

# Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen $O(^3P)$ with Sulfur Containing Compounds

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# Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen $O(^3P)$ with Sulfur Containing Compounds

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Chemical kinetic data for reactions of  $O(^3P)$  atoms with sulfur containing compounds are compiled and critically evaluated. Specifically, the reactions considered include the interactions of the ground electronic state of oxygen atoms,  $O(^3P)$ , with  $S_2$ ,  $SF_2$ ,  $SF_3$ ,  $SOF$ ,  $S_2O$ ,  $SO$ ,  $SO_2$ ,  $SO_3$ ,  $SH$ ,  $H_2S$ ,  $D_2S$ ,  $H_2SO_4$ ,  $CS$ ,  $CS_2$ ,  $COS$ ,  $CH_3SH$ ,  $C_2H_5SH$ ,  $C_3H_7SH$ ,  $C_4H_9SH$ ,  $C_5H_{11}SH$ ,  $CH_3SCH_3$ ,  $cy-CH_2SCH_2$ ,  $cy-CHCHSCHCH$ ,  $CH_3SSCH_3$ ,  $SCF_3$ ,  $SCCl_2$ , and  $cy-CF_2SCF_2S$ . With one exception, the liquid phase reaction  $O(^3P) + H_2SO_4 \rightarrow$  products, all the data considered were for gas phase reactions. Where possible, "Recommended" values of the rate parameters have been assessed and conservative uncertainty limits assigned to them.

Key words: Arrhenius parameters; atomic oxygen; chemical kinetics; evaluated kinetic data;  $O(^3P)$ ; rate of reaction; recommended kinetic parameters; sulfur.

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## 1. Introduction

### 1.1. Overview

The present evaluation of chemical kinetic data for the elementary reactions of  $O(^3P)$  atoms with sulfur containing compounds follows a recent evaluation of kinetic data for the  $O(^3P)$  reactions with unsaturated hydrocarbons<sup>1</sup>. As pointed out there, these evaluations represent a part of a larger effort directed towards the development of a comprehensive general evaluated chemical kinetic data base. More specifically, they are a part of the broader data base for all  $O(^3P)$  reactions with organic and inorganic reactants. They are thus also a part of an extensive data base, currently developed by the Chemical Kinetics Data Center of the National Bureau of Standards, dealing with chemical oxidation processes, in

particular those involved in thermal combustion and in atmospheric chemistry.

The main object of the present evaluation has been to compile as many as possible of the published values of reaction rates of the elementary steps involved in the reactions of  $O(^3P)$  atoms with organic and inorganic sulfur containing compounds and to use them to arrive at an estimate of the "recommended" (or "preferred") values of the kinetic parameters and their uncertainties.

### 1.2. Reaction Mechanisms

There are some far-reaching similarities between the  $O(^3P)$  reactions with some of the sulfur containing compounds, especially when sulfur is in a low oxidation state, and those with unsaturated hydrocarbons. As discussed in the earlier evaluation<sup>1</sup>, interaction of a ground state oxygen atom,  $O(^3P)$ , with an organic or inorganic compound may in principle lead to any of the following three types of chemical change: 1) "Abstraction" by the

O atom of an atom from the compound, 2) "Addition" of the O atom to the compound, and 3) "Replacement" (or "displacement") by the O atom of an atom or atomic group (radical) from the compound. "Replacement" itself is of necessity initially an addition, combined with subsequent or simultaneous fragmentation of the initial adduct. "Insertion" is a particular type of addition in which the atom inserts into a bond of a compound; for  $O(^3P)$  atoms this may be sometimes spin forbidden and not likely to occur (although it is not spin forbidden for  $O(^1D_2)$  atoms reacting with hydrocarbons and occurs readily<sup>2</sup>).

Rapid addition of  $O(^3P)$  atoms to the CC double bond is the main and perhaps frequently the exclusive initial process in their reactions with alkenes<sup>3-5,6</sup>. Similarly, in the  $O(^3P)$  reactions with a number of sulfur containing compounds rapid addition of  $O(^3P)$  to an S atom in the compound is the main and perhaps sometimes the exclusive initial process. At least at not too elevated temperature and with  $O(^3P)$  atoms not kinetically excited ("hot"), abstraction cannot compete effectively with the very rapid  $O(^3P)$  addition to the double bond. However, at sufficiently high temperature, or with sufficiently "hot"  $O(^3P)$  atoms, abstraction of H atoms may be expected to become more important<sup>5</sup>.

Kinetic behavior of methyl sulfide<sup>7,8</sup> and dimethyl disulfide<sup>8</sup> and of alkenes in their reactions with  $O(^3P)$  atoms is very similar: oxygen atoms add very rapidly to S atoms and to CC double bonds, respectively, and, moreover, the activation energies tend to be negative in both cases, especially so in the more rapid of these reactions. In both cases the exothermicities are relatively high and initial adducts tend to undergo rapid fragmentation. In view of these similarities and the type of products formed, it can be assumed that the primary process in the reaction of  $O(^3P)$  with methyl sulfide and dimethyl disulfide is  $O(^3P)$  attachment to S to form an energy-rich adduct which readily fragments.

The addition mechanism appears to apply also, at least in part, to alkane thiols and probably to some other sulfur organics, as well as to  $H_2S$ . However, since the initial adduct rapidly fragments, it is difficult to differentiate, for example, between a primary abstraction and a primary addition. A good example<sup>9</sup> of such mechanistic ambiguity is the reaction  $O + H_2S \rightarrow$  products, in which the observed products are OH and SH, i.e. the expected "abstraction" products. In view of such ambiguities, and the considerable analytical difficulties frequently associated with S containing compounds, there remain serious uncertainties in the literature regarding the reaction channels, the branching ratios and finer details of the reaction mechanisms. As a consequence, the primary emphasis in the present evaluation is on the overall rate constants, as it has been also in the earlier evaluation of the related series of  $O(^3P)$  reactions with unsaturated hydrocarbons<sup>1</sup>. At the same time, when information is available, alternative reaction channels are indicated in the present evaluation and their rates are listed and the pertinent references given.

### 1.3. Selection of Recommended Rate Parameters and Their Uncertainty Factors

Reliability of the kinetic data used in the present evaluation has been assessed in particular by scrutinizing the experimental techniques employed, the thoroughness of investigation, the number and precision of measurements, and the consistency with other reported values in the literature when these are available. Although single experimental values have been reported for a number of the reactions considered, some of them are believed to be sufficiently reliable to justify their inclusion into the list of recommended values and assignment of conservatively estimated uncertainty limits. In such cases, as well as when no recommendation is considered possible, or when the derived recommended values are based on more than one reported value but the estimated uncertainty limits are large, further experimental measurements of the rate constants will evidently be needed.

