k_{\mathrm{w}}}{=} \mathrm{O}_2.
\end{aligned}$$

A steady state analysis leads to the following expression for the intensity of the Herzberg emission:

$$I_{\mathrm{Herzberg}} = \frac{k_1[\mathrm{M}]\,[\mathrm{O}]^2}{1 + \tau(k_{\mathrm{M}}[\mathrm{M}] + k_{\mathrm{O}}[\mathrm{O}] + k_{\mathrm{w}})}.$$

For the laboratory data with N_2 and O_2 quenchants, k_{obs} is independent of pressure in the measured 130–1330 Pa range, indicating that the quenching term in the denominator is dominant and k_{obs} relates directly to $k_1/(k_{\mathrm{M}}\tau)$. The value of k_1 remains unknown. It is possible, as noted in figure 24, that recombining O atoms may channel into any of the six possible electronic states of O_2. If these were populated according to their various degeneracies it would suggest a 19% probability for the channel producing $\mathrm{O}_2(A\,^3\Sigma_u^+)$. However, it seems more likely that the more strongly bound states are favored and the actual probability may be in the 1–10% range (Slanger & Black, 1977). The rate constant for the overall recombination process is

$$\begin{aligned}
\mathrm{O} + \mathrm{O} + \mathrm{M} \rightarrow \mathrm{O}_2 + \mathrm{M} \quad k_{\mathrm{N}_2} &\cong 10 \times 10^{-33}\ \mathrm{cm}^6\ \mathrm{molecule}^{-2}\ \mathrm{s}^{-1}\ (200\ \mathrm{K})\\
&\cong 3 \times 10^{-33} \qquad (300\ \mathrm{K})
\end{aligned}$$

with third body efficiencies ($k_{\mathrm{Ar}}:k_{\mathrm{O}_2}:k_{\mathrm{N}_2} = 1:1:1.9$) being somewhat uncertain (Baulch et al., 1976). This places an upper limit on the magnitude of k_1 and, neglecting any third body effects, a 5% probability leads to those values of k_{M} listed in table 30. Until k_1 becomes better known, together with its M dependency, a detailed analysis of the data does not appear merited. Nevertheless, some relative measures for k_{M} are available, namely

$$k_{\mathrm{N_2O}}/k_{\mathrm{N}_2} \cong 14 \qquad k_{\mathrm{O}} \text{ may be significant}$$

$$k_{\mathrm{O}_2}/k_{\mathrm{N}_2} > 5 \qquad k_{\mathrm{He,\,Ar}} \text{ small}$$

$$k_{\mathrm{CO}_2} > k_{\mathrm{O}_2}.$$

These suggest the general ordering for k_{M} of

$$k_{\mathrm{N_2O,\,CO_2,\,O}} > k_{\mathrm{N_2,\,O_2}} > k_{\mathrm{He,\,Ar}}.$$

In the case of He and Ar, McNeal and Durana (1969) found that k_{obs} was pressure dependent, indicating that collisional quenching is no longer a dominant factor in such systems and a different rate expression is appropriate. This was also indicated in the resolved spectrum which included bands originating from $v'=1$ to 9. Vibrational relaxation within the $A\,^3\Sigma_u^+$ state was much more important in O_2/He or Ar mixtures than in pure oxygen.

The value for k_{O} derived by Vlasov (1969) from a comparison of the atmospheric nightglow intensities of the $\mathrm{O}(^1\mathrm{S})$ 557.7 nm and Herzberg emissions is based on the assumption that quenching by atomic oxygen produces predominantly $\mathrm{O}(^1\mathrm{S})$

$$\mathrm{O}_2(A\,^3\Sigma_u^+) + \mathrm{O} = \mathrm{O}_2 + \mathrm{O}(^1\mathrm{S}) \quad \Delta H^\circ_{298\,\mathrm{K}} = -14.5\ \mathrm{kJ\ mol}^{-1}\ (-3.5\ \mathrm{kcal\ mol}^{-1})$$

Slanger and Black (1976; 1977) have most recently discussed the relative merits of the Barth and Chapman mechanisms for $\mathrm{O}(^1\mathrm{S})$ production. If $\mathrm{O}_2(A\,^3\Sigma_u^+)$ is the precursor state, their data imply that $k_{\mathrm{O}} \gg k_{\mathrm{N}_2}$.

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5.7. Atomic Phosphorus $P(3^2D_{3/2,5/2}, 3^2P_{1/2,3/2})$

Only limited kinetic data are yet available for these low lying metastable states. Although reaction products have not yet been measured, the probability of reaction versus physical quenching has been tentatively inferred from an analysis of the correlation diagrams.

5.7.1. Recommended Rate Constant Values

Only single datum points, at 300 K, are available for each interaction and are listed in table 32. No products have been monitored and the suggested nature of the interactions is speculative.

Chemical reaction:

CH_4	probable	PCl_3	fast reaction
CF_3H	H abstraction possible?	CO_2	reaction for $P(^2D)$
CF_3Cl	Cl abstraction possible	NO	reaction to PN + O for $P(^2D)$?
C_2H_6	fast reaction	O_2	fast reaction
C_2H_4	fast addition mechanism	H_2	reaction for $P(^2D)$
C_3H_6	fast addition mechanism	HCl	two reactive channels for $P(^2D)$ $P(^2P)$ may produce $PH(^1\Delta) + Cl$
C_2H_2	fast addition mechanism		
N_2O	two reactive channels	Cl_2	fast reaction
NH_3	fast reaction probable		

Physical quenching:

CF_4, CF_3H?, SF_6, CO, N_2, He, Ar, Kr, Xe for $P(^2D, ^2P)$.
CO_2, NO?, H_2? with $P(^2P)$ only.

5.7.2. Discussion

The only reaction rate data for the metastable states of phosphorus have been generated in three related studies using the same flash photolysis-atomic absorption technique. Experimental conditions essentially remained the same and data were obtained only at 300 K.

The most recent of these studies (Acuna et al., 1973b) included an examination of the effective second order rate constants for the individual $^2P_{1/2}$,$^2P_{3/2}$ levels by resolving the 253.40 and 253.57 nm absorption transitions. The values were identical, indicating either similar specific rates for the two states or confirming the rapid equilibration that is expected between the components of the $^2D_{3/2,\,5/2}$ and $^2P_{1/2,\,3/2}$ states which are separated by only 15.6 and 25.3 cm^{-1}, respectively.

Correlation diagrams are again a useful means of explaining the variations in the measured rate data for diatomic molecules. With the more complex polyatomics, where in general such diagrams cannot be readily constructed, the decay of $P(^2D)$ and $P(^2P)$ states appear to proceed with comparable rates. It is expected that correlations for atomic phosphorus will not be quite as restrictive as those for atomic nitrogen states owing to the slightly larger spin-orbit coupling with the heavier phosphorus atom which will facilitate some mixing of A′ and A″ surfaces.

These studies did not monitor the products and could not therefore distinguish directly between chemical or physical quenching processes. Nevertheless, in many cases possible mechanisms can be inferred from considerations of the reaction enthalpy and the availability of correlating surfaces. However, it cannot be resolved as to whether nonadiabatic transitions proceed to products or are purely physical quenching.

Table 33 lists the calculated enthalpy changes for possible reactions that might occur. Kinetic data for ground state $P(^4S_{3/2})$ have also become available recently (Husain & Norris, 1977a, b). Its inefficient interactions with H_2, CO, NH_3 and C_2H_6 result in part from unfavorable reaction enthalpies. Likewise, reactions of $P(^2D)$ and $P(^2P)$ with CO and N_2 are sufficiently endothermic to rule out reaction as indicated. Consequently, CO is quite notable in that it quenches $P(^2D)$ efficiently.

a. $P(^2D,^2P)$ + CH_4, CF_4, CF_3H, CF_3Cl, C_2H_6, C_2H_4, C_3H_6, C_2H_2, SF_6

In spite of favorable energetics, CF_4 and SF_6 are inefficient in quenching either $P(^2D)$ or $P(^2P)$ and are in sharp contrast to the behavior with CH_4. The processes involved with CF_3H and CF_3Cl are uncertain but H or Cl abstraction reactions appear favored if chemical channels are operative.

Although not yet fully characterized for atomic nitrogen, chemical reactions with hydrocarbons appear equally likely for phosphorus. The fast quenching of $P(^2D,^2P)$ by C_2H_4, C_3H_6 and C_2H_2 presumably arises through initial addition across the unsaturated bonds, possibly leading to ring formation rather than by H abstraction.

b. $P(^2D, ^2P)$ + N_2O

The rather interesting order of reactivity with N_2O, $P(^2D) > P(^2P) > P(^4S)$ reflects that of the corresponding states of atom nitrogen. Moreover, correlation diagrams similarly illustrate the availability of exothermic surfaces in all cases, figure 25, but differ from nitrogen in that alternate channels are possible to either PN + NO or PO + N_2 products. The diagram originally published by Acuna et al. (1973b) for PN + NO products has been modified since it neglected to in-

Table 31. Energies and radiative lifetimes of low-lying electronic states of atomic phosphorus.[a]

Electronic State	Energy Level (cm^{-1})	Radiative Lifetime (s)
$^2P_{3/2}$	18,748.0	3.4
$^2P_{1/2}$	18,722.7	5.1
$^2D_{5/2}$	11,376.4	5.0×10^3
$^2D_{3/2}$	11,360.8	3.4×10^3
$^4S_{3/2}$	0.0	-

[a] Wiese et al., 1969

Table 32. Rate constants for interactions of $P(3^2D_{3/2,\,5/2},\ 3^2P_{1/2,\,3/2})$, $cm^3\ molecule^{-1}\ s^{-1}$, 300 K

M	^2D_J	^2P_J	M	^2D_J	^2P_J
CH_4	$1.1(\pm0.1)x10^{-11}$	$2.8(\pm0.5)x10^{-12}$	CO	$1.5(\pm0.4)x10^{-11}$	$7(\pm6)x10^{-16}$
CF_4	$7.3(\pm0.8)x10^{-15}$	$5x10^{-15}$	NO	$5.5(\pm0.6)x10^{-11}$	$3.0(\pm0.5)x10^{-11}$
CF_3H	$3.9(\pm0.7)x10^{-13}$	$1.9(\pm0.2)x10^{-12}$	N_2	$<5x10^{-16}$	$<5x10^{-16}$
CF_3Cl	$1.5(\pm0.1)x10^{-11}$	$2.0(\pm0.3)x10^{-12}$	O_2	$1.4(\pm0.2)x10^{-11}$	$2.6(\pm0.2)x10^{-11}$
C_2H_6	$6.0(\pm0.7)x10^{-11}$	$2.7(\pm0.5)x10^{-11}$	H_2	$4.0(\pm0.7)x10^{-12}$	$3.1(\pm0.8)x10^{-13}$
C_2H_4	$1.5(\pm0.1)x10^{-10}$	$4.2(\pm1.2)x10^{-11}$	HCl	$2.4(\pm0.2)x10^{-11}$	$6.0(\pm0.3)x10^{-12}$
C_3H_6	$1.3(\pm0.1)x10^{-10}$	$1.4(\pm0.2)x10^{-10}$	Cl_2	$1.8(\pm0.2)x10^{-11}$	$2.9(\pm0.4)x10^{-11}$
C_2H_2	$8.7(\pm0.7)x10^{-11}$	$3.6(\pm0.4)x10^{-11}$	He	$<5x10^{-16}$	$<5x10^{-16}$
N_2O	$1.2(\pm0.2)x10^{-11}$	$3.1(\pm0.6)x10^{-13}$	Ar	$<5x10^{-16}$	$<5x10^{-16}$
PCl_3	$9.7(\pm0.9)x10^{-11}$	$1.1(\pm0.1)x10^{-10}$	Kr	$2.6(\pm1.1)x10^{-15}$	$<5x10^{-16}$
SF_6	$1.5(\pm0.3)x10^{-15}$	$2.4(\pm0.5)x10^{-14}$	Xe	$1.7(\pm0.3)x10^{-11}$	$2.0(\pm0.3)x10^{-13}$
CO_2	$3.3(\pm1.0)x10^{-12}$	$7.3(\pm1.9)x10^{-14}$			
Method	Vacuum uv flash photolysis, λ>160 nm Kr lamp 905-980 J. Static system, 0.1-0.2 Pa PCl_3 in excess He at 3.33 kPa. Atomic absorption, monitoring [^2D] by 213.55, 213.62 nm and [^2P] by 253.40, 253.57 nm lines using flowing microwave discharge line source.				
Comments	First order kinetic analysis, valid assumption of negligible cascading from ^2P to ^2D states, [^2D]:[^2P]≃10:1 initially. Data for resolved $^2P_{3/2}$ level.				
Reference	Acuna & Husain, 1973; Acuna et al., 1973a, b.				

Table 33. Enthalpies for possible reactions of atomic phosphorus, $\Delta H^{o}_{298\ K}$ kJ mol^{-1}.