As discussed earlier<sup>1</sup>, as a result of potential presence of unknown ("hidden") systematic errors in the measured values of rate constants of a reaction, there are no standard statistical methods for a quantitative evaluation from the data reported in the literature of the expected "best" value and its confidence limits. When two or preferably more values obtained by different techniques have been reported, and there is close agreement between them (within the combined imprecisions), it is reasonable to assume that systematic errors are probably less important than the random errors. In such cases use of standard weighted least squares techniques may be justified and is equivalent to treating any residual systematic errors as random errors.<sup>10</sup> As was done previously<sup>1</sup>, in the present evaluation the "recommended values" were generally obtained as the mean weighted least squares values. Depending on the estimated reliability of the data, smaller (and, in rare cases, zero) statistical weights were assigned to some literature values of rate parameters. Thus, for example, for the O atom reaction with dimethyl sulfide at 300 K, the  $k$  value of 74 CAD/WIC is two orders of magnitude smaller than the other values for the same reaction and is therefore assigned zero weight.

Since the procedure used is of necessity subjective, conservatively estimated probable overall uncertainties were assigned to the selected "recommended" values of  $k$  and the Arrhenius  $A$  factor. It was found convenient to express these uncertainties in  $k$  and  $A$  in the form of uncertainty factors (which must not be taken to imply that the errors in the rate constants are necessarily log-normally distributed). The uncertainties assigned to the Arrhenius  $B$ , expressed as additive ( $\pm$ ) deviations, are also approximate estimates.

The evaluation covers the investigated (and documented in the literature)  $O(^3P)$  reactions with organic and inorganic sulfur containing compounds. With one exception, only gas phase reactions have been considered. For previous evaluations of kinetic data for some of these reaction systems see, for example, Reference 11.

### 1.4. Organization

The material presented in this article is divided into four sections. Section 1 is the Introduction. Section 2 gives a brief summary of the adopted symbols and units. Section 3 contains a table of all recommended kinetic parameters and the page numbers indicating the locations of the detailed tabulations of the kinetic data for the listed reactions. Section 4 contains the data sheets for O(<sup>3</sup>P) reactions with organic and inorganic sulfur containing compounds with the lists of references.

### 1.5. Guide to Summary of Recommended Rate Parameters

The Table in Section 3 summarizes the recommended values of the kinetic parameters for the listed gas phase second and third order reactions. The information is displayed in 7 columns. Column 1 ("Reaction") contains the reaction formula and the chemical name of the species reacting with O(<sup>3</sup>P) atoms. If Column 2 ("T/K") contains a single temperature, e.g. 298, the value in Column 3 ("k, A") is *k* at that temperature; if it contains a temperature range, e.g. 200–500, the value in Column 3 is the Arrhenius *A*. The units of *k* and *A* for the second and third order reactions are cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> and cm<sup>6</sup> mol<sup>-2</sup> s<sup>-1</sup>, respectively. The values are given in exponential form, written as (1.00±0.10)(11), which signifies (1.00±0.10)×10<sup>11</sup>.

Columns 4 ("n") and 5 ("B") contain, if applicable, the *n* and *B* parameters in the extended Arrhenius Eq.  $k = A(T/298)^n \exp(-B/T)$ . Column 6 ("k err. factor") contains the assigned uncertainty factors of *k* and *A*, and Column 7 ("Page") lists the page number showing the location of the detailed tabulation of kinetic data for the reaction.

### 1.6. Guide to the Reaction Data Sheets

With one exception, all kinetic data listed are for gas phase reactions. The data in the Data Sheets are divided into eight columns. Column 1 ("Reference Code, Notes") contains Reference Code and Notes relevant to the data entered and the techniques employed. When, for brevity, the reference code is omitted from Column 1 of a data line, it is the same as the closest reference code in Column 1 in one of the preceding data lines. The Reference Code consists of the last two digits of the year of publication, followed by the first three letters of the names of the first and second author (if present) separated by a slash. An integer index is attached at the end when it is necessary to differentiate between otherwise identical Codes. This is illustrated by the Code 80 LEE/TAN2. Column 2 ("Data type") contains the two-character Data Type Codes listed in Section 2. If Column 3 ("T/K") contains a single temperature, e.g. 298, the value in Column 4 ("k, k/k(ref), A, A/A(ref)") is *k* (or *k/k*(ref)) at that temperature; if it contains a temperature range, e.g. 200–500, the value in Column 4 is the Arrhe-

nus *A* parameter (or *A/A*(ref)). Column 5 ("n") and Column 6 ("B, B-B(ref)"), respectively, contain, when applicable, the *n* and *B* (or *B-B*(ref)) parameters in the extended Arrhenius Eq.  $k = A(T/298)^n \exp(-B/T)$ . *k*(ref), *A*(ref) and *B*(ref) are the kinetic parameters of the reference reaction in relative rate determinations. Column 7 ("k, A units") specifies the reaction order and thus defines the units of *k* and *A*, as listed in Section 2. Column 8 ("k err. factor") lists the overall uncertainty factors assigned to *k* and *A*.

### 1.7. Acknowledgments

This work was supported by the Department of Energy, Division of Basic Energy Sciences and the Office of Standard Reference Data, National Bureau of Standards.

### 1.8. References to the Introduction

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## 2. Summary of Symbols and Units

#### Reaction Phase Codes:

G=gas, L=liquid, S=solid, M=mixed phases (gas-liquid, gas-solid, liquid-solid, gas-liquid-solid)

#### Data Type Codes:

EX (experimentally measured absolute value),  
 RL (experimentally measured relative value),  
 RN (RL normalized to absolute value),  
 TH (theoretical value),

- DE (derived indirectly, e.g. using reverse rate and equilibrium constant, or computer simulation of a complex mechanism)
- CO (computed numerically),
- ES (estimated, by analogy etc.),
- SE (selected in the literature as probable "best" value),
- RE (currently recommended value).
- Type of excitation:  
 (EXV) (vibrationally excited)  
 (EXT) (translationally excited)  
 (EXE) (electronically excited)  
 (EXEV) (electronically and vibrationally excited), etc.
- Decadic exponent notation:  
 1.2(11) (stands for  $1.2 \times 10^{11}$ )
- Temperature ( $T$ ): in kelvins (K).
- Arrhenius parameters are defined by  
 $k = A(T/298)^n \exp(-B/T)$
- Unit Codes for  $k$ ,  $k/k(\text{ref})$ ,  $A$ ,  $A/A(\text{ref})$ :  
 1 ( $\text{s}^{-1}$ )  
 2 ( $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ )  
 3 ( $\text{cm}^6 \text{mol}^{-2} \text{s}^{-1}$ )  
 1/1, 2/2 etc. (dimensionless)  
 2/1 ( $\text{cm}^3 \text{mol}^{-1}$ ), etc.
- ( $T/298$ ) and  $n$  (the exponent of  $T$ ) are dimensionless.
- Units for  $B$ ,  $B-B(\text{ref})$ : kelvins (K). (Arrhenius parameter  $E = R \times B$ ).
- $k(\text{ref})$ ,  $A(\text{ref})$  and  $B(\text{ref})$  are the values for the "reference reaction" in relative rate determinations.
- $k$  err. factor: Estimated overall Uncertainty Factor. It multiplies and divides  $k$  or  $A$  to indicate approximate error limits. It does not imply that errors in  $k$  are necessarily lognormally distributed.