Reaction	Reactant $P(^4S_{3/2})$	$P(^2D)$	$P(^2P)$
$P+CH_4 = PH+CH_3$	+140	+4.2	-83.9
$P+CF_4 = PF+CF_3$	+70.5	-65.5	-154
$P+CF_3H = PH+CF_3$	+138	+1.7	-86.4
$= PF+CF_2H$	≃+70	≃-65	≃-150
$P+CF_3Cl = PCl + CF_3$	+36.8	-99.3	-187
$= PF + CF_2Cl$	≃+70	≃-65	≃-150
$P+C_2H_6 = PH+C_2H_5$	+109	-27.0	-115
$P+C_2H_4 = PH+C_2H_3$	+147	+11.1	-77.0
$P+C_3H_6 = PH+C_3H_5$	+45.3	-90.7	-179
$P+C_2H_2 = PH+C_2H$	+170	+33.9	-54.2
$= HCP+CH$	+201	+64.9	-23.2
$P+N_2O = PN+NO$	-221	-357	-445
$= PO+N_2$	-428	-564	-652
$P+NH_3 = PH+NH_2$	+133	-2.8	-90.9
$P+PCl_3 = PCl+PCl_2$	≃0	≃-136	≃-224
$P+SF_6 = PF+SF_5$	-156	-292	-380
$P+CO_2 = PO+CO$	-63.0	-199	-287
$P+CO = CP+O$	+493	+357	+269
$= PO+C$	+480	+344	+255
$P+NO = PN+O$	-70.2	-206	-294
$= PO+N$	+36.4	-99.6	-188
$P+N_2 = PN+N$	+244	+108	+19.4
$P+O_2 = PO+O$	-96.8	-233	-321
$P+H_2 = PH+H$	+138	+1.7	-86.4
$P+HCl = PH+Cl$	+133	-2.7	-90.8
$= PCl+H$	+123	-13.1	-101
$P+Cl_2 = PCl+Cl$	-66.1	-202	-290

clude the PN($^3\Sigma_u^+$, $^3\Pi$) states which undoubtedly exist. Although not yet characterized, these may lie, by comparison with isoelectronic CS, P_2, SiO and N_2 molecules, at about 30,000 to 35,000 cm^{-1} above PN($X\,^1\Sigma^+$). This illustrates the care that sometimes has to be taken to include all possible low lying electronic states in such correlations otherwise some adiabatic surfaces may be overlooked. According to the exact ordering of these PN($a\,^3\Sigma^+$, $b\,^3\Pi_g$) states, P(^{2}D) and P(^{2}P) + N_2O correlate either to both of these or to $b\,^3\Pi_g$ only.

Likewise, this same problem arises in deriving the exact correlation diagram for the highly exothermic reactions producing PO electronic states. Although much progress has been made in identifying the nature of its low lying states (Verma et al., 1971; Verma & Singhal, 1975) the exact position of the lowest $a\,^4\Pi$ state is uncertain although certainly below $B\,^2\Sigma^+$ (Roche & Lefebvre-Brion, 1973; Tseng & Grein, 1973). It has been assumed here to lie ≅25,000 cm^{-1} (≅300 kJ mol^{-1}) above the ground state. Of more consequence is the potential importance of the theoretically predicted but as yet unobserved $^2\Phi$ bound state at about 30,000 cm^{-1}. Nevertheless, in spite of these uncertainties, numerous exothermic surfaces are undoubtedly available and by comparison with atomic nitrogen, chemical reaction is very probable by any of these allowed processes. The unreactive nature of the ground ($^4S_{3/2}$) state and the inefficient interaction with (^{2}P) remains unexplained for phosphorus and nitrogen atoms.

c. P(^{2}D, ^{2}P) + NH_3

The reaction of ground state P($^4S_{3/2}$) with NH_3 is endothermic by ≅ 130 kJ mol^{-1} (≅30 kcal mol^{-1}), $k_{298\ K} < 5 \times 10^{-15}$ (Husain & Norris, 1977b). However, possible reactions for P(^{2}D, ^{2}P) are exothermic (table 33) and although not yet studied, comparison with N(^{2}D) ($k_{298\ K} \cong 5 \times 10^{-11}$) indicates that fast chemical interactions might be expected.

d. P(^{2}D, ^{2}P) + CO_2

Figure 26 illustrates the available surfaces for P(^{2}D) and the necessary nonadiabatic transition for P(^{2}P) which are in accord with the measured rate constants and with the behavior of atomic nitrogen. The rate constant for P(^{2}D) most probably refers to this chemical reaction and may indicate a small activation energy.

e. P(^{2}D, ^{2}P) + NO

These interactions are very efficient, are similar for P(^{2}D) and P(^{2}P), and identical with the corresponding reactions of atomic nitrogen. It suggests that the same mechanism may be operative for both P(^{2}D) and P(^{2}P). Considering the probable chemical channels, possible products are PN + O or PO + N. However, exothermic adiabatic surfaces are available for P(^{2}D) only to PN + O(^{3}P, ^{1}D) and are probably the preferred pathway for this state (Husain & Norris, 1977a). Likewise, the fast interaction of P(^{2}P) with NO is not in accord with either correlation diagram based on these weak spin orbit coupling approximations and indicates the availability of only endothermic surfaces unless the predicted PN($b\,^3\Pi$) state lies ≤ 25,000 cm^{-1} above its ground state.

f. P(^{2}D, ^{2}P) + O_2

Although there is a slightly different ordering of reactant states in figure 27 from the corresponding correlation diagram for atomic nitrogen, the exothermic surfaces connecting P(^{2}D, ^{2}P) to PO + O(^{3}P, ^{1}D) have a similar appearance and indicate allowed transitions in both cases. Fast chemical reactions are implied. The exact energy positioning of the PO($a\,^4\Pi$) state is still uncertain and pathways to this may or may not be exothermic.

g. P(^{2}D, ^{2}P) + H_2

The correlation diagram with H_2 (Acuna et al., 1973a) is basically identical to that for N + H_2, figure 19. It predicts one approximately thermoneutral adiabatic surface for P(^2D_J), with a small activation energy, leading to ground state products, and only nonadiabatic curve crossing transitions for P(^2P_J), which might result in either chemical or physical quenching.

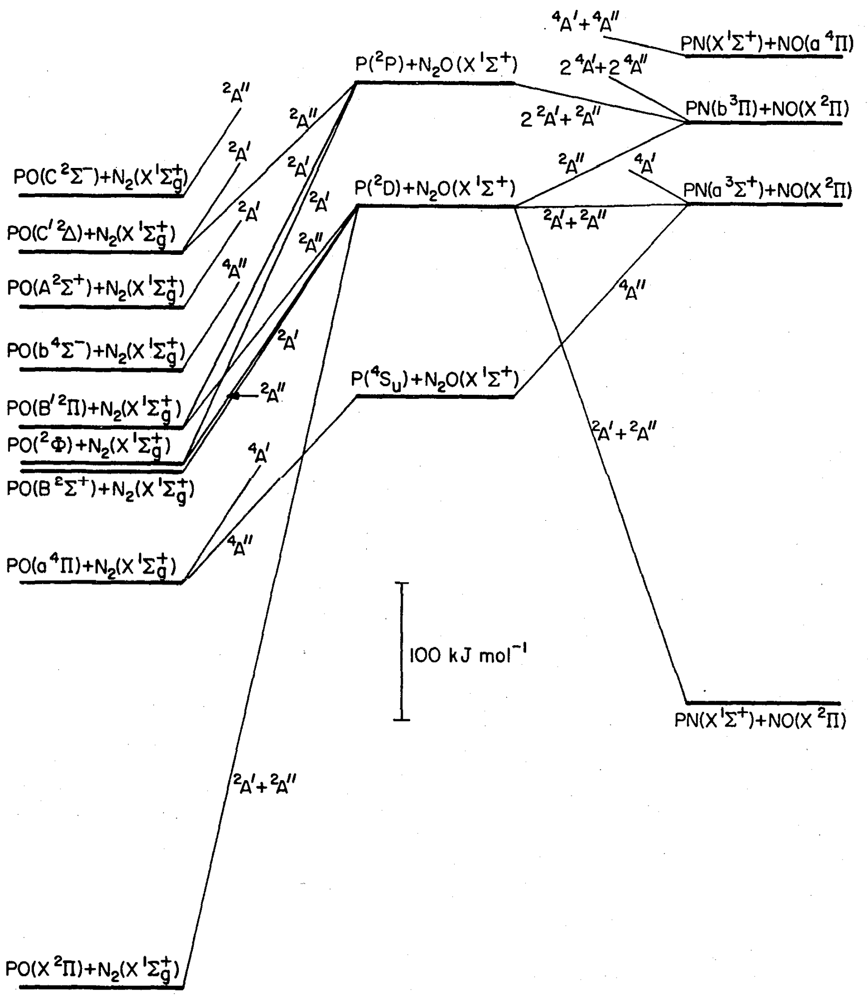
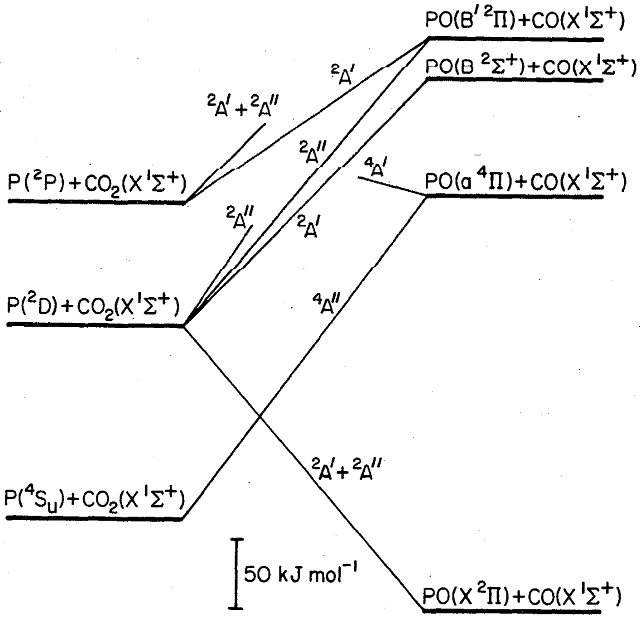


FIGURE 25. Correlation diagram connecting P + N_2O states to either PO + N_2 or PN + NO reaction products.



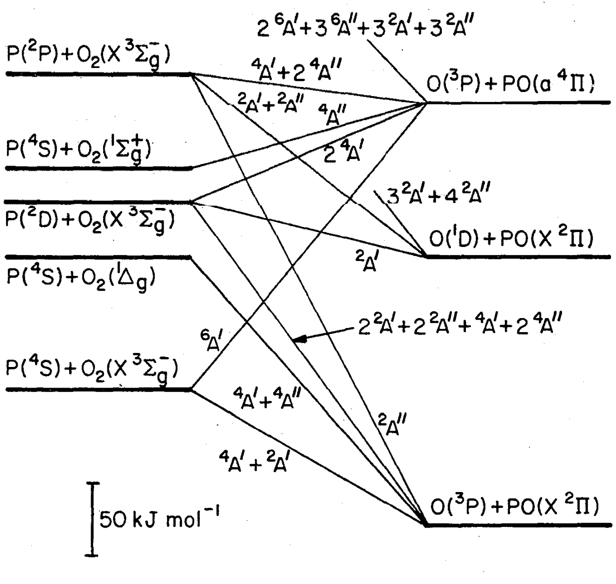


FIGURE 26. Correlation diagram connecting the states of P + CO_2 and PO + CO (from Acuna et al., 1973b).

FIGURE 27. Correlation diagram connecting the states of P + O_2 and PO + O (modified from Acuna et al., 1973a).

h. $P(^2D, ^2P) + HCl, Cl_2, PCl_3$

With HCl, two reactive channels are possible to either PH + Cl or PCl + H. $P(^2D)$ correlates to the ground states of either of these products and reaction is probable. $P(^2P)$ correlates only to $PH(a\,^1\Delta)$ + Cl if the $PH(a\,^1\Delta)$ state lies at or less than about 7600 cm^{-1} above its ground state, which it may do (Barrow & Lemanczyk, 1975). Correlations to PCl + H for this are endothermic.

In the case of Cl_2, exothermic surfaces are available for $P(^2D)$ to $PCl(X\,^3\Sigma^-, a\,^1\Delta)$ and for $P(^2P)$ to $PCl(a\,^1\Delta, b\,^1\Sigma^+)$ states. Chemical reaction is most probable.

Likewise, with PCl_3, fast reactions appear to occur to PCl + PCl_2 even with $P(^4S_{3/2})$. Mathur et al. (1976) have determined the PCl_2 - Cl bond strength as 316 ± 15 kJ mol^{-1} (75.6 ± 3.5 kcal mol^{-1}) implying that the as yet uncertain value for the diatomic P - Cl strength is comparable to or larger than the 306 kJ mol^{-1} (73 kcal mol^{-1}) suggested by the JANAF tables (Stull & Prophet, 1971; Chase et al., 1974).

i. $P(^2D, ^2P)$ + Inert Gases

As is also the case for example with $C(^1D)$ + Kr and $As(^2D)$, $O(^1D)$, $S(^1D)$ + Xe, relaxation of $P(^2D)$ and $P(^2P)$ by Xe is relatively efficient requiring about 10 and 10^3 collisions, respectively. In such cases, the inert gases of large atomic weight can induce efficient relaxation of electronic to translational energy. Presumably this is favored by an extensive mixing of the doublet and quartet surfaces producing an extremely efficient crossing mechanism.

5.7.3. References

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5.8. Atomic Sulfur $S(3^1D_2, 3^1S_0)$

Although the spin orbit splitting for ^3P_J is larger than kT at 300 K, little is yet known concerning the differences in the chemical or physical behavior of these spin components. The ^3P_J components can be formed with nonthermal distributions but their relaxation appears to be sufficiently rapid to maintain equilibrium on most experimental time scales (Donovan, 1969).