## 3. Index of Reactions and Summary of Recommended Rate Parameters

Reaction	T/K	k, A cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	n	B	k err. factor	Page
O + S <sub>2</sub> → products	409	7(12)			1.2	1384
O + Sulfur dimer (Tentative suggestion for 298K)	298	1(13)			4	
O + SF <sub>2</sub> → products	298	6.5(13)			1.3	1385
O + Sulfur fluoride (SF <sub>2</sub> )						
O + SF <sub>5</sub> → products	298	1.2(13)			1.3	1385
O + Sulfur fluoride (SF <sub>5</sub> )						
O + SOF → products	298	4.8(13)			2	1386
O + Sulfur fluoride oxide						
O + S <sub>2</sub> O → products	298	9.3(11)			1.3	1386
O + Sulfur oxide (S <sub>2</sub> O)						
O + SO + M → SO <sub>2</sub> + M (k <sub>∞</sub> )	298	3.2(13)			1.5	1387
O + Sulfur monoxide (M=Ar)	298	1.85(17)cm <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup>			1.2	
k relative to k(M=Ar) at 298K: Ar=1.0, Ne=0.88, Kr=1.18, He=1.25, Xe=1.28, N <sub>2</sub> =1.51, CF <sub>4</sub> =7.84, CO <sub>2</sub> =8.22, CH <sub>4</sub> =8.65, SF <sub>6</sub> =9.62, C <sub>3</sub> F <sub>8</sub> =12.2, H <sub>2</sub> =13.7, D <sub>2</sub> =13.7.						
O + SO → SO <sub>2</sub> + hv	298	2(8)			3	1389
O + Sulfur monoxide						
O + SO <sub>2</sub> + M → SO <sub>3</sub> + M (M=Ar)	299	3.7(14)cm <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup>			1.3	1390
O + Sulfur dioxide (M=Ar)	299-440	1.1(16)cm <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup>		1010±200	1.5	
(M=Ar)	1700-2500	1.06(13)cm <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup>		-7870	2	
(M=He)	298	3.5(14)cm <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup>			1.3	
(M=He)	248-415	4.0(16)cm <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup>		1400±200	1.5	
k relative to k(M=Ar) at 298K: Ar=1.0, He=0.9, N <sub>2</sub> =1.3, O <sub>2</sub> =1.3. N <sub>2</sub> O=3, SO <sub>2</sub> =10, within about 30%, for SO <sub>2</sub> up to a factor of 3.						
O + SO <sub>2</sub> → SO + O <sub>2</sub>	440-3000	5(12)		9800	3	1396
O + Sulfur dioxide						
O + SO <sub>3</sub> → products						1397
O + Sulfur trioxide						

## Index of Reactions and Summary of Recommended Rate Parameters -- Continued

Reaction	T/K	k, A cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	n	B	k err. factor	Page
O + SO <sub>3</sub> + M → SO <sub>2</sub> + O <sub>2</sub> + M O + Sulfur trioxide						1399
O + SH → H + SO O + Mercapto	298	1.4(14)			3	1400
O + SH → OH + S O + Mercapto						1401
O + H <sub>2</sub> S → products O + Hydrogen sulfide	298 263-502	1.5(10) 6.0(12)			1.3 1.8	1401
O + D <sub>2</sub> S → OD + SD O + Deuterium sulfide	298 298-450	4.7(9) 6.3(12)		1789±200 2144±200	1.4 2	1405
O + H <sub>2</sub> S → SO + H <sub>2</sub> O + Hydrogen sulfide						1405
O + H <sub>2</sub> S → HSO + H O + Hydrogen sulfide *) Branching ratio (nondimensional)	298	<0.2 *)			1.1	1406
O + H <sub>2</sub> SO <sub>4</sub> → products O + Sulfuric acid #) Rn. probability per collision < 1.0(-6) (nondimensional).	298	#)				1407
O + CS → products O + Carbon monosulfide	298 156-305	1.2(13) 1.5(14)			1.2 1.5	1408
O + CS <sub>2</sub> → products O + Carbon disulfide	298 218-920	2.3(12) 3.55(13)		751±100 821±100	1.2 1.5	1411
O + CS <sub>2</sub> → COS + S O + Carbon disulfide	298 249-500	2.1(11) 2.2(12)		701±100	1.3 2	1415
O + CS <sub>2</sub> → CO + S <sub>2</sub> O + Carbon disulfide k(298K) *) Branching ratio (nondimensional)	298 298	1.4(-2) *) 3.5(10)			1.2 1.3	1416
O + COS → products O + Carbon oxide sulfide	298 239-523 239-1900	8.0(9) 1.6(13) 4.7(13)		2257±200 2621±200	1.2 1.3 1.5	1417
O + COS → CO <sub>2</sub> + S O + Carbon oxide sulfide	1200 1200-1900	5(11) 5(13)			3 3	1422

## Index of Reactions and Summary of Recommended Rate Parameters -- Continued

Reaction	T/K	k, A cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	n	B	k err. factor	Page
O + CH <sub>3</sub> SH → products	298	1.2(12)			1.2	1422
O + Methanethiol	252-661	*)	*)	*)	1.3	
*) Strongly curved Arrhenius plot: k=A1+A2exp(-B/T) with A1=9.0(11), A2=1.8(13), B=1261.						
O + C <sub>2</sub> H <sub>5</sub> SH → products	298	1.7(12)			1.2	1424
O + Ethanethiol	256-574	*)	*)	*)	1.4	
*) Strongly curved Arrhenius plot: k=A1+A2exp(-B/T) with A1=1.6(12), A2=1.0(14), B=2198.						
O + C <sub>3</sub> H <sub>7</sub> SH → products	298	1.6(12)			1.3	1427
O + 1-Propanethiol	303-421	8.3(12)		494±50	1.5	
O + C <sub>4</sub> H <sub>9</sub> SH → products	298	2.0(12)			1.3	1427
O + 1-Butanethiol	306-419	5.8(12)		321±50	1.5	
O + C <sub>5</sub> H <sub>11</sub> SH → products	298	2.1(12)			1.3	1428
O + 1-Pentanethiol	302-409	6.2(12)		328±50	1.5	
O + CH <sub>3</sub> SCCH <sub>3</sub> → products	298	3.1(13)			1.2	1429
O + Methane, thiobis-	252-557	8.2(12)		-397±100	1.3	
O + cy-CH <sub>2</sub> SCCH <sub>2</sub> → products	298	7.6(12)			1.3	1431
O + Ethylene episulfide	268-424	8.1(12)		18±50	1.5	
O + cy-CHCHSCCH → products						1432
O + CH <sub>3</sub> SSCH <sub>3</sub> → products	298	6.0(13)			1.2	1433
O + Disulfide, dimethyl-	298-570	2.6(13)		-250±100	1.5	
O + SCF <sub>2</sub> → products	298	2.1(12)			1.5	1435
O + Carbonothioic difluoride	259-493	7.4(12)		376±100	1.5	
O + SCCl <sub>2</sub> → products	298	2.3(13)			1.3	1436
O + Carbonothioic dichloride	251-493	1.9(13)		-60±100	1.5	
O + cy-CF <sub>2</sub> SCF <sub>2</sub> S → products	298	8.1(11)			1.3	1437
O + 1,3-dithietane, 2,2,4,4-tetrafluoro-	253-493	1.4(13)		855±100	1.5	



## 4. Reaction Data Sheets

 $O + S_2 \rightarrow$  productsO + Sulfur dimer

The assumed reaction product is SO+S (68 HOM/KRO, 87 HIL/CIC).