$S(^1D)$ has been quite extensively studied with a large number of quenching species, however, data are still insufficient for any one collision partner and restricted to room temperature values.

Even less information is available for $S(^1S)$ but sufficient to indicate its completely different behavior.

These factors should be borne in mind when considering the values that have been recommended.

Table 34. Energies and radiative lifetimes of low-lying electronic states of atomic sulfur[a, c].

Electronic State	Energy Level (cm^{-1})	Radiative Lifetime (s)
$^1S_0$	22,179.95	0.47[b]
$^1D_2$	9,238.61	28.0
$^3P_0$	573.64	3310
$^3P_1$	396.06	714
$^3P_2$	0.00	-

[a] Weise et al., 1969

[b] Kernahan & Pang, 1975

[c] Eriksson, 1978

5.8.1. Recommended Rate Constant Values, 300 K, cm^3 $molecule^{-1}$ s^{-1}.

	$S(^1D_2)$[a]	$S(^1S_0)$
CH_4	$\geq 5\times10^{-12}$,R predominant	$\cong 1.5\times10^{-15}$,R or Q?
C_2H_6	$\cong 1\times10^{-11}$,R & Q activation energy $\cong 4.2$ kJ mol^{-1}	$\cong 4.4\times10^{-14}$,R or Q?
C_nH_{2n+2}		
$c-C_nH_{2n}$		
C_2H_4	$\cong 7\times10^{-11}$,R dominant	$\cong 1.3\times10^{-13}$,R or Q?
C_3H_6	$\cong 2\times10^{-10}$,R	
C_nH_{2n}	$\cong$ gas kinetic frequency,R	
$c-C_nH_{2n-2}$		
$C_nH_{2n-m}F_m$		
$c-C_4F_6$	$\cong 2\times10^{-11}$R or Q?	
C_2H_2	$\cong 5\times10^{-11}$,R	$\cong 1.6\times10^{-13}$,R or Q?
NO_2	no data, R probably fast	$\cong 6\times10^{-10}$,R
N_2O	$\cong 1.3\times10^{-11}$,R & Q	$< 3\times10^{-15}$,R or Q?
OCS	$\cong 1\times10^{-10}$,R & Q $\geq 6.6\times10^{-11}$,R	$1\times10^{-11}/4\times10^{-13}$,R & Q? discrepant data
CS_2	$\cong 1.9k_{OCS}$,R or Q?	$\cong 8.1\times10^{-10}$,R?
SO_2	no data,R?	$\cong 1\times10^{-10}$,R
H_2S	no data,R?	$\cong 4.9\times10^{-10}$,R
SF_6	$< 7\times10^{-14}$,Q	$\leq 3.5\times10^{-16}$,Q
CO_2	$\cong 2\times10^{-11}$,R or Q?	$< 6\times10^{-17}$,Q
CO	$\cong 3\times10^{-11}$,Q	$< 3.5\times10^{-16}$,Q
NO	$\cong 4.5\times10^{-11}$,R or Q?	$\cong 3.2\times10^{-10}$,R or Q?
N_2	$\cong 4\times10^{-12}$,Q	$\leq 1\times10^{-17}$,Q[b]
O_2	no data,R probable	$\cong 6\times10^{-13}$,R or Q?
H_2	$1.7(\pm0.9)\times10^{-11}$,R	$\cong 8\times10^{-16}$,R or Q?
Cl_2	no data,R probable	$\cong 4.8\times10^{-10}$,R?
He	$< 1\times10^{-14}$,Q	$\leq 6\times10^{-18}$,Q
Ne	$< 7\times10^{-14}$,Q	no data,Q
Ar	6.5×10^{-13},Q	$\leq 6\times10^{-18}$,Q[b]
Kr	1.9×10^{-12},Q	$\leq 6\times10^{-17}$,Q[b]
Xe	1.1×10^{-11},Q	$\leq 1.6\times10^{-16}$,Q[b]

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[a] R Reaction; Q physical quenching. Accuracy uncertain, see discussion.

[b] Collision induced emission is important.

5.8.2. Discussion

Invariably, OCS photolysis is used in kinetic studies as the source for either $S(^1D)$ or $S(^1S)$. Wavelength thresholds for their respective productions are at about 290 and 210 nm (Klemm et al., 1975; Black et al., 1975c).

Generally, $S(^1D)$ is found to be a more reactive species than $S(^1S)$, however there are numerous interactions for the latter that occur at gas kinetic collision frequency rates.

Many reactions of $S(^1D)$ are fast. Their quantitative values are still in a somewhat unsatisfactory state and more data are required. Generally, only relative rates have been measured, most often against that of k_{OCS}, the overall value of which is still not known to better than about a factor of two. In contrast to $S(^3P)$ which reacts only slowly with OCS ($k_{300\,K} \cong 3.0 \times 10^{-15}$, Baulch et al., 1976) and can produce only $S_2(X\,^3\Sigma_g^-)$, the interaction with $S(^1D)$ has several possible channels, all which appear to occur to various extents:

$$S(^1D) + OCS \overset{k_Q}{=} S(^3P) + OCS \quad \Delta H^\circ_{298\,K} = -110.5 \text{ kJ mol}^{-1} \; (-26.4 \text{ kcal mol}^{-1})$$

$$\overset{k_\Delta}{=} S_2(^1\Delta_g) + CO \quad \cong -170 \text{ kJ mol}^{-1} \; (-41 \text{ kcal mol}^{-1})$$

$$\overset{k_\Sigma}{=} S_2(^1\Sigma^+) + CO \quad \cong -122 \text{ kJ mol}^{-1} \; (-29 \text{ kcal mol}^{-1})$$

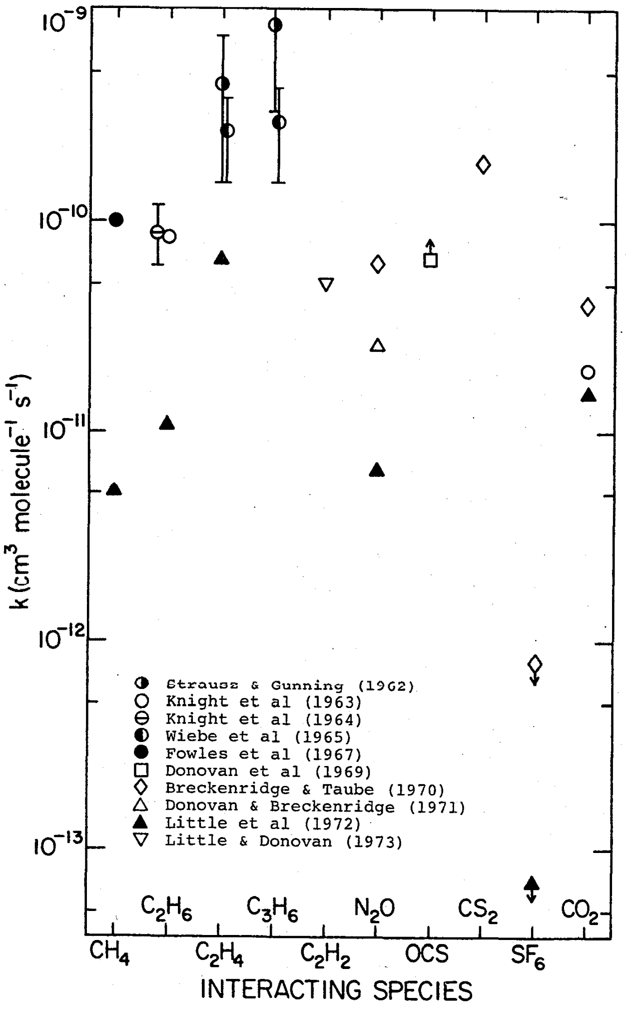

FIGURE 28. Rate constants for the interactions of $S(3^1D_2)$ with various polyatomic species, 300 K.

Breckenridge and Taube (1970) have indicated that $k_Q/(k_\Delta + k_\Sigma) \geq 0.3$ in spite of the spin forbidden nature of the physical quenching process. A value for k_Δ, the channel producing $S_2(^1\Delta_g)$, has been measured as $> 6.6 \times 10^{-11}$ (Donovan et al., 1969) which is approximately 1 collision in 4 or less. Consequently, in those investigations which report values for k_M relative to the overall decay of $S(^1D)$ with OCS, k_{OCS}, a value for the latter of 1×10^{-10} has been assumed and should be within a factor of two. In those other cases where $S(^1D)$ is followed by monitoring $S_2(^1\Delta_g)$, the value of 6.6×10^{-11} is used for k^Δ_{OCS}. The actual measured ratios also have been tabulated for ready conversion if these assumed values become better specified. Consequently, this feature should be remembered when considering absolute values.

In all studies of $S(^1D)$ its concentration is inferred by monitoring a secondary species, either $S_2(^1\Delta_g)$ or NS in absorption. For $S(^1S)$ this is not the case and it is monitored directly either via atomic absorption or its "forbidden" emission. Although fewer studies are reported concerning $S(^1S)$ these are of recent vintage.

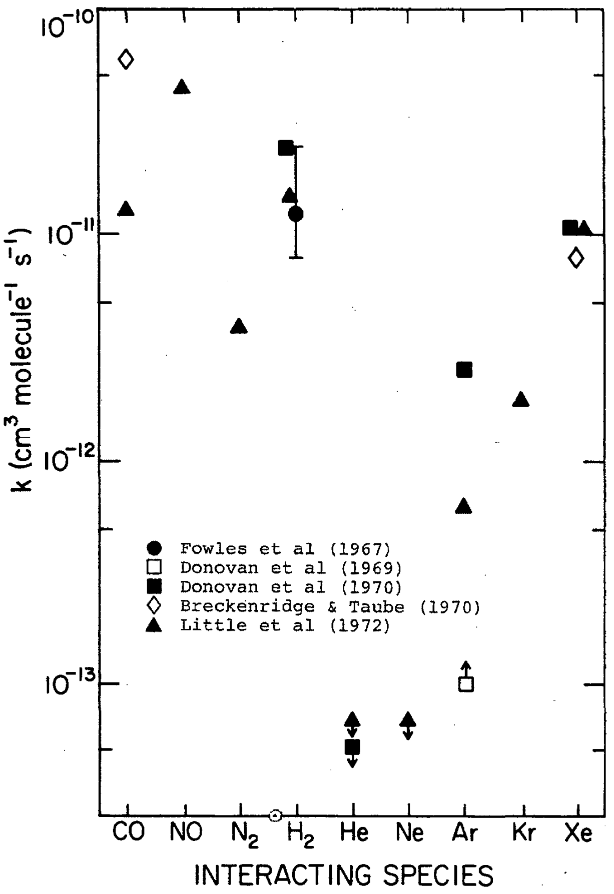

FIGURE 29. Rate constants for the interactions of $S(3^1D_2)$ with various atomic and diatomic species, 300 K.

a. $S(^1D, ^1S)$ + Alkanes

These reactions with $S(^1D)$ were among the first to be studied by Gunning's group and have been extensively reviewed (Gunning, 1965; Gunning & Strausz, 1966; Strausz, 1967; Strausz & Gunning, 1968). However, their data are necessarily somewhat approximate owing to the nature of the product analyzing technique and the kinetic treatment based on final product concentrations. Nevertheless, their values do give a rough indication of the interaction efficiencies and showed at an early stage the different nature of $S(^1D)$ to that of $S(^3P)$. In view of more recent work it appears that their rates were somewhat overestimated.

Whereas ground state $S(^3P)$ is unreactive to the paraffins, $S(^1D)$ reacts rapidly and with the exception of CH_4 yields only the corresponding alkyl mercaptan, formed by indiscriminate insertion into the C-H bond. This fact was apparent because where the possibility of different isomeric mercaptans arose these were noted in the expected statistical ratios (Knight et al., 1963). Reaction with CH_4 appears more complex owing to the decomposition and subsequent reactions of the initially formed vibrationally excited methyl mercaptan.

Rates for isotopically substituted paraffins (C_3H_8, $C_3H_6D_2$, $C_3H_2D_6$, C_3D_8) are similar (Knight et al., 1963, 1964) and the reactions are all described by low activation energies of no more than 4.2 kJ mol^{-1} (Knight et al., 1964).

Both reaction (insertion) and physical quenching occur to various extents with $S(^1D)$. Reaction is dominant for CH_4 but both channels are important for the other alkanes. Measured rates for C_2 to C_4 chain and C_3 to C_5 cyclic alkanes are similar and are probably all $\cong 1 \times 10^{-11}$ or faster (Little et al., 1972). There is an apparent discrepancy for CH_4 between the slower rate established by Little et al. (1972), 5×10^{-12}, and the very efficient interaction implied by Fowles et al. (1967), 1×10^{-10}.

Only a single study has reported data for $S(^1S)$ indicating an inefficient interaction with CH_4 and C_2H_6, with a 30 fold difference between the two.

b. $S(^1D, ^1S)$ + Alkenes

Reactions of $S(^1D)$ with alkenes are markedly different from those with alkanes, and are about two orders of magnitude more reactive than ground state S^3P (Davis et al., 1972). They have been extensively studied and reviewed by Gunning and Strausz (Gunning, 1965; Gunning & Strausz, 1966; Strausz, 1967; Strausz & Gunning, 1968). Reaction is either by addition across the double bond to form cyclic episulfides or by insertion into a C-H to produce the mercaptan. Theoretical calculations have indicated the competing nature of these two possible channels (Hoffman et al., 1970). The insertion mechanism is characteristic for $S(^1D)$ and not observed with $S(^3P)$. Although C_2H_4 produces vinyl mercaptan (CH_2CHSH) and the episulfide in the ratio of about (0.7–1.0):1 (Wiebe et al., 1965) the importance of the vinylic type mercaptans (insertion into the unsaturated carbon-hydrogen bond) rapidly decreases as the number of carbon groups increases and a preference is apparent rather for insertion into saturated carbon-hydrogen bonds. For example, C_4 olefines give little if any vinylic mercaptans, final products are ≅ 70% episulfide and ≅ 30% alkyl type mercaptans (Sidhu et al., 1966). C_3H_6 is intermediate in nature and rates of production of the vinyl to alkyl type mercaptan are of about the same magnitude (Wiebe et al., 1965).

To obtain accurate kinetic rate data for fundamental reactions is difficult from an analysis of final products. Rate coefficients so determined were found to be pressure dependent indicating a more complex mechanism than assumed. The probably more reliable flash photolysis measurements of Little et al. (1972) quote a value for $k_{C_2H_4}$ of about 0.7 k_{OCS} ($\cong 6.7 \times 10^{-11}$) a factor of at least two below values derived from product analyses.

Episulfide and mercaptan products have been identified for the reactions of $S(^1D)$ with 1-butene, cis and trans 2-butene, isobutylene, 1-3 butadiene (Sidhu et al., 1966), cyclopentene, cyclohexene, perfluorocyclobutene, trimethylethylene, tetramethylethylene, vinyl chloride, cis and trans 1-2 dichloroethylene (Lown et al., 1967). Of these, only perfluorocyclobutene has reduced reactivity of the double bond due to the presence of the F atoms. For this, a rate comparable to k_{CO_2} was indicated. Otherwise, partially fluorinated alkenes are similar to the corresponding hydrocarbon.

Activation energies are small and $\leq$ 4 kJ mol^{-1} for episulfide formation. Channels forming mercaptans likewise have values no more than 2 kJ mol^{-1} higher. Reaction rates

Table 35. Rate constants for interactions of $S(3^1D_2)$

M	k_M, $cm^3 molecule^{-1} s^{-1}$ [a]		
CH_4		k_R $5.6 \times 10^{-12\dagger}$ (k_{OCS}/k_R=17.8)† k_Q 3×10^{-13} (k_R/k_Q=20)	
C_2H_6		k_R 5×10^{-11} (k_{OCS}/k_R=2.04) k_Q 3.5×10^{-11} (k_R/k_Q=1.4)	k^*_R $(4.5-9.1) \times 10^{-11}$ (k_{OCS}/k_R=1.1-2.2) k^*_Q $(1.5-2.7) \times 10^{-11}$ (k_R/k_Q=3.2)
C_3H_8		k_R $(C_3H_8)=k_R(C_3D_8)$	k^*_R 5.3×10^{-11} (k_{OCS}/k_R=1.9) k^*_Q 8.4×10^{-12} (k_R/k_Q=6.2)
C_2H_4	$(1.5-7.5) \times 10^{-10}$ ($k_{C_2H_4}/k_{OCS}$=1.5-7.5) $k_{C_2H_4}/k_{C_3H_6} \approx 0.28$		
C_3H_6	$(3.2-14) \times 10^{-10}$ ($k_{C_3H_6}/k_{OCS}$=3.2-14)		
$c-C_3H_6$, $c-C_4H_8$ $c-C_5H_{10}$			k_R 5×10^{-11} (k_{OCS}/k_R=2.0) k_Q 2.5×10^{-11} (k_R/k_Q=2.0)
$i-C_4H_{10}$		k_R 5×10^{-11} (k_{OCS}/k_R=2.04) k_Q 3.1×10^{-11} (k_R/k_Q=1.6)	
CO_2		2×10^{-11} ($\approx 0.2 k_{OCS}$)	
Exp. Temp. K	298	298	298
Method	Static OCS photolysis system, 229-255 nm medium pressure arc. 6.7-26.7 kPa OCS, 1.5-52.4 kPa C_2H_4, C_3H_6. Exposure times 6-300 min. Final products analyzed by mass spectrometer.	Static photolysis system, medium pressure Hg arc >229 nm. 0.7-10 hrs exposure times. 6.7 kPa OCS, <187 CH_4, <116 C_2H_6, <74 kPa $i-C_4H_{10}$. Gas chromatography-mass spectrometric final product analysis.	Static photolysis system, Cd* 228.8 nm & Hg arc >229 nm. 1-2 hr exposure times 5.5-26.7 kPa OCS, <240 C_2H_6, C_3H_8, <51 kPa $c-C_3H_6$, $c-C_4H_8$, $c-C_5H_{10}$. Gas chromatography-mass spectrometric product analysis.
Comments	Mean values for $S(^1D)+S(^3P)$ present in system, however, $k(^1D) >> k(^3P)$	†value in error, did not include H_2S product yield; later work gave $k_R \approx k_{OCS}$ (Fowles et al., 1967)	Slight dependence on exciting wavelength. Values must be considered as only approximate owing to the nature of the kinetic treatment. $E^A_R = E^A_Q = E^A_{OCS} + 4.2(\pm 0.8)$ kJ mol^{-1} (C_2H_6, C_3H_8 298-497 K)
Reference	Strausz & Gunning, 1962	Knight et al., 1963	Knight et al., 1964

[a] Value for k_{OCS} (all reaction channels) taken as 1×10^{-10} $cm^3 molecule^{-1} s^{-1}$.
k_R refers to the insertion reaction $S(^1D)+RH=RSH$, k_Q refers to physical deactivation.

Table 35. Rate constants for interactions of $S(3^1D_2)$ -- continued

M	k_M, $cm^3 molecule^{-1} s^{-1}$		
CH_4		k_R 1×10^{-10} ($k_{OCS}/k_R \simeq 1$)	
C_2H_4	$(1.5-3.8) \times 10^{-10}$ ($k_{C_2H_4}/k_{OCS}$=1.5-3.8) $k_{C_2H_4}/k_{C_2H_6}$=0.75-1.60		$k_{C_2H_4} : k_{C_3H_6} : k_{i-C_4H_8}$=1:2.9:7.5
C_3H_6	$(1.5-4.3) \times 10^{-10}$ ($k_{C_3H_6}/k_{OCS}$=1.5-4.3)		
$C_2H_2F_2$	$(2.9-4.4) \times 10^{-10}$ ($k_{C_2H_2F_2}/k_{OCS}$=2.9-4.4)		
H_2		$(0.8-2.5) \times 10^{-11}$ ($4 \leq k_{OCS}/k_{H_2} \leq 12$)	
Exp. Temp. K	297	298	297
Method	Static OCS photolysis system, 229-255 nm medium pressure Hg arc. 6.7-16.9 kPa OCS/3.3-106.7 kPa olefin. Exposure times 10-60 min. Gas chromatography-mass spectrometric analysis of final products.	Flash photolysis OCS, >220 nm, E=1660 J. Plate photometry SH (0,0) 323.7 and (1,0) 305 nm bands, S_2(13,0) 271.3 nm band in absorption. 2.3-2.7 kPa OCS/ <79 kPa H_2, CH_4. Final products analyzed by gas chromatography.	Static OCS photolysis system, 229-255 nm low pressure Hg lamp. 10.3 & 12.1 kPa OCS, ≃20 kPa olefin. Gas chromatography-mass spectrometric analysis of final products.
Reference	Wiebe et al., 1965	Fowles et al., 1967	Lown et al., 1967.

Table 35. Rate constants for interactions of $S(3^1D_2)$ -- continued

M	k_M, $cm^3 molecule^{-1} s^{-1}$		
N_2O			$6.3x10^{-11}(k_{N_2O}/k_{OCS}=0.63)$
SF_6			$<8x10^{-13}(k_{SF_6}/k_{OCS}<0.008)$
CS_2			$k_{CS_2}/k_{OCS}=1.9$
OCS	$>6.6x10^{-11}$*		
CO_2			$4.1x10^{-11}(k_{CO_2}/k_{OCS}=0.41)$
CO			$6x10^{-11}(k_{CO}/k_{OCS}=0.6\pm0.3)$
H_2		$2.4x10^{-11}(0.37k^{\Delta}_{OCS})$	
He		$<1x10^{-14}(<1.7x10^{-4}k^{\Delta}_{OCS})$	
Ar	$>10^{-13}$	$2.6x10^{-12}(0.04k^{\Delta}_{OCS})$	
Xe		$1.1x10^{-11}(0.17k^{\Delta}_{OCS})$	$8x10^{-12}(k_{Xe}/k_{OCS}=0.08)$
Exp. Temp. K	300	300	300
Method	Flash photolysis OCS/excess He or Ar. Plate photometry, $S_2(^1\Delta_g)$ monitored in absorption.	Flash photolysis static system, N_2 lamp 500 J. OCS/M/excess He mixtures ≤53.2 kPa. Plate photometry, $S(^1D)$ indirectly by monitoring either $S_2(C-X)$, $S(^3P_2)$ or $S_2(^1\Delta_g)$ by vacuum uv absorption.	Static photolysis cell 228.8 nm Cd or 253.7 nm Hg lines. OCS 1.7-18, N_2O 5.3, CO<26.7, CO_2, Xe, SF_6 < 113.3 kPa. Exposure times 3-35 min., gas chromatography-mass spectrometric product analysis.
Comments	*k_{OCS} specifically relates to channel producing $S_2(^1\Delta_g)$+ CO.	Based on $k^{\Delta}_{OCS}=6.6x10^{-11}$. ($S_2{}^1\Delta_g$ channel)	Based on $k_{OCS}=1x10^{-10}$ (all channels)
Reference	Donovan et al., 1969	Donovan et al., 1970	Breckenridge & Taube, 1970

Table 35. Rate constants for interactions of $S(3^1D_2)$ -- continued

M		k_M, cm^{3}molecule^{-1}s^{-1}	
CH_4		$5.1x10^{-12}(k_M/k_{C_2H_4}=0.076)$	
C_2H_6		$1.1x10^{-11}($ $=0.17)$	
C_2H_4		$6.7x10^{-11}($ $=1.0)$	
C_2H_2			$5.0x10^{-11}(k_{C_2H_2}/k_{CO_2}=2.5)$
N_2O	$2.6x10^{-11}(k_{N_2O}/k^{\Delta}_{OCS}=0.4)$	$\approx 6.7x10^{-12}($ $\approx 0.1)$	
SF_6		$<7x10^{-14}$ $($ $<10^{-3})$	
OCS		$1x10^{-10*}$ $($ $=1.5)$	
CO_2		$1.6x10^{-11}($ $=0.24)$	
CO		$1.3x10^{-11}($ $=0.19)$	
NO		$4.5x10^{-11}($ $=0.68)$	
N_2		$4.1x10^{-12}($ $=0.062)$	
H_2		$1.5x10^{-11}($ $=0.22)$	
He		$<7x10^{-14}$ $($ $<10^{-3})$	
Ne		$<7x10^{-14}$ $($ $<10^{-3})$	
Ar		$6.5x10^{-13}($ $=9.7x10^{-3})$	
Kr		$1.9x10^{-12}($ $=0.028)$	
Xe		$1.1x10^{-11}($ $=0.16)$	
Exp. Temp. K	300	300	295
Method	Flash photolysis E=2000 J. OCS 0.27/N_2O 1.6/He 9.1 kPa. Plate photometry $S(^3P)$, NS(A-X) 250 nm, (C-X) 230 nm, in absorption, $S(^1D)$ inferred from $S_2(^1\Delta_g)$ absorption.	Flash photolysis E=1000 J. OCS 0.065/N_2O 0.61/SF_6 6.7 kPa. Plate photometry. Relative rates, $S(^1D)$ inferred from NS C-X(0,0) 230 nm absorption.	Flash photolysis OCS/N_2O/ excess SF_6 mixture. $C_2H_2 \leq$ 400 Pa, $CO_2 \leq$ 800 Pa. NS C-X (0,0)230 nm absorption used as measure of $S(^1D)$.
Comments	With N_2O, ratio of physical quenching to reaction forming NS is 5:1. No effects due to N_2O photolysis. Based on $k^{\Delta}_{OCS}=6.6x10^{-11}$ $(S_2{}^1\Delta_g$ channel).	Measured relative to $k_{C_2H_4}$, absolute values based on $*k_{OCS}=1x10^{-10}$. $S(^1D)+N_2O=NO+NS$ produces NS; no reactions noted between NS and the gases added.	Relative to k_{CO_2} taken as $2x10^{-11}$.
Reference	Donovan & Breckenridge, 1971	Little et al., 1972	Little & Donovan, 1973

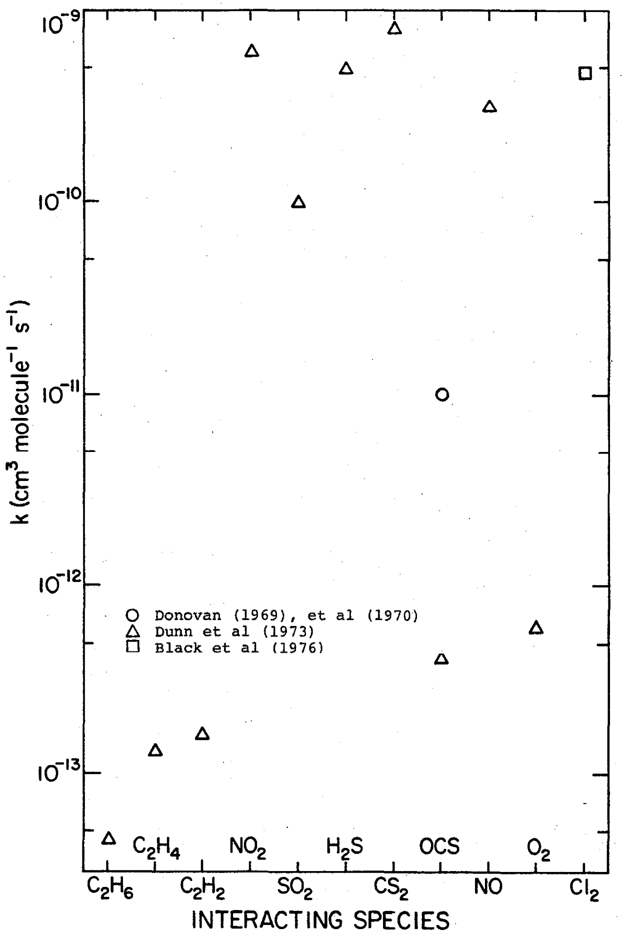

FIGURE 30. Rate constants for the various interactions of $S(3^1S_0)$, $k_{300\ K} > 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

appear to increase with carbon number and relative rates have been given as $k_{C_2H_4} : k_{C_3H_6} : k_{i\text{-}C_4H_8} \cong 1{:}3{:}7$ (Lown et al., 1967). That for i-C_4H_8 must approximate to a gas kinetic collision frequency.