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
68 HOM/KRO Discharge flow. O formed by microwave discharge in N <sub>2</sub> /Ar, followed by N+NO→O+N <sub>2</sub> . SO formation monitored by mass spec. Excess [S <sub>2</sub> ] over [O]. P=2 Torr. Uncertainty is an order of magnitude.	EX	1050	4(12)			2
73 SCH Only one reported value (68 HOM/KRO).	SE	1050	4(12)			2
87 HIL/CIC Discharge flow. Decay of S <sub>2</sub> in excess O monitored by mass spec. O formed by microwave discharge in O <sub>2</sub> . For absolute k measurement, [O] was determined by titration with excess NO <sub>2</sub> . For relative rate measurement, O + NO <sub>2</sub> was used as the reference rxn. (taking k <sub>ref</sub> =5.6(12) from 85 DEM/MAR). Decay of NO <sub>2</sub> was measured in excess O. P = 0.89-1.60 Torr.	EX RN	409 409	(6.62±0.78)(12) (7.17±1.02)(12)			2 2
Recommended value of k	RE	409	7(12)			2 1.2
Suggested tentative value of k at 298 K	RE	298	1(13)			2 4
Based on the data of 87 HIL/CIC and potential extreme values of 68 HOM/KRO. More determinations are needed.						

References for reaction  $O + S_2 \rightarrow$  products

- 68 HOM/KRO Homann, K.H., Krome, G., and Wagner, H.G., "Schwefelkohlenstoff-oxydation, geschwindigkeit von elementarreaktionen. Teil 1," Ber. Bunsenges. Phys. Chem. **72**, 998 (1968).
- 73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data **2**, 25 (1973).
- 85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. **85-37** (1985).
- 87 HIL/CIC Hills, A.J., Cicerone, R.J., Calvert, J.G., and Birks J.W., "Kinetics of the reactions of S<sub>2</sub> with O, O<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O, NO, and NO<sub>2</sub>," J. Phys. Chem., **91**, 1199 (1987).

$O + SF_2 \rightarrow$  products $O +$  Sulfur fluoride ( $SF_2$ )

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
86 PLU/RYA Discharge flow-mass spec. Decay rate of $SF_2$ in excess O. O and $SF_2$ formed by microwave discharge in $O_2/He$ and in $SF_6/He$ . SOF, SO, and $SO_2$ were detected as products.	EX	295	(6.5±1.2)(13)			2
Recommended value of k Based on the only data available (86 PLU/RYA). Additional determinations would be useful.	RE	298	6.5(13)			2 1.3

Reference for reaction  $O + SF_2 \rightarrow$  products

86 PLU/RYA Plumb I.C., and Ryan K.R., "Gas-phase reactions of  $SF_5$ ,  $SF_2$ , and SOF with  $O(^3P)$ : their significance in plasma processing," Plasma Chem. Plasma Processing, 6, 247-258 (1986).

 $O + SF_5 \rightarrow$  products $O +$  Sulfur fluoride ( $SF_5$ )

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
86 PLU/RYA Discharge flow-mass spec. Decay rate of $SF_5$ in excess O. O and $SF_5$ formed by microwave discharge in $O_2/He$ and in $SF_6/He$ . Products are assumed to be $SOF_4 + F$ .	EX	295	(1.2±0.3)(13)			2
Recommended value of k Based on the only data available (86 PLU/RYA). Additional determinations would be useful.	RE	298	1.2(13)			2 1.3

Reference for reaction  $O + SF_5 \rightarrow$  products

86 PLU/RYA Plumb I.C., and Ryan K.R., "Gas-phase reactions of  $SF_5$ ,  $SF_2$ , and SOF with  $O(^3P)$ : their significance in plasma processing," Plasma Chem. Plasma Processing, 6, 247-258 (1986).

## O + SOF → products

O + Sulfur fluoride oxide

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
86 PLU/RYA Discharge flow-mass spec. Analysis of the formation and decay of SOF in the rn. O+SF <sub>2</sub> . O and SF <sub>2</sub> formed by microwave discharge in O <sub>2</sub> /He and in SF <sub>6</sub> /He.	EX	295	(4.8±1.2)(13)			2
Recommended value of k Based on the only data available (86 PLU/RYA). Additional determinations would be useful.	RE	298	4.8(13)			2 2

## Reference for reaction O + SOF → products

86 PLU/RYA Plumb I.C., and Ryan K.R., "Gas-phase reactions of SF<sub>5</sub>, SF<sub>2</sub>, and SOF with O(<sup>3</sup>P): their significance in plasma processing," Plasma Chem. Plasma Processing, 6, 247-258 (1986).

O + S<sub>2</sub>O → productsO + Sulfur oxide (S<sub>2</sub>O)

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
74 STE/ALV Reference rn. is O+NO <sub>2</sub> →NO+O <sub>2</sub> . Discharge flow. O formed by microwave discharge of O <sub>2</sub> /Ar or by N+NO rn. The RL value obtained by comparing the O+SO and O+NO chemiluminences for different flow rates of S <sub>2</sub> O and NO <sub>2</sub> . [RN value has been updated using k <sub>ref</sub> =5.6(12) (65 DEM/MAR)]. SO observed as a product.	RL RN	298 298	0.17±0.02 (9.3±1.2)(11)			2/2 2
Recommended value of k Based on the only data available (74 STE/ALV). Additional determinations would be useful.	RE	298	9.3(11)			2 1.3

References for reaction O + S<sub>2</sub>O → products

74 STE/ALV Stedman, D.H., Alvord, H., and Baker-Blocker, A., "Chemiluminescent reactions of di-sulfur monoxide," J. Phys. Chem. 78, 1248 (1974).

References for reaction  $O + S_2O \rightarrow$  products -- Continued

- 85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).

O + Sulfur monoxide

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
66 HAL/THR Discharge flow. O and SO formed by microwave discharge in $SO_2/Ar$ . [O] and [SO] monitored by O+NO and O+SO chemiluminescences.	EX	300	(3.2±0.4)(17)			3
67 SHA/PAD *) Room T. M=Ar. P=0.8 Torr. Obtained SO in the rn. O+COS. Rate of light emission measured relative to the reaction $O+NO \rightarrow NO_2+h\nu$ . The second order rate constant was derived using $k(O+NO \rightarrow NO_2+h\nu)$ , $k(O+COS \rightarrow CO+SO)$ , and relative emission intensities of the $O+NO \rightarrow NO_2+h\nu$ and $O+SO \rightarrow SO_2+h\nu$ rns. The listed termolecular k was obtained by dividing the second order constant by P. (See also 67 SHA/PAD in the next data sheet).	RN	*)	8.0(16)			3
70 TAK M=Ar. P(Ar)=4.2 Torr. Discharge flow. O formed by microwave discharge of $N_2O/Ar$ . [O] monitored by chemiluminescence from $O+NO_2$ and $O+NO$ Rns. SO formed by reaction of excess O with $H_2S$ , and its decay monitored by chemiluminescence from O+SO reaction.	EX	293	5.8(16)			3
71 MIY/TAK *) Room temperature. M=Ar. P=3.8 Torr. Discharge flow. O formed by microwave discharge of $N_2O/Ar$ . SO formed by reaction of O with $CS_2$ . Formation of $SO_2$ monitored by its chemiluminescence. k calculated from the integrated rate equation for initially equal [O] and [SO].	EX	*)	7.3(16)			3
73 SCH Based on only one measurement (66 HAL/THR).	SE	300	3.2(17)			3

O + SO + M → SO<sub>2</sub> + M -- Continued

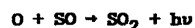
Reference Code, Notes		Data type	T/K	k, k(k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
76 BAU/DRY		SE	298	(6.7±2.0)(16)			3
M=Ar.							
78 HAM/GAR		SE	298	6.7(16)			3 1.3
M=Ar. Accepted recommendation of 76 BAU/DRY.							
85 COB/HIP	(M=Ar P=0.2-200 bar)	EX	300	1.85(17)			3
	(M=N <sub>2</sub> P=0.2-200 bar)	EX	300	2.79(17)			3
	(M=C <sub>3</sub> F <sub>8</sub> P=0.2-3 bar)	EX	300	2.25(18)			3
	(M=He P=0.2-25 bar)	EX	300	2.32(17)			3
	(M=Ne P=0.5-5 bar)	EX	300	1.63(17)			3
	(M=Kr P=1-5 bar)	EX	300	2.18(17)			3
	(M=Xe P=0.2-5 bar)	EX	300	2.36(17)			3
	(M=H <sub>2</sub> P=0.5-5 bar)	EX	300	2.54(18)			3
	(M=D <sub>2</sub> P=0.5-5 bar)	EX	300	2.54(18)			3
	(M=CO <sub>2</sub> P=0.2-5 bar)	EX	300	1.52(18)			3
	(M=CH <sub>4</sub> P=0.5-5 bar)	EX	300	1.60(18)			3
	(M=CF <sub>4</sub> P=0.2-5 bar)	EX	300	1.45(18)			3
	(M=SF <sub>6</sub> P=0.2-5 bar)	EX	300	1.78(18)			3
	(k <sup>∞</sup> , high P limit)	EX	300	3.2(13)			2
O and SO formed by laser photolysis of SO <sub>2</sub> at 193nm. k values obtained from 2nd order plots of uv absorption, used to monitor SO <sub>2</sub> reformation. Pressure of third body ranged from 0.2 to 200 bar. k <sup>∞</sup> (high pressure limit) is based on data for M=Ar, N <sub>2</sub> , and C <sub>3</sub> F <sub>8</sub> . Used broadening factors (Fc) of 0.55, 0.58 and 0.76 to fit the data for N <sub>2</sub> , Ar and C <sub>3</sub> F <sub>8</sub> , respectively.							
Recommended value of k <sup>∞</sup> (high P limit)		RE	298	3.2(13)			2 1.5
Recommended value of k(M=Ar)		RE	298	1.85(17)			3 1.2
Recommended third body efficiencies at 298 K (i.e. k values relative to k(M=Ar)): Ar=1.00, Ne=0.88, Kr=1.18, He=1.25, Xe=1.28, N <sub>2</sub> =1.51, CF <sub>4</sub> =7.84, CO <sub>2</sub> =8.22, CH <sub>4</sub> =8.65, SF <sub>6</sub> =9.62, C <sub>3</sub> F <sub>8</sub> =12.2, H <sub>2</sub> =D <sub>2</sub> =13.7. The recommended values are based on the extensive data of 85 COB/HIP. (The average of the listed k(M=Ar) values, excluding the value of 67 SHA/PAD, which is apparently for the rate of the third order light emission, is only 16% smaller than the recommended value of 1.85(17)).							

References for reaction O + SO + M → SO<sub>2</sub> + M

- 66 HAL/THR Halstead, C.J. and Thrush, B.A., "The kinetics of elementary reactions involving the oxides of sulphur. II. Chemical reactions in the sulphur dioxide afterglow," Proc. Roy. Soc. A 295, 363 (1966).
- 67 SHA/PAD Sharma, A., Padur, J.P., and Warneck, P., "The chemiluminescent reactions of atomic oxygen with carbonyl sulfide and hydrogen sulfide," J. Phys. Chem. 71, 1602 (1967).

References for reaction  $O + SO + M \rightarrow SO_2 + M$  -- Continued

- 70 TAK Takahashi, S., "The study of the reaction of hydrogen sulphide with atomic oxygen using emission spectrum," Mem. Nat. Def. Acad. Japan 10, 369 (1970).
- 71 MIY/TAK Miyazaki, S., and Takahashi, S., "On the reaction of oxygen atom with carbon disulfide (Part 2)," Mem. Nat. Def. Acad. Japan 11, 307 (1971), C.A. 78, 62771w (1973).
- 73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).
- 76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the  $O_2$ - $O_3$  system, the  $CO$ - $O_2$ - $H_2$  system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).
- 78 HAM/GAR Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," Nat. Bur. Stand. Spec. Publ. 513 (1978).
- 85 COB/HIP Cobos, C.J., Hippler, H., and Troe J., "Falloff curves of the recombination reaction  $O + SO + M \rightarrow SO_2 + M$  in a variety of bath gases," J. Phys. Chem. 89, 1778 (1985).

O + Sulfur monoxide

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
65 ROL/REE *) Room temperature. $P < 0.02$ Torr. Rate constant for light emission. Discharge flow. Excess O, formed by discharge in $O_2$ . SO obtained from $O+COS$ rn. Rate constant determined relative to light emission from $O+NO$ .	RN	*)	4.2(8)			2
66 HAL/THR Rate constant for light emission. Discharge flow. Excess O, formed by discharge in $O_2/Ar$ . SO obtained from $O+COS$ rn. k determined relative to light emission from $O+NO$ . Intensity was independent of Ar pressure, at $P=0.2-1.6$ Torr.	RN	298	1.5(8)			2
67 SHA/PAD *) Room T. Discharge flow in $O_2$ or $O_2/Ar$ . $O+COS$ gives SO. Measured light emission at 0.8 Torr relative to $O+NO-NO_2+h\nu$ . Listed k derived using $k(O+NO-NO_2+h\nu)$ , $k(O+COS-CO+SO)$ , and relative emission intensities of $O+NO-NO_2+h\nu$ and $O+SO-SO_2+h\nu$ rns. Measured light emission is assumed to be sum of contributions from a small second order and a larger third order process. (See also 67 SHA/PAD in the preceding data sheet).	RN	*)	3.4(9)			2

O + SO → SO<sub>2</sub> + hv -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
69 FLE/LEV Shock tube study of SO <sub>2</sub> /Ar mixtures. Calibrated the optical system with tungsten and hydrogen lamps. [O] and [SO] calculated assuming equilibrium for the species SO <sub>2</sub> , Ar, SO, O, O <sub>2</sub> , and SO <sub>3</sub> . Adopting k=1.5(8) at 298 K (66 HAL/THR), the authors calculate A=1.5(8), n=-1.0, B=0. Total P ~ 0.5 atm.	EX	3500	(1.4±0.4)(7)			2
Recommended value of k Additional experimental work is desirable.	RE	298	2(8)			2 3

References for reaction O + SO → SO<sub>2</sub> + hv

- 65 ROL/REE Rolfes, I.R., Reeves, R.R., Jr., and Harteck, P., "The chemiluminescent reaction of oxygen atoms with sulfur monoxide at low pressures," J. Phys. Chem. 69, 849 (1965).
- 66 HAL/THR Halstead, C.J. and Thrush, B.A., "The kinetics of elementary reactions involving the oxides of sulphur. II. Chemical reactions in the sulphur dioxide afterglow," Proc. Roy. Soc. A 295, 363 (1966).
- 67 SHA/PAD Sharma, A., Padur, J.P., and Warneck, P., "The chemiluminescent reactions of atomic oxygen with carbonyl sulfide and hydrogen sulfide," J. Phys. Chem. 71, 1602 (1967).
- 69 FLE/LEV Fletcher, S.R., and Levitt, B.P., "O + SO recombination emission at 3500K," Trans. Faraday Soc. 65, 1544 (1969).