A single value has been reported for $S(^1S) + C_2H_4(k_{C_2H_4} \cong 1.3 \times 10^{-13})$ indicating a 500-fold lower efficiency than with $S(^1D)$.

c. $S(^1D, {}^1S) + C_2H_2$

Little and Donovan (1973) using flash photolysis methods have indicated for $S(^1D)$ a value of $k_{C_2H_2}$ 2.5 times that of k_{CO_2} for the overall interaction. It is predominantly reactive and a complex system owing to the various initial channels (Strausz et al., 1978) and the subsequent chemistry (Strausz et al., 1967; Strausz & Gunning, 1968). This is the only value available and is stated here as 5.0×10^{-11} using the suggested value for k_{CO_2}.

Likewise, only a single value for $S(^1S)$ is published, 1.6×10^{-13}, a 300-fold smaller cross section than that for $S(^1D)$.

d. $S(^1D, {}^1S) + NO_2$

Reaction of $S(^1S)$ with NO_2, like $O(^1S)$, is extremely rapid ($k_{NO_2} \cong 6 \times 10^{-10}$). By comparison, reaction with $S(^1D)$, as yet unmeasured, is expected to be equally fast ($k(O^1D + NO_2) = 1.4 \times 10^{-10}$, Schofield, 1978). However, unlike oxygen, two possible reaction channels are possible.

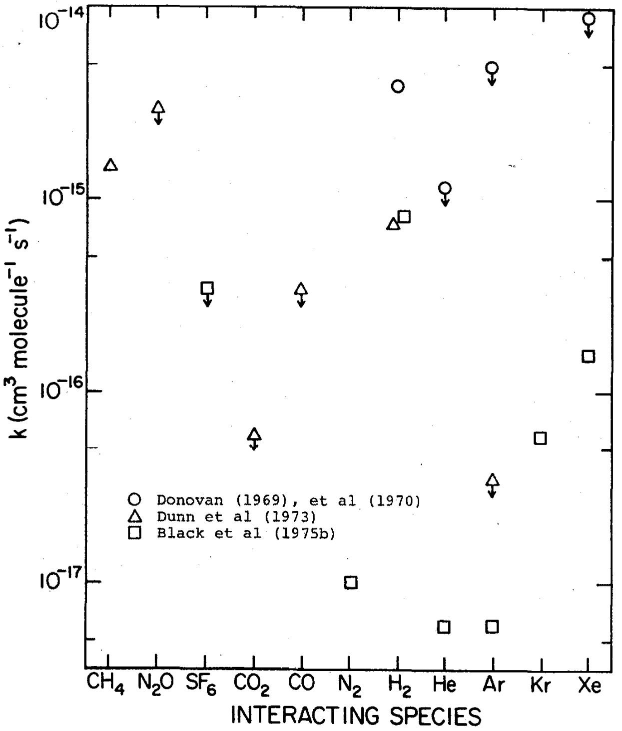

FIGURE 31. Rate constants for the various interactions of $S(3^1S_0)$, $k_{300\ K} < 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

$$S(^1D) + NO_2 = NO + SO \quad \Delta H^\circ_{298\ K} = -326 \text{ kJ mol}^{-1} \ (-77.9 \text{ kcal mol}^{-1})$$

$$= NS + O_2 \quad = -157 \text{ kJ mol}^{-1} \ (-37.6 \text{ kcal mol}^{-1})$$

Based on energetic and spin considerations alone, these reactions can produce the SO or O_2 products in any of the $a\,^1\Delta$, $b\,^1\Sigma^+$ or $X\,^3\Sigma_g^-$ states. $S(^1S)$ can behave similarly and in addition might produce $SO(A\,^3\Pi)$.

e. $S(^1D, {}^1S) + N_2O$

An order of magnitude spread exists for $S(^1D)$ between the three measures of k_{N_2O}, the largest and possibly least reliable value resulting from an analysis of final product composition (Breckenridge & Taube, 1970). The fact that the three rates are expressed in different ways, relative to k_{OCS}, k^{Δ}_{OCS} (reaction producing $S_2\,^1\Delta$ only), and to $k_{C_2H_4}$ complicates the issue but cannot explain the discrepancy. A value $\cong 1.3 \times 10^{-11}$, based on the two more recent studies appears a best estimate at present. These two values would only come closer into agreement if the value here taken for k_{OCS} was larger and that for k^{Δ}_{OCS} smaller.

Two reaction pathways other than physical quenching are possible as in the case of $O(^1D)$.

Table 36. Rate constants for interactions of $S(3^1S_0)$.

M	k_M, cm^3 molecule^{-1} s^{-1}			
CH_4		1.5x10^{-15}		
C_2H_6		4.4x10^{-14}		
C_2H_4		1.3x10^{-13}		
C_2H_2		1.6x10^{-13}		
NO_2		6.1x10^{-10}		
N_2O		<3 x10^{-15}		
SO_2		1.0x10^{-10}		
H_2S		4.9x10^{-10}		
CS_2		8.1x10^{-10}		
OCS	1.0x10^{-11}	4 x10^{-13}		
SF_6			≤3.5x10^{-16}	
CO_2		<6 x10^{-17}		
CO		<3.5x10^{-16}		
NO		3.2x10^{-10}		
N_2			≤1 x10^{-17}	
O_2		6.0x10^{-13}		
H_2	4.0x10^{-15}	7.7x10^{-16}	≤8.6x10^{-16}	
Cl_2				4.8x10^{-10}
He	<1.2x10^{-15}		≤6 x10^{-18}	
Ar	<5 x10^{-15}	<3.5x10^{-17}	≤6 x10^{-18}	
Kr			≤6 x10^{-17}	
Xe	<10^{-13}		≤1.6x10^{-16}	
Exp. Temp. K	300	298	296	
Method	Vacuum uv flash photolysis N_2 lamp, >110 nm E=500 J. 3.3-10.7 Pa OCS in 26.7 kPa Ar. Plate photometry, $S(^1S)$ 178.2 nm in absorption.	Flow system, 147 nm Xe pulsed photolysis of ≈0.2 Pa OCS in ≈1.3 kPa Ar carrier gas. $S(^1S)$ emission 772.5 and 458.9 nm.	OCS pulsed photolysis 161 nm H_2 source. 5.3 Pa OCS/≤67 kPa M. 690-840 nm filter (for 772.5 nm emission) and 420-620 nm filter (458.9 nm emission).	OCS pulsed photolysis $S(^1S_0)$ emission.
Comments	SH 167.3 nm absorption detected with H_2	Refers to total loss rates of $S(^1S)$.	Quenching + reaction only. Collision induced emission important for N_2 and the inert gases.	Unpublished data.
Reference	Donovan, 1969; Donovan, et al., 1970.	Dunn et al., 1973.	Black et al., 1975b.	Black et al., 1976.

$$(1)\quad S(^1D) + N_2O = NS + NO \quad \Delta H^\circ_{298\,K} = -116.0\ \mathrm{kJ\ mol^{-1}}\ (-27.7\ \mathrm{kcal\ mol^{-1}})$$

$$(2)\quad = SO(^1\Delta) + N_2 \quad \cong -389\ \mathrm{kJ\ mol^{-1}}\ (-93\ \mathrm{kcal\ mol^{-1}})$$

SO is required to be formed in a singlet state to conserve spin and can be either $^1\Delta$ or $^1\Sigma^+$. Adiabatic surfaces are available for both reactions to these products. Breckenridge and Taube (1970) estimated that only 15 ±10% proceeded via reaction (2). Likewise, Donovan and Breckenridge (1971) established that $k_1/k_Q = 0.2 \pm 0.05$, indicating that both reactive channels appear equally important with physical quenching dominant. However, these values cannot yet be considered quantitatively firm. Nevertheless, it does contrast with the corresponding reactions of $O(^1D)$ where although the two channels do have very similar cross sections, relaxation to $O(^3P)$ is negligible (Boxall et al., 1972). The intermediacy of an SN_2O collision complex has been discussed (Breckenridge & Taube, 1970; Donovan & Breckenridge, 1971).

In contrast, the interaction of $S(^1S)$ with N_2O is very inefficient, $k_{N_2O} < 3 \times 10^{-15}$. A correlation diagram for the corresponding chemical reactions indicates that collisions involving such a planar interaction complex can only occur by nonadiabatic transitions.

f. $S(^1D, ^1S)$, + OCS, CS_2

The interaction of $S(^1D)$ with OCS has been discussed already in the introduction to this section due to its importance as the measuring rod for other reactions of $S(^1D)$ and due to the fact that OCS is used as the cleanest photochemical source of both $S(^1D)$ and $S(^1S)$. Of the many reactions studied, that of $S(^1D)$ with OCS appears to be one of the fastest. Of the three interactive channels only that for reaction producing $S_2(^1\Delta_g)$ has been measured, $k^{\Delta}_{\mathrm{OCS}} > 6.6 \times 10^{-11}$. Construction of the potential energy surfaces assuming all four atoms collide in a plane (C_s symmetry) indicates allowed transitions leading to either $S_2(^1\Delta_g$ or $^1\Sigma_g^+)$. That to the latter may have a greater activation energy associated with it and so lessen its importance (Donovan et al., 1969).

The corresponding interaction of OCS with $S(^1S)$ only correlates endothermically with excited states of the products and a nonadiabatic transition must occur (Donovan et al., 1969). The factor of 25 discrepancy between the two measured values is difficult to explain and requires further measurement.

Quenching of $S(^1D)$ by CS_2 has been reported only by Breckenridge and Taube (1970) at a rate 1.9 times that of k_{OCS}. Although reaction via

$$S(^1D) + CS_2 = CS + S_2(^1\Delta g) \quad \Delta H^\circ_{298\,\mathrm{K}} \cong -22\ \mathrm{kJ\ mol^{-1}}\ (-5.2\ \mathrm{kcal\ mol^{-1}})$$

is exothermic there is no evidence for production of measurable amounts of CS. Rather it appears that simple atom exchange or direct physical quenching are the decay process for $S(^1D)$.

Likewise, the single measure of k_{CS_2} with $S(^1S)$ appears very large, 8.1×10^{-10}, and probably indicative of chemical reaction.

g. $S(^1D, ^1S) + SO_2, H_2S$

Although not yet measured for $S(^1D)$ these interactions with $S(^1S)$ are very fast and may be chemical in nature, for example

$$S(^1D) + SO_2 = SO + SO \quad \Delta H^\circ_{298\,\mathrm{K}} = -82.5\ \mathrm{kJ\ mol^{-1}}\ (-19.7\ \mathrm{kcal\ mol^{-1}})$$

$$S(^1D) + H_2S = SH + SH \quad = -88.7\ \mathrm{kJ\ mol^{-1}}\ (-21.2\ \mathrm{kcal\ mol^{-1}})$$

h. $S(^1D, ^1S) + CO_2$, CO

CO has no thermodynamically favorable reactive channels for either sulfur state. Whereas an efficient relaxation mechanism is evident for $S(^1D)$ that for $S(^1S)$ is very slow.

In comparison, reaction with CO_2 is exothermic in both cases and is sufficiently energetic to produce $SO(^1\Delta)$ with $S(^1D)$ or both singlet SO states with $S(^1S)$. However, $S(^1S)$ correlates endothermically only with higher energy states, probably explaining its extremely low collision cross section. The interaction between $S(^1D)$ and CO_2 may or may not be reactive

$$S(^1D) + CO_2 = SO(^1\Delta) + CO \quad \Delta H^\circ_{298\,\mathrm{K}} \cong -24\ \mathrm{kJ\ mol^{-1}}\ (-5.7\ \mathrm{kcal\ mol^{-1}})$$

but its rate coefficient, $k_{\mathrm{CO}_2} \cong 2 \times 10^{-11}$, is not significantly different from that of CO, $k_{\mathrm{CO}} \cong 3 \times 10^{-11}$.

i. $S(^1D, ^1S) + N_2, SF_6$

No reactions are expected for these species and physical relaxation must be dominant. The scant data indicate that for $S(^1D)$, $k_{N_2} \cong 4 \times 10^{-12}$ and $k_{SF_6} < 7 \times 10^{-14}$.