O + SO<sub>2</sub> + M → SO<sub>3</sub> + MO + Sulfur dioxide

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
58 KAU *) Room temperature. M=O <sub>2</sub> . Discharge flow. O formed by microwave discharge in O <sub>2</sub> . Decay of O in excess SO <sub>2</sub> determined from intensity of the O+NO chemiluminescence. Detailed experimental conditions not reported.	EX	*)	3(16)			3

O + SO<sub>2</sub> + M → SO<sub>3</sub> + M -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
65 LEV/MER Microprobe study of H <sub>2</sub> S/O <sub>2</sub> /N <sub>2</sub> or of H <sub>2</sub> S/O <sub>2</sub> /Ar flames. Mass spec. analyses for O <sub>2</sub> , H <sub>2</sub> S, H <sub>2</sub> O, H <sub>2</sub> , and SO <sub>2</sub> ; wet analyses for SO + SO <sub>2</sub> and SO <sub>3</sub> . Calculated equilibrium concentrations of atoms and radicals. k's derived from observed [SO <sub>2</sub> ] and [SO <sub>3</sub> ] profiles. The value for B is assumed.	DE	300-1300	(2.2-22)(15)		3019	3
65 WEB/WAL M=H <sub>2</sub> +O <sub>2</sub> . P=27.9 Torr. Reference rn. O+H <sub>2</sub> →OH+H (used k=2.0(10)). Determined second explosion limits for H <sub>2</sub> /O <sub>2</sub> mixtures with and without SO <sub>2</sub> .	RN	784	1.1(16)			3
66 CAD/POW M=N <sub>2</sub> . Discharge flow. O from microwave discharge in O <sub>2</sub> or in N <sub>2</sub> followed by N+NO→O+N <sub>2</sub> . k determined from initial decrease in [O] (measured by O+NO luminescence) and [SO <sub>2</sub> ] decrease (measured by gas chromatography). Activation energy reported as near 0. N <sub>2</sub> and O <sub>2</sub> are equally efficient as third bodies.	EX	300	4.7(15)			3
66 HAL/THR M=Ar. Discharge flow. O formed by microwave discharge in O <sub>2</sub> /Ar mixture. Monitored O in excess SO <sub>2</sub> by O+NO chemiluminescence. The efficiency of Ar relative to O <sub>2</sub> is 1.0±0.2. Pressure range is not reported.	EX	293	(4.7±0.8)(15)			3
66 JAF/KLE M = SO <sub>2</sub> . Photolysis of NO <sub>2</sub> in presence of SO <sub>2</sub> . k derived from quantum yield of NO <sub>2</sub> consumption, <sup>18</sup> O isotope exchange, and rate constant for the O+NO <sub>2</sub> rn. The k value is for P=2 Torr.	DE	297	1.4(16)			3
67 MUL/STE (M=SO <sub>2</sub> P=0.7-3 Torr)	EX	299	(1.0±0.4)(16)			3
(M=Ar P=0.7-3 Torr)	EX	299	(2.4±0.15)(15)			3
(M=O <sub>2</sub> P=0.7-3 Torr)	EX	299	(2.7±0.5)(15)			3
Stirred flow - ESR detection of O. Excess SO <sub>2</sub> . Allowance not made for influence of SO <sub>3</sub> on the wall recombination of O atoms (see 69 MUL/STE).						



O + SO<sub>2</sub> + M → SO<sub>3</sub> + M -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
69 MUL/STE Supercedes 67 MUL/STE for M=Ar. P(Ar)=2-6 Torr. Stirred flow. O formed by microwave discharge in O <sub>2</sub> in excess Ar and monitored by O+NO chemiluminescence and ESR. Allowance made for influence of SO <sub>3</sub> on the wall recombination of O.	EX	300	(1.1±0.3)(15)			3
69 NET/STI M=N <sub>2</sub> . Sampled with an alumina tube the flames composed of either CH <sub>4</sub> or CO with O <sub>2</sub> , SO <sub>2</sub> , and N <sub>2</sub> . Determined CO, CO <sub>2</sub> , O <sub>2</sub> , SO <sub>3</sub> , and SO <sub>2</sub> . Rate constant is based on the SO <sub>3</sub> production, the calculated equilibrium concentrations of O, and the value k=1(12) for O+SO <sub>3</sub> → SO <sub>2</sub> +O <sub>2</sub> rn. The authors suggest that the value of k is a lower limit.	DE	2150	≥2(15)			3
71 HEI/WOO *) Room temperature. M=N <sub>2</sub> O. O formed by Hg-photosensitized decomposition of N <sub>2</sub> O in the presence of COS. SO <sub>2</sub> produced in secondary reactions. Rate constant determined relative to O+COS, based on yields of N <sub>2</sub> and CO. The authors indicate a large experimental uncertainty.	RL	*)	5(6)			3/2
71 TIM/LEF (M=SO <sub>2</sub> )	EX	298	4.10(16)			3
(M=Ar)	EX	298	1.0(15)			3
(M=He)	EX	298	8(14)			3
Discharge flow-EER detection of O. Excess SO <sub>2</sub> . Allowance is made for the third body effect of SO <sub>2</sub> . An Arrhenius plot is given for M=SO <sub>2</sub> at 205K-T-298K (values of A and B are not quoted).						
73 SCH M=Ar. Estimated a factor of 2 error at 300 K, greater at other temperatures. Third body efficiencies taken to be about the same for Ar, O <sub>2</sub> , N <sub>2</sub> , He, and from 6 to 40 times greater for SO <sub>2</sub> , NO <sub>2</sub> , N <sub>2</sub> O.	SE	250-1000	3.6(14)		-503	3

O + SO<sub>2</sub> + M → SO<sub>3</sub> + M -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
74 ATK/PIT M=N <sub>2</sub> O. P(N <sub>2</sub> O)=54-135 Torr. Phase shift technique. O atoms generated by the Hg-photosensitized decomposition of N <sub>2</sub> O. O monitored by the O+NO chemiluminescence. An upper limit of k(SO <sub>2</sub> )/k(N <sub>2</sub> O) = 5 assessed for SO <sub>2</sub> and N <sub>2</sub> O as third bodies (see also 78 ATK/PIT).	EX	299-392	3.32(16)		1006±200	3
74 DAV M=N <sub>2</sub> . Flash photolysis-resonance fluorescence. Relative third body efficiencies N <sub>2</sub> :He:Ar:SO <sub>2</sub> =1.0:0.45:0.87:60. Few details. Reference to unpublished data of D.D. Davis, R. Schiff, and S. Fischer.	EX	220-353	1.2(16)		1120	3
75 WES/DEHZ (M=He P=0.7-6.7 Torr) (M=N <sub>2</sub> P=0.7-6.7 Torr) (M=SO <sub>2</sub> k <sub>rel</sub> =k/k(M=He))	EX EX RL	248-415 297 297	(3.9±0.9)(16) (7.2±0.3)(14) 9.5±2.7		1400±50	3 3 3/3
Discharge flow-ESR detection of O. Excess SO <sub>2</sub> . Allowance is made for the third body effect of SO <sub>2</sub> .						
76 BAU/DRY *) No new recommendation. Suggest using Davis's data (see entry for 74 DAV).	SE		*)			3
78 ATK/PIT M=Ar. P(Ar)=25-50 Torr. Flash photolysis - NO <sub>2</sub> chemiluminescence. O formed by photolysing SO <sub>2</sub> and NO. [O] was followed by the O+NO chemiluminescence. The effect of SO <sub>2</sub> as third body was taken into account. Relative k values for different M at 300 K are Ar:N <sub>2</sub> :N <sub>2</sub> O:SO <sub>2</sub> = 1.0:1.3:3.0:0.0.	EX	299-440	1.12(16)		1009±151	3
78 HAM/GAR M=N <sub>2</sub> . Relative k values for different M are: N <sub>2</sub> :He:Ar:SO <sub>2</sub> =1.0:0.45:0.87:56.	SE	220-353	1.2(16)		1130	3
78 TRO M=Ar. Derived by fitting a modified Arrhenius expression to the experimental data of 75 WES/DEH and 79 AST/GLA.	DE	250-2500	4.9(18)	-4	2646	3

O + SO<sub>2</sub> + M → SO<sub>3</sub> + M -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
79 AST/GLA M=Ar. Shock wave decomposition of SO <sub>3</sub> . Monitored SO <sub>2</sub> formed by uv absorption. Calculated k for the reverse rn. (O+SO <sub>2</sub> +M→SO <sub>3</sub> +M) using the equilibrium constant.	EX	1700-2500	1.06(13)		-7870	3
80 BAU/COX *) M=Ar. Estimated error factor: 3 for 200-500K, 2 for 300K.	SE	200-2500	2.8(19)	-3.75	2650	3 *)
84 ATK/LLO M=N <sub>2</sub> and M=O <sub>2</sub> M=N <sub>2</sub> and M=O <sub>2</sub> The third body efficiencies of N <sub>2</sub> and O <sub>2</sub> are assumed equal.	SE	298	4.9(14)			3 1.3
	SE	300-440	(1.5±0.4)(16)		1009	3
84 BAU/COX M=N <sub>2</sub> and M=O <sub>2</sub> M=N <sub>2</sub> and M=O <sub>2</sub>	SE	298	5.1(14)			3 2
	SE	200-400	1.5(16)		1000	3
Recommended value of k for M=Ar	RE	299	3.7(14)			3 1.3
Recommended values of Arrhenius A and B for M=Ar	RE	299-440	1.1(16)		1010±200	3 1.5
Recommended values of Arrhenius A and B for M=Ar	RE	1700-2500	1.06(13)		-7870	3 2
Recommended value of k for M=He	RE	298	3.5(14)			3 1.3
Recommended values of Arrhenius A and B for M=He	RE	248-415	4.0(16)		1400±200	3 1.5
Based recommendations on the data of 78 ATK/PIT, 75 WES/DEH2 and (for 1700-2500K) of 79 AST/GLA. Tentatively recommended relative third body efficiencies at 298K are Ar:He:N <sub>2</sub> :O <sub>2</sub> :N <sub>2</sub> O:SO <sub>2</sub> = 1.0:0.9:1.3:1.3:3:10, within about 30% and, for SO <sub>2</sub> , up to a factor of 3.						
Arrhenius plots for O+SO <sub>2</sub> +M→products are shown in Fig. 1 (1a for M=He and 1b for M=Ar (at 299-440K)).						

References for reaction O + SO<sub>2</sub> + M → SO<sub>3</sub> + M

- 58 KAU Kaufman, F., "The air afterglow and its use in the study of some reactions of atomic oxygen," Proc. Roy. Soc. A 247, 123 (1958).
- 65 LEV/MER Levy, A., and Merryman, E. L., "The microstructure of hydrogen sulphide flames," Combustion and Flame 9, 229 (1965).
- 65 WEB/WAL Webster, P., and Walsh, A.D., "The effect of sulfur dioxide on the second pressure limit of explosion of hydrogen-oxygen mixtures," Tenth Symposium (International) on Combustion, p. 463, The Combustion Institute (1965).
- 66 CAD/POW Cadle, R.D., and Powers, J.W., "Some aspects of atmospheric chemical reactions of atomic oxygen," Tellus 18, 176 (1966).
- 66 HAL/THR Halstead, C.J. and Thrush, B.A., "The kinetics of elementary reactions involving the oxides of sulphur. II. Chemical reactions in the sulphur dioxide afterglow," Proc. Roy. Soc. A 295, 363 (1966).
- 66 JAF/KLE Jaffe, S., and Klein, F.S., "Photolysis of NO<sub>2</sub> in presence of SO<sub>2</sub> at 3660Å," Trans. Faraday Soc. 62, 2150 (1966).