The single measure for $S(^1S)$ with N_2 reports a value $\leq 1 \times 10^{-17}$ for non-radiative quenching. However, relaxation via collision induced emission also has been shown to be significant in the $S(^1S) - N_2$ system ($k = 3.3 \times 10^{-18}$) and may be a major if not exclusive channel for $S(^1S)$ decay. Corresponding values for SF_6 are $< 3.5 \times 10^{-16}$ for physical relaxation and 8.5×10^{-18} for collision induced emission (Black et al., 1975b).

j. $S(^1D) + C_2N_2$

Although no quantitative data are yet available, McGrath et al. (1967) have observed NCS in absorption following COS/C_2N_2 photolysis and conclude that an insertion reaction producing this and CN may be responsible.

k. $S(^1D, ^1S)$ + NO

Although only single datum points have been obtained for the two sulfur states these show efficient relaxation processes that necessarily involve nonadiabatic transitions.

With $S(^1D)$, potential reaction to NS + O is endothermic by 34.60 kJ mol⁻¹, that to N + SO is slightly exothermic, 0.6 kJ mol⁻¹. However, the correlation diagram, basically identical to that for O + NO, figure 18, shows only endothermic surfaces to excited states of N. Consequently, the rate coefficient, $\cong 4.5 \times 10^{-11}$, probably relates to an efficient curve crossing mechanism.

Similarly, although the above mentioned reactions both become exothermic with $S(^1S)$, again only endothermic surfaces are available in each case. The rate constant, $\cong 3.2 \times 10^{-10}$, if accepted, either indicates a curve crossing mechanism that approximates to the gas kinetic collision frequency, or illustrates the inadequacy of these theoretical descriptions.

l. $S(^1D, ^1S) + O_2$

No data are available for $S(^1D)$. However, by comparison with $O(^1D)$ reaction is feasible, being allowed and producing $SO(b\,^1\Sigma^+)$ unless the surface has an appreciable activation energy

$$S(^1D) + O_2 = SO(b\,^1\Sigma^+) + O \quad \Delta H^\circ_{298\,\mathrm{K}} = -8.58\ \mathrm{kJ\ mol^{-1}}\ (-2.05\ \mathrm{kcal\ mol^{-1}})$$

The correlation diagram generated originally by Donovan and Husain (1970) is illustrated in figure 32. It also offers the explanation for the slower rate for S(^{1}S), $k_{O_2} \cong 6 \times 10^{-13}$ suggesting a nonadiabatic transition. Additionally, Dunn et al. (1973) have ruled out the possibility of this relating to the almost thermoneutral nonadiabatic decay to S(^{1}D) and O$_2$($b\,^1\Sigma_g^+$).

m. S(^{1}D, ^{1}S) + H_2

Three measures of these rate constants have been made in each case. Those for S(^{1}D) are in substantial agreement indicating a value of about 1.7($\pm$0.9) $\times 10^{-11}$. Fast exothermic reaction is expected although it appears not to be as fast as for O(^{1}D) (Schofield, 1978).

A lack of suitably correlating surfaces explains the much reduced rate with S(^{1}S). The result obtained by Donovan (1969; et al., 1970) appears too large and a value of $\cong 8 \times 10^{-16}$ is suggested.

Although there is evidence for collision induced emission of S(^{1}S) by H_2 its rate is about 500 fold less than that for physical quenching (Black et al., 1975b).

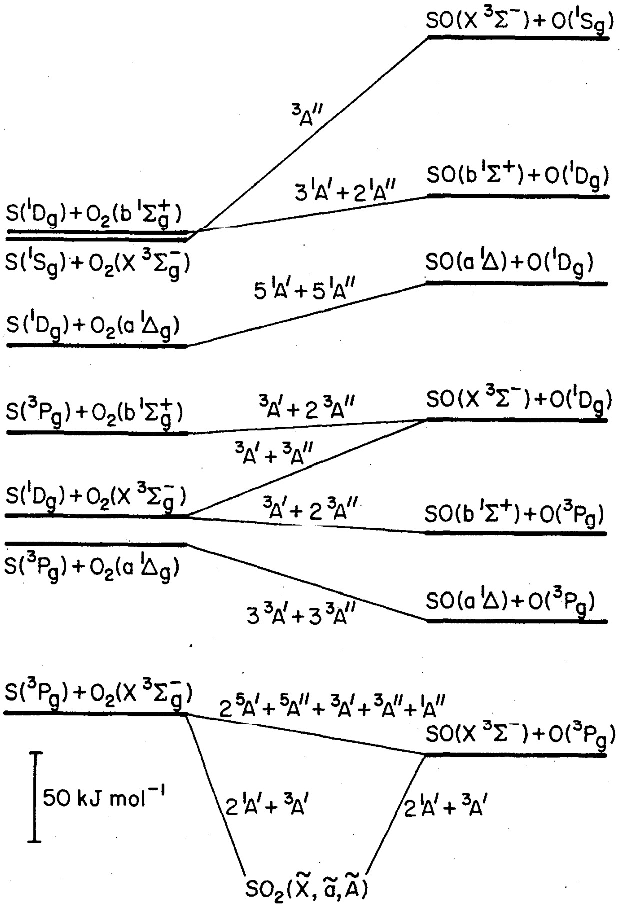

FIGURE 32. Correlation diagram connecting the states S + O_2 and SO + O (from Donovan & Husain, 1970).

n. S(^{1}D, ^{1}S) + Cl_2

Although the thermodynamics and spectroscopy of SCl are not well specified, reaction is exothermic and highly probable in both these cases. The rate constant has been reported only with S(^{1}S), $\cong 4.8 \times 10^{-10}$, but indicates a unit collision efficiency with slightly larger than gas kinetic cross section.

Reaction with S(^{1}D) correlates to ground state SCl + Cl products and is also expected to be fast. That for S(^{1}S) correlates *adiabatically and exothermically only to an excited* state of SCl that may lie at or below 25,000 cm^{-1}. Otherwise it must react by a nonadiabatic process.

o. S(^{1}D, ^{1}S) + Inert Gases

Donovan et al. (1969) noted in their uv flash photolysis study of OCS that S(^{3}P) was virtually absent with He diluent but was abundant in Ar as a result of an enhanced relaxation rate of S(^{1}D).

The results clearly show that quenching efficiencies of the inert gases increase with atomic number, as for O(^{1}D), and with Xe require only about 20 collisions. Similar arguments as presented for O(^{1}D) appear involved (Donovan et al., 1970) and the potential energy surfaces must cross or closely approach one another. Data are still quite limited but suggest for S(^{1}D) the 300 K values of $k_{He} < 1 \times 10^{-14}$, $k_{Ne} < 7 \times 10^{-14}$, Ar $\cong 6.5 \times 10^{-13}$, Kr $\cong 1.9 \times 10^{-12}$, Xe $\cong 1.1 \times 10^{-11}$.

With S(^{1}S), like O(^{1}S), transient radiating excimers can be formed with the inert gases which have higher transition probabilities than for the normal ^{1}S–^{1}D atomic radiation (Julienne, 1978). Consequently, such collision induced emission offers an alternate if not exclusive relaxation mechanism. As with O(^{1}S) it appears to be dominant, particularly for Ar, Kr and Xe (Black et al., 1975a). Measured values for physical quenching and collision induced emission are respectively, He ($\leq 6 \times 10^{-18}$, 5.6×10^{-20}), Ar ($\leq 6 \times 10^{-18}$, 4.2×10^{-18}, Kr ($\leq 6 \times 10^{-17}$, 1.5×10^{-17}) and Xe ($\leq 1.6 \times 10^{-16}$, 1.1×10^{-16}) clearly illustrating this conclusion.

p. S(^{1}D) + *Other Molecules*

The reactions of S(^{1}D) with Si–H and B–H bonds have been examined briefly (Gunning & Strausz, 1966; Strausz, 1967) and appear to be of value in synthesizing various complex cage-structured organo-boron compounds (Plotkin & Sneddon, 1977). CH_3SiH_3 gives predominantly the corresponding mercaptan CH_3SiH_2SH. From product ratios the rate constants for Si–H to C–H bond insertion is reported to be approximately of the order of 50 implying an extremely fast, collision frequency rate. $(CH_3)_3SiH$ behaves similarly. $(CH_3)_4Si$ on the other hand is comparable to the alkanes but has about twice their value for the rate constant ratio of quenching to reaction.

B_2H_6 also appears to undergo an insertion reaction with a rate similar to that for the alkanes.

5.8.3. References

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5.9. Diatomic Sulfur, $S_2(a\,^1\Delta_g,\ b\,^1\Sigma_g^+,\ A\,^3\Sigma_u^+,\ B\,^3\Sigma_u^-)$

The electronic energy states of S_2 although similar to isoelectronic O_2 are not as well characterized. Levels above $v'=9$ in the $B\,^3\Sigma_u^-$ state are predissociated (Ricks & Barrow, 1969). Estimates of the energy positions of the $A\,^3\Sigma_u^+$, $b\,^1\Sigma_g^+$, and $a\,^1\Delta_g$ states have been discussed by Barrow and duParcq (1965, 1968).

Limited kinetic data are available only for the $B\,^3\Sigma_u^-$ and $a\,^1\Delta_g$ states.

5.9.1. Radiative Lifetimes

According to the more recent studies of McGee and Weston (1978), lifetime measurements for $S_2(B\,^3\Sigma_u^-)$ appear to indicate the effects of a coupled state. According to the experimental conditions, radiative lifetimes of either $\cong$ 15–40 ns or $\cong$ 100 ns can be determined from the fluorescence decay, table 38. Unfortunately, their data were obtained with a broadband excitation source (9.6 nm FWHM) implying a severe averaging over several vibrational and numerous rotational levels. Although this possibility of mixed states exists, the long lifetimes may yet be solely a characteristic of some experimental peculiarity of these broadband excitation systems.

Consequently, until additional data are obtained for specific levels, a value of about 20–40 ns is suggested for the $v'=0$–9 levels.

Radiative lifetimes for the other states of S_2, all of which are metastable, are not available. Although their optical selection rules may be less stringent than those for O_2, their lifetimes appear relatively long.

Table 37. Energies and radiative lifetimes of low-lying electronic states of molecular sulfur.

	T_e	T_0	D_0^0	τ
		cm^{-1}		s
$B^3\Sigma_u^-$	31,689	31,905	12,936	$\approx 40 \times 10^{-9}$ (b)
$A^3\Sigma_u^+$	$\approx$22,700	$\approx$22,900	$\approx$12,670	? metastable
$b^1\Sigma_g^+$	$\approx$ 9,140	$\approx$ 9,490	$\approx$26,100	? metastable
$a^1\Delta_g$	$\approx$ 5,140	$\approx$ 5,490	$\approx$30,100	? metastable
$X^3\Sigma_g^-$	0	385.8[a]	35,216[a]	-

[a] Ricks and Barrow, 1969 (Dissociation to ground state sulfur atoms)

[b] See table 38

Table 38. Radiative lifetimes for $S_2(B^3\Sigma_u^-)$

State	τ, ns	Method	Reference
v'=0-3	16.9	e-Bombardment-phase shift	Smith, 1969
v'=4, N'=40	18.3	Hanle effect	Meyer & Crosley, 1973[a]
v'=3, N'=42	20.7		
v'=4, N'=12	$\approx$20	Hanle effect	Caughey & Crosley, 1977
v'=4, N'=40	36		
v'=3, N'=42	36		
v'$\approx$5-8	45.0	Broad band excitation-fluorescence decay	McGee & Weston, 1977[b]
v'$\approx$5-8	$\approx$15-30 $\approx$110	Broad band excitation-fluorescence decay	McGee & Weston, 1978[c]

[a] Incorrect by about a factor of two (Caughey & Crosley, 1977)

[b] Similar value for excitation in v'=0-3 or 7-12

[c] Decay characterized by two components in experiments with S_2/quenchant gas mixtures

5.9.2. Suggested Rate Constant Values, cm^3 molecule^{-1} s^{-1}

a. $S_2(B\,^3\Sigma_u^-)$, 900 K

$k_{elect} \gg k_{vib,rot}$ (H_2S, SO_2, S_2).
$k_{rot} > k_{vib} \gg k_{elect}$ (H_2, N_2, inert gases).
Rotational relaxation exhibits orientation memory.
$k_{elect} \cong (1\text{-}5) \times 10^{-10}$ (CF_4, C_2F_6, N_2, inert gases).
$\cong (6\text{-}10) \times 10^{-10}$ (H_2S, SO_2, S_2).
$k_{vib} \cong (1.2\text{-}5.3) \times 10^{-10}$ (H_2, N_2, inert gases).
$k_{rot} \cong (5.7\text{-}15) \times 10^{-10}$ (H_2, N_2, inert gases).

b. $S_2(A\,^3\Sigma_u^+, b\,^1\Sigma_g^+)$

No available data.

c. $S_2(a\,^1\Delta_g)$, 300 K

$k_{He,\,OCS} \cong 2 \times 10^{-14}$.
$k_{CH_4,\,H_2S,\,H_2S_2} > k_{OCS,\,CO_2}$.
$k_{H_2} > k_{D_2}$.
Little data available.

5.9.3. Discussion

a. $S_2(B\,^3\Sigma_u^-)$

Although limited data are available for the $B\,^3\Sigma_u^-$ state, listed in table 39, indications are that quenching or relaxation can proceed with high efficiencies. For S_2, SO_2, H_2S, k_{elect}

Table 39. Rate constants for interactions of $S_2(B^3\Sigma_u^-)$, cm^3 $molecule^{-1}$ s^{-1}.

M	k_M, cm^3 $molecule^{-1}$ s^{-1}				
CF_4				1.5×10^{-10}	3.6×10^{-13}
C_2F_6				4.7×10^{-10}	5.7×10^{-13}
H_2S			$\approx6\times10^{-10}$		
SO_2			$\approx6\times10^{-10}$		
N_2			$(11\times10^{-10})^a$	3.5×10^{-10}	2.0×10^{-13}
S_2			13×10^{-10}	6.2×10^{-10}	
He	1.9×10^{-10}		$(10\times10^{-10})^a$	2.5×10^{-10}	small
Ne	8.3×10^{-11}		$(6.6\times10^{-10})^a$		
Ar	5.8×10^{-11}	2.1×10^{-10}	$(6.9\times10^{10})^a$	1.2×10^{-10}	3.6×10^{-13}
Kr	6.8×10^{-11}		$(7.5\times10^{-10})^a$		
Xe	8.8×10^{-11}		$(7.3\times10^{-10})^a$	1.6×10^{-10} (b)	13×10^{-13} (c)
Exp. Temp. K	873	298	900	873	
Method	Static cell, 150Pa sulfur vapor, M≤5 kPa. 292.9, 293.6 nm Mg^+ source excites (8,1)N' = 37,41 levels. (8,0)-(8,12) fluorescence recorded photographically.	Fast flow system, RF discharge in H_2/Ar mixture ≤320 Pa. S from $H+H_2S$ reactions. S_2 emission, v'=0-9 monitored via filters centered at 366 nm.	Static cell, ≈80 Pa sulfur vapor, M≤ few hundred Pa. 307.6 nm Zn line induced fluorescence of v'=4, N'=40, J'=41 resolved.	Static cell, ≈80 Pa sulfur vapor, M≤80 kPa, H_2 light source, broadband (292 nm, 9.6 nm FWHM) excitation of S_2 fluorescence, v'=5-8. Monitored at 370 nm (33 nm FWHM bandpass).	
Comments	$k \propto \tau^{-1}$, based on τ = 40 ns.	$k \propto \tau^{-1}$, based on τ = 40 ns.	Rot. relaxation exhibits orientation memory. $k_{elect} >> k_{vib, rot}$ (S_2,SO_2,H_2S) $k_{rot} > k_{vib} >> k_{elect}$ (rare gases, N_2).	Mixed state behavior.	
Reference	Durand, 1940	Fair & Thrush, 1969	Caughey & Crosley, 1977	McGee & Weston, 1977, 1978	

[a] $k_{vib+rot}$ (see also Caughey and Crosley, 1978).

[b] Relate to short-lived fluorescence component ($\tau \approx$ 20-40 ns)

[c] Relate to long-lived fluorescence component ($\tau \approx$ 100 ns)

$\gg k_{vib,\,rot}$, whereas with the inert gases, H_2 or N_2 rotational relaxation is dominant and $k_{rot} > k_{vib} \gg k_{elect}$.

Caughey and Crosley (1978) now report individual rates for the total transfer out of $v' = 4$, vibrational rates for $v'=4 \rightarrow 3$ and for $v'=4 \rightarrow 5$ together with total rotational transfer rates out of $v'=4$, $N'=40$, $J'=41$. These values for k_{vib}, $k_{v'}=4 \rightarrow 3$, $k_{v'}=4 \rightarrow 5$ and k_{rot} are, respectively, He 2.0, 1.09, 0.54, 8.2; Ne 1.55, 0.70, 0.33, 6.2; Ar 1.22, 0.61, 0.29, 5.7; Kr 2.08, 0.97, 0.38, 6.4; Xe 2.6, 1.06, 0.52, 4.8; H_2 5.3, 2.4, 1.08, 15 and N_2 2.5, 1.15, 0.49, 7.9×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, for conditions similar to their 1977 paper listed in table 39. The fact that the sum of the $k_{v'}=4 \rightarrow 3$ and $k_{v'}=4 \rightarrow 5$ vibrational relaxation rates is less than the total vibrational transfer rate is suggested as an indication of some multi-quantum vibrational transfer.

Caughey and Crosley (1977, 1978) note that the rotational relaxation exhibits a pronounced orientation memory, even for changes of several quanta. Also multiquantum rotational transfer can occur in a single collision ($\Delta J \leq 14$ was observed with He). The coherence (orientation) retention, 85% probable for collisions with He decreasing to ≅ 40% for Xe is noted not only in $F_1 \rightarrow F_1$ transitions (F_1 levels, $J = N+1$) but also for $F_1 \rightarrow F_2, F_3$ (F_2, $J=N$; F_3, $J=N-1$). However, it could not be specifically concluded that such a retention also occurred during vibrational relaxation.

The existence of a longer-lived component that shows two to three orders of magnitude smaller quenching rates must be regarded with some skepticism at present although perturbed states undoubtedly do exist. Further studies utilizing narrow band excitation are desirable.

Efficient quenching is consistent with the observations of Tewarson and Palmer (1971) who noted that the $B\,^3\Sigma_u^- - X\,^3\Sigma_g^-$ emission, $v' \leq 9$, from K or Na/SCl_2 or $SOCl_2$ diffusion flames at 1100 K was not affected by Ar pressures over a range of a few hundred Pa but that the levels were quenched at higher pressures. At 1100 K the time between collisions of S_2 and Ar becomes equal to a radiative lifetime of 40 ns at about 1 kPa. They noted also that the addition of a few hundred Pa of OCS or O_2 to a K/SCl_2 flame had no noticeable affect on the S_2 emission. Also, lasing action of the $S_2(B\,^3\Sigma_u^-)$ state from a heated cell containing sulfur has been noted to rapidly fall off due to quenching as the sulfur pressure is increased above

1.3 kPa, indicative of an efficient interaction (Leone & Kosnik, 1977).

The nature of the electronic quenching mechanism remains unclear. McGee and Weston (1978) have noted that $V-V$ transfer appears unimportant since $S_2(B\,^3\Sigma_u^-)$ and CF_4 have almost equal vibrational quanta yet show no enhanced resonance quenching rates. Whether collision induced predissociation is an important process awaits examination. The $v'=0$, 4–8 levels are reportedly perturbed by a $^3\Pi_u$ state (Ricks & Barrow, 1969).

b. $S_2(A\,^3\Sigma_u^+, b\,^1\Sigma_g^+)$

At present these states are poorly characterized. No absorption systems have been reported for them, nor has the forbidden emission from $A\,^3\Sigma_u^+$ been observed. That from $b\,^1\Sigma_g^+$ has been tentatively assigned to the lasing wavelengths in the vicinity of 1 μm observed in photodissociation studies of OCS (Zuev et al., 1972). This lack of analytical means for monitoring their concentrations is responsible for the absence of chemical kinetic data.

c. $S_2(a\,^1\Delta_g)$

The small amount of data concerning the chemistry of $S_2(a\,^1\Delta_g)$ is presented in table 40. It derives mainly from preliminary observations of the decay behavior of $S_2(a\,^1\Delta_g)$ or the growth of $S_2(X\,^3\Sigma_g^-)$ in various flash photolysis systems and must be regarded as approximate. For example, the values of Fowles et al. (1967) are pressure dependent varying by an order of magnitude over the 60-fold pressure range indicating the incomplete nature of their mechanism, a fact noted also by Basco and Pearson (1967). These studies monitored only ground state S_2 relating this back to the $S_2(a\,^1\Delta_g, b\,^1\Sigma_g^+)$ both of which are presumably formed initially (Strausz et al., 1968; Zuev et al., 1972). CO_2 has been noted as inefficient in quenching $S_2(a\,^1\Delta_g)$ (Donovan & de Sorgo, 1967).

Little can be said at present concerning these rates except that even though small they do indicate a markedly different behavior from that of inefficiently quenched $O_2(a\,^1\Delta_g)$ (Leiss et al., 1978).

5.9.4. References

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b. $Se(4^1D_2)$

Reaction of Hydrogen Atoms with Hydrogen Sulfide," Trans. Faraday Soc. **65**, 1208(1969).

Table 40. Rate constants for interactions of $S_2(a^1\Delta_g)$, cm^3 $molecule^{-1}$ s^{-1}.

M	k_M	Exp. Temp. K	Method	Reference
OCS	5.8×10^{-14} (0.93 kPa)	≈330	Flash photolysis Kr-N_2 lamp >220 nm, E=1660 J. S_2 monitored by $B^3\Sigma_u^-\leftarrow X^3\Sigma_g^-$(13,0) 271.3 nm absorption band. Plate photometry. Pure OCS, 0.93-54.7 kPa. $S_2(^1\Delta_g, ^1\Sigma_g^+)$ states implied but not resolved.	Fowles et al., 1967
	3.2×10^{-14} (2.27)	≈320		
	1.4×10^{-14} (8.67)	≈310		
	5.4×10^{-15} (54.7)	≈295		
	$k_{CH_4} > k_{OCS}$			
	$k_{H_2S,\ H_2S_2} > k_{OCS,\ CO_2}$	300	Flash photolysis H_2S or H_2S_2/CO_2 and OCS/inert gases. $^1\Delta_g$ monitored in absorption 234-252 nm. Plate photometry.	Strausz et al., 1968
	$k_{H_2} > k_{D_2}$			
N_2	$>2\times10^{-15}$	300	Flash photolysis E=2112 J. 13 Pa S_2Cl_2/80 kPa N_2. Plate photometry, $S_2(^1\Delta_g)$ in absorption 238-250 nm. Short lived, survives <50 μs.	Donovan et al., 1968
He	$\approx2\times10^{-14}$	300	Flash photolysis E=500 J. 13 Pa OCS/5.3 kPa He. Plate photometry, $S_2(^1\Delta_g)$ in absorption. Estimated from decay rate.	Donovan et al., 1969, 1970

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5.10. Atomic Selenium, Se($4^3P_{1,0}$, 4^1D_2, 4^1S_0)

The energies of these four excited metastable states are such that their individual nature can be characterized. At present, only a limited amount of room temperature data are available for $^1S_0$, $^1D_2$ and $^3P_0$. However, this is sufficient to provide an initial insight to their comparative behaviors.

Table 41. Energies and radiative lifetimes of low-lying electronic states of atomic selenium

Electronic State	Energy[a] Level (cm^{-1})	Radiative[b] Lifetime (s)
$^1S_0$	22,446.03	0.098
$^1D_2$	9,576.08	1.36
$^3P_0$	2,534.35	115
$^3P_1$	1,989.49	5.88
$^3P_2$	0.00	-

[a] Moore, 1971

[b] Garstang, 1964; Kernahan & Pang, 1976

5.10.1. Recommended Rate Constant Values, 300 K

It is pointless to suggest recommended values since only single sets of data are available for each of the $^3P_0$, $^1D_2$ or $^1S_0$ states. At present, there is no obvious reason for questioning the reliability of these published values.

Se(4^3P_0): efficient interactions,
$k_{N_2O,\,CO_2,\,H_2} > k_{CO,\,N_2,\,O_2} > k_{Ar}$.
Se(4^1D_2): efficient interactions,
$k_{OCSe,\,CO_2,\,CO,\,N_2,\,O_2,\,H_2,\,D_2,\,Kr,\,Xe} > k_{SF_6,\,He,\,Ne,\,Ar}$.
Se(4^1S_0): generally inefficient interactions
with the exceptions of OCSe, NO_2 and Cl_2.

5.10.2. Discussion

a. Se(4^3P_0)

The far uv photolysis of CSe_2 has been observed to produce Se atoms with a nonthermal distribution over the 4^3P_J spin components (Callear & Tyerman, 1964). Of the excited $^3P_0$ and $^3P_1$ states, data have been obtained only for the former and, as indicated in table 42, imply generally rapid collisional decay mechanisms.

Chemical reactions are not possible for these species and the quenching mechanisms are uncertain. The Se($^3P_0$–$^3P_1$) decay involves a 544.86 cm^{-1} energy dissipation, that for ($^3P_0$–$^3P_2$) corresponds to 2534.35 cm^{-1}. This compares with vibrational quanta, in cm^{-1}, of 588.8 (N_2O), 667.4 (CO_2), 2143 (CO), 2330 (N_2), 1556 (O_2) and 4160 (H_2). Electronic-vibrational energy transfer has been suggested for N_2O and CO_2 which have energy defects of only 44 and 122 cm^{-1}, respectively. CO and N_2 may involve $^3P_0$–$^3P_2$ relaxation. The rates for O_2 and particularly H_2 indicate unexpected efficiencies that might involve electronic-rotational energy transfer (Callear & Tyerman, 1966).

b. Se(4^1D_2)

Analogous to sulfur chemistry, the uv photolysis of OCSe produces Se($^1D_2$) in a system suitable for detailed kinetic analysis (Callear & Tyerman, 1965). Only one set of quantitative data, illustrated in table 43, are yet available for its collisional quenching. These show similar trends to S($^1D_2$), although rates do appear to be consistently faster. With the inert gases, the familiar pattern is noted of collisional cross sections increasing with atomic number but rates are about 5-10 times faster. SF_6, rather unreactive with S(^1D), is still relatively inefficient but about 50 fold less so. OCSe shows the similar highly efficient reaction and undoubtedly yields $Se_2(a\,^1\Delta$ or $b\,^1\Sigma^+)$. CO and N_2 are surprisingly efficient for nonreactive, nonadiabatic transitions; k_{N_2} is about 40 fold faster than for S($^1D_2$). Likewise, the interaction with O_2 is very fast but the adiabatic surfaces, that lead solely to SeO($b\,^1\Sigma^+$), are endothermic and this must also involve a curve crossing mechanism. The rates for H_2 and D_2 are fast and suggest reaction as the dominant channel. Se(^1D) + H_2 correlates to ground state SeH + H products and requires for thermoneutrality a value for D_0°(Se-H) of $\geq$ 317 kJ mol^{-1} (75.9 kcal mol^{-1}) which lies within the error bars of an experimental estimate of 311 ± 12 kJ mol^{-1} (Lindgren, 1968).

Efficient quenching by CO_2 has been noted but not quantitatively measured. Reactions of Se($^1D_2$) with propane, cyclopropane, cyclobutane, ethane, methylsilane and isobutane have been studied using a flash photolysis-time resolved mass spectrometric technique (Tyerman et al., 1966).

Table 42. Rate constants for interactions of Se(4^3P_0).

M	k_M, cm^3 $molecule^{-1}$ s^{-1}
N_2O	1.2×10^{-10}
CO_2	1.4×10^{-10}
CO	1.1×10^{-12}
N_2	3.0×10^{-12}
O_2	1.5×10^{-12}
H_2	3.5×10^{-10}
Ar	$\leq 2.4 \times 10^{-14}$
Exp. Temp. K	298
Method	Flash photolysis 6.7 Pa CSe_2/3.3-6.7 kPa Ar, M<200 Pa. Plate photometry Se($^3P_0$) 206.3 nm atomic absorption
Comments	Pseudo first order kinetic analysis
Reference	Callear & Tyerman, 1966

Table 43. Rate constants for interactions of Se(4^1D_2).

M	k_M, cm^3 $molecule^{-1}$ s^{-1}
SF_6	$\approx 3 \times 10^{-12}$
OCSe	$\approx 1 \times 10^{-10}$
CO	1.4×10^{-10}
N_2	1.7×10^{-10}
O_2	1.2×10^{-10}
H_2	2.1×10^{-10}
D_2	7.6×10^{-11}
He	$\approx 3.0 \times 10^{-14}$
Ne	$\approx 4.0 \times 10^{-13}$
Ar	$7.0\ (\pm 4.9) \times 10^{-12}$
Kr	$2.3\ (\pm 1.2) \times 10^{-11}$
Xe	$6.7\ (\pm 3.0) \times 10^{-11}$
Exp. Temp. K	293
Method	Flash photolysis of 0.03 Pa OCSe/300 Pa He mixtures. 0.3-3 Pa Ar, Kr and Xe. Time resolved 185.8 nm atomic absorption of Se(4^1D_2). Pseudo first order conditions.
Reference	Donovan & Gillespie, 1975; Donovan & Little, 1978

Insertion to form selenomercaptans appears the dominant mechanism. Reaction with C_2D_4 and other alkenes predominantly forms the episelenide adduct (Strausz & Gunning, 1968). No kinetic data for these have been reported.

c. Se(4^1S_0)

At present, only Black et al. (1976a,b) have studied the reactions of Se($^1S_0$). Quantum yield measurements for the production of Se($^1S_0$) from OCSe in the 110–200 nm range indicate a maximum of >0.75 between 164 and 180 nm, gradually falling away at both shorter and longer wavelengths. The threshold for Se($^1S_0$) production is at ≅ 210 nm (Black et al., 1976a).

Although the forbidden Se($^1S_0$–$^3P_1$) emission at 488.8 nm can be observed, this is superimposed on a more pronounced and extensive molecular system stretching from 380–750 nm and attributed to $Se_2(B\,^3\Sigma_u^-–X\,^3\Sigma_g^-)$. The intensity of this molecular emission correlates with the Se($^1S_0$) concentration and has been used by them to derive the quenching cross sections for the large series of species listed in table 44.

Table 44. Rate constants for interactions of Se(4^1S_0).

M	k_M, cm^3 $molecule^{-1}$ s^{-1}
CH_4	$\leq 1.6 \times 10^{-15}$
C_2H_6	1.3×10^{-14}
C_2H_4	1.4×10^{-13}
C_2H_2	$\leq 1.8 \times 10^{-15}$
N_2O	$\leq 1.6 \times 10^{-16}$
NH_3	5.5×10^{-12}
OCSe	1.6×10^{-10}
SF_6	$\leq 2.1 \times 10^{-15}$
CO_2	$\leq 1.6 \times 10^{-16}$
CO	$\leq 1.6 \times 10^{-16}$
NO	1.2×10^{-10}
N_2	$\leq 1.6 \times 10^{-16}$
O_2	4.9×10^{-12}
H_2	2.2×10^{-15}
Cl_2	1.6×10^{-10}
He	$\leq 1.6 \times 10^{-16}$
Ar	$\leq 1.6 \times 10^{-16}$
Kr	$\leq 1.6 \times 10^{-16}$
Xe	$\leq 1.6 \times 10^{-16}$
Exp. Temp. K	296
Method	Pulsed photolysis OCSe/He mixtures, slow flow, H_2 lamp 165 nm(1.7 nm bandpass), (170 nm for O_2 case). 0.02-0.08 Pa OCSe/400 Pa He. $Se_2(B^3\Sigma_u^- - X^3\Sigma_g^-)$ 380-750 nm emission used as measure of Se($^1S_0$).
Reference	Black et al., 1976b

It has been implied by Black et al. (1976a) that the $Se_2(B\,^3\Sigma_u^-)$ is produced with ≤ 17% yield from the possibly thermoneutral reaction

$$Se(^1S_0) + OCSe(X\,^1\Sigma^+) = CO(X\,^1\Sigma^+) + Se_2(B\,^3\Sigma_u^-).$$

However, this is clearly a spin forbidden process. Although the corresponding reaction with S($^1S_0$) is similarly ≅ 6.7 kJ mol^{-1} (1.6 kcal mol^{-1}) exothermic, no indication has been reported of observing the corresponding $S_2(B\,^3\Sigma_u^-–X\,^3\Sigma_g^-)$ emission in such OCS systems. Rather, the S_2 appears to be formed mainly in the $a\,^1\Delta_g$ and possibly $b\,^1\Sigma_g^+$ states. Consequently, unless it so happens that an efficient nonadiabatic curve crossing mechanism is operative, another precursor may be responsible for the Se_2 emission. Nevertheless, the measured quenching cross sections appear reasonable and like $S(^1S)$ show very fast reactions with OCSe, NO and Cl_2, although a nonadiabatic transition may be involved with NO. Interactions with O_2, NH_3, C_2H_4 and C_2H_6 are less efficient and again reflect the behavior of $S(^1S)$, however, that for O_2 does appear to be about 8 times faster. The inert gases, N_2, CO, CO_2, N_2O, SF_6, H_2, CH_4 and C_2H_2 are all inefficient quenchants which undoubtedly reflects nonadiabatic transitions. Only with C_2H_2 is quenching significantly slower than is the case for $S(^1S)$.

5.10.3. References

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5.11. Atomic Tellurium, $Te(5^3P_{1,0}, 5^1D_2, 5^1S_0)$

The $^3P_1$ and $^3P_0$ states, although examined individually, do appear to be equilibrated for all purposes owing to their close lying nature. Only limited room temperature data are available for $^3P_{1,0}$ and $^1D_2$. No studies have been reported yet for $Te(^1S_0)$.

5.11.1. Recommended Rate Constant Values, 300 K

Too little data exist at present for any kind of reliability assessment.

$Te(5^3P_{1,0})$: intermultiplet relaxation, $^3P_1 \leftrightarrow {}^3P_0$, fast.

For relaxation to $^3P_2$, $k_{CH_4, i-C_4H_{10}, H_2} > k_{CO_2, O_2, D_2, He, Ar, Xe}$.

$k_{H_2} \gg k_{D_2}$.

$Te(5^1D_2)$: $k_{D_2Te} \gg k_{Ar}$.

Table 45. Energies and radiative lifetimes of low-lying electronic states of atomic tellurium.

Electronic State	Energy[a] Level (cm^{-1})	Radiative[b] Lifetime (s)
$^1S_0$	23,199	0.025
$^1D_2$	10,559	0.28
$^3P_1$	4,751	0.45
$^3P_0$	4,707	137
$^3P_2$	0	-

[a] Moore, 1971

[b] Garstang, 1964

5.11.2. Discussion

a. $Te(5^3P_{1,0})$

The study of Donovan and Little (1973) listed in table 46 provides the only quantitative data yet available for these states. Although they resolved the $^3P_1$ and $^3P_0$ atomic absorptions, deriving data for each, no significant difference could be observed. It was concluded that these close lying levels are equilibrated and that the observed decay is a measure of the sum of the relaxation rates for the two states. This lends support to the general belief that intermultiplet relaxation cross sections are large for closely spaced electronic levels.

In this H_2Te flash photolysis system it was concluded that the populations produced in the $^3P_{1,0}$ levels are <10% of that in $^3P_2$. Consequently, no additional information can be derived by monitoring $^3P_2$. It was not possible to distinguish between reaction or physical quenching and no products were monitored.

The data confirm the preliminary and qualitative study by Connor et al. (1969) which indicated that although relaxation

Table 46. Rate constants for interactions of $Te(5^3P_{1,0})$.

M	k_M, cm^3 $molecule^{-1}$ s^{-1}
O_2	1.3×10^{-14}
H_2	1.0×10^{-11}
D_2	8.8×10^{-15}
He	$\leq 3.0 \times 10^{-15}$
Ar	1.4×10^{-15}
Xe	$\leq 2.7 \times 10^{-15}$
Exp. Temp. K	295
Method	Flash photolysis >200 nm, 400 J, 1.73 Pa H_2Te/3.34 kPa Ar. $Te(^3P_0)$ and $(^3P_1)$ via atomic absorption 238.40 and 238.65 nm respectively using sealed Ar/Te microwave discharge lamp.
Comments	Data collected at least 300 μs after flash to allow $Te(^1D_2)$ and $HTe(X^2\Pi_{1/2})$ to decay.
Reference	Donovan & Little, 1973

by H_2, CH_4 and i-C_4H_{10} was relatively fast, that with O_2, CO_2 and Ar appeared inefficient. Reactions to form TeH or TeO are endothermic. Likewise a direct insertion reaction with O_2 to give TeO_2 appears equally unlikely (Donovan & Little, 1973).

The most remarkable observation in this work concerns the relative rate constants with H_2 and D_2 which indicate an 840 fold difference between the two cross sections, the largest such isotope effect yet observed. This has been explained in terms of a near resonant electronic to vibrational energy transfer process for H_2 (Donovan & Gillespie, 1975). This is energetically deficient by only 6 cm^{-1} in the case of

$$Te(5^3P_0) + H_2(v''=0, J''=1) \rightarrow Te(5^3P_2) + H_2(v''=1, J''=3).$$

This is a reasonable explanation. Moreover, the $v''=0$, $J''=1$ level of H_2 is the most densely populated at room temperature. It indicates that the ortho-H_2 component will be responsible for the quenching. The corresponding interaction with D_2, involving a $v''=0, J''=2 \rightarrow v''=1, J''=4$ transition, is about 1320 cm^{-1} exothermic for $Te(5^3P_0)$ and other transitions are no closer to resonance.

Such interactions have been treated theoretically by Ewing (1974), invoking long range attractive forces theory based on quadrupole-quadrupole coupling which involves a selection rule of $\Delta J=0, \pm 2$. This predicts a negative temperature dependence for the rate constant. It also implies that the $^3P_1$ cross section is the dominant contributor although this is not quite in such close resonance as for $^3P_0$. It therefore appears that this chance resonance with H_2 is all important and controls the relative rates with H_2 and D_2.

b. $Te(5^1D_2)$

The single preliminary study by Donovan et al. (1972) listed in table 47 provides the very limited data available for this state. Photolysis of D_2Te was used as the source of $Te(^1D_2)$ to eliminate a spectral interference arising from an overlapping H_2Te absorption band. Decay of $Te(^1D_2)$ is attributed to the reaction

$$Te(5^1D_2) + D_2Te = DTe + DTe.$$

Ar quenches rather inefficiently and at a much slower rate than expected from comparison with $S(^1D_2)$ or $Se(^1D_2)$.

Obviously, more extensive investigations are required.

Table 47. Rate constants for interactions of $Te(5^1D_2)$

M	k_M, cm^3 molecule^{-1} s^{-1}
D_2Te	1.0×10^{-11}
Ar	$<1.6 \times 10^{-15}$
Exp. Temp.	300 K
Method	Flash photolysis >200 nm, 800 J. 4.0 Pa D_2Te/50 kPa He. $Te(^1D_2)$ 175.8 nm atomic absorption, plate photometry.
Comments	$Te(5^3P_2)$ and DTe concentrations also monitored in absorption; both increase as $^1D_2$ decreases.
Reference	Donovan et al., 1972

5.11.3. References

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