References for reaction  $O + SO_2 + M \rightarrow SO_3 + M$  -- Continued

- 67 MUL/STE Mulcahy, M.F.R., Steven, J.R., and Ward, J.C., "The kinetics of reaction between oxygen atoms and sulfur dioxide: an investigation by electron spin resonance spectrometry," *J. Phys. Chem.* **71**, 2124 (1967).
- 69 MUL/STE Mulcahy, M.F.R., Steven, J.R., Ward, J.C., and Williams, D.J., "Kinetics of interaction of oxygen atoms with sulfur oxides," Twelfth Symposium (International) on Combustion, p. 323, The Combustion Institute, 1969.
- 69 NET/STI Nettleton, M.A., and Stirling, R., "Formation and decomposition of sulfur trioxide in flames and burned gases," Twelfth Symposium (International) on Combustion, p. 635, The Combustion Institute (1969).
- 71 HEI/WOO Heicklen, J., Wood, W.P., Olszyna, K.J., and Cehelnik, E., "The reactions of unstable intermediates in the oxidation of  $CS_2$ ," in 'Chemical Reactions in Urban Atmospheres' (C.S. Tuesday, editor), p. 191 (1971).
- 71 TIM/LEF Timmons, R.B., LeFevre, H.F., and Hollinden, G.A., "Reactions of sulfur dioxide of possible atmospheric significance," in 'Chemical Reactions in Urban Atmospheres' (C.S. Tuesday, editor), p. 159 (1971).
- 73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," *J. Phys. Chem. Ref. Data* **2**, 25 (1973).
- 74 ATK/PIT Atkinson, R., and Pitts, J.N., Jr., "Rate constants for the reaction of  $O(^3P)$  atoms with  $SO_2$  ( $M=N_2O$ ) over the temperature range 299-392K," *Chem. Phys. Lett.* **29**, 28 (1974).
- 74 DAV Davis, D.D., "A kinetics review of atmospheric reactions involving  $HxOy$  compounds," *Can. J. Chem.* **52**, 1405 (1974).
- 75 WES/DEH2 Westenberg, A.A., and deHaas, N., "Rate of the reaction  $O + SO_2 + M \rightarrow SO_3 + M$ ," *J. Chem. Phys.* **63**, 5411 (1975).
- 76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the  $O_2$ - $O_3$  system, the  $CO$ - $O_2$ - $H_2$  system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).
- 78 ATK/PIT Atkinson, R., and Pitts, J.N., Jr., "Kinetics of the reaction  $O(^3P) + SO_2 + M \rightarrow SO_3 + M$  over the temperature range of 299-440K," *Int. J. Chem. Kinet.* **10**, 1081 (1978).
- 78 HAM/GAR Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," *Nat. Bur. Stand. Spec. Publ.* **513** (1978).
- 78 TRO Troe, J., "Atom and radical recombination reactions," *Ann. Rev. Phys. Chem.* **29**, 223 (1978).
- 79 AST/GLA Astholz, D.C., Glanzer, K., and Troe, J., "The spin-forbidden dissociation-recombination reaction  $SO_3 = SO_2 + O$ ," *J. Chem. Phys.* **70**, 2409 (1979).
- 80 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry," *J. Phys. Chem. Ref. Data* **9**, 295 (1980).
- 84 ATK/LLO Atkinson, R., and Lloyd, A.C., "Evaluation of kinetic and mechanistic data for modeling of photochemical smog," *J. Phys. Chem. Ref. Data* **13**, 315 (1984).
- 84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," *J. Phys. Chem. Ref. Data* **13**, 1259 (1984).

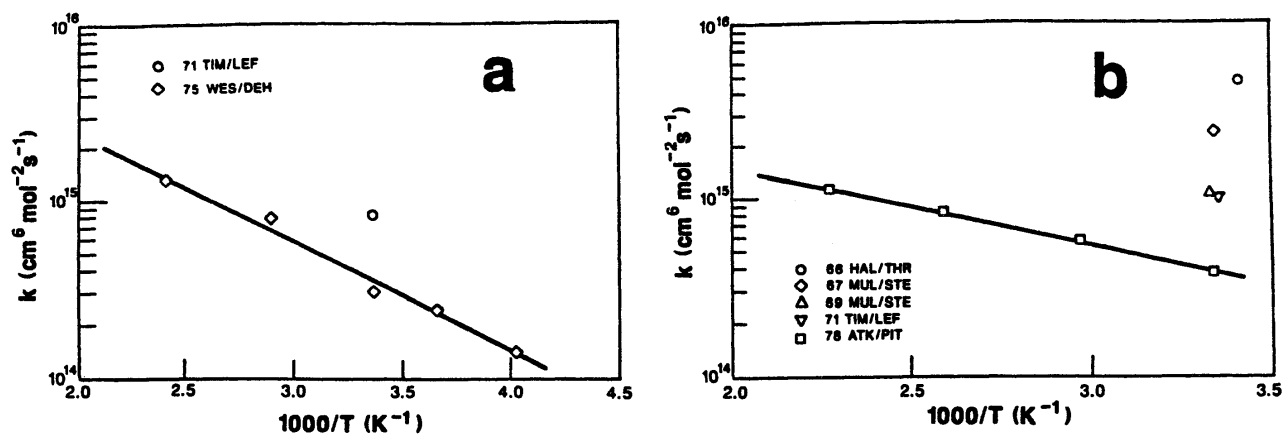
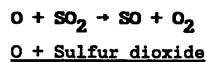


Fig. 1. Arrhenius plots for  $O+SO_2+M \rightarrow \text{products}$  with  $M=He$  (1a) and  $M=Ar$  at 299–440K (1b).  
The lines are calculated using the recommended A and B values.



Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
73 WAG Derived from the rate parameters (A=1.3(12), B=3986) for the reverse reaction and the equilibrium constant.	DE		5(12)		9813	2
76 BAU/DRY Based on the recommended rate constant expression for the reverse reaction (76 BAU/DRY) and the equilibrium constant expression of 73 SCH.	SE	440-2100	6.80(12)	-0.511	9980	2
78 HAM/GAR Accepted recommendation of 76 BAU/DRY.	SE	440-2100	7.3(12)	-0.5	9980	2 1.8

O + SO<sub>2</sub> → SO + O<sub>2</sub> -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
80 SLA/GRI Reflected shock waves in mixture of SO <sub>2</sub> /N <sub>2</sub> O/Ar. P=2-5 atm. Monitored decay of SO <sub>2</sub> by IR emission at 7.347 microns. [O], used to calculate k values, computed from a model of 8 reactions.	EX	3320-3760	(3.8±0.5)(11)			2
Recommended values of Arrhenius A and B Based on the indirectly derived parameters of 73 WAG and 76 BAU/DRY. Additional experimental work is needed.	RE	440-3000	5(12)		9800	2 3

References for reaction O + SO<sub>2</sub> → SO + O<sub>2</sub>

- 73 WAG Wagner, H.Gg., "Elementary reactions in the combustion of small inorganic molecules," Fourteenth Symposium (International) on Combustion, p. 27, The Combustion Institute (1973).
- 76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the O<sub>2</sub>-O<sub>3</sub> system, the CO-O<sub>2</sub>-H<sub>2</sub> system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).
- 78 HAM/GAR Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," Nat. Bur. Stand. Spec. Publ. 513 (1978).
- 80 SLA/GRI Slack, M., and Grillo, A., "Rate coefficient measurements for SO<sub>2</sub> + O = SO + O<sub>2</sub>," J. Chem. Phys. 73, 987 (1980).

O + SO<sub>3</sub> → productsO + Sulfur trioxide

The product is always assumed to be SO<sub>2</sub>+O<sub>2</sub>. (See 75 WES/DEH1 for suggestion that rn. is third order, i.e. O+SO<sub>3</sub>+M→SO<sub>2</sub>+O<sub>2</sub>+M).

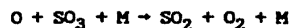
Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
58 KAU Discharge flow. O formed by microwave discharge in O <sub>2</sub> and monitored by O+NO chemiluminescence. No reaction was detectable between O and SO <sub>3</sub> in the gas phase, and the estimate of B is a lower limit. SO <sub>3</sub> was observed to change the rate of recombination of O on the reactor walls.	EX	300			≥3500	

O + SO<sub>3</sub> → products -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
62 REU/LIN Reference rn. O+SO <sub>2</sub> →SO <sub>3</sub> (assumed to be bimolecular). Thermal decomposition of N <sub>2</sub> O mixed with SO <sub>2</sub> and either Ar, He, or CO <sub>2</sub> . [SO <sub>2</sub> ] determined by uv absorption. Monitored total pressure (up to about 500 Torr).	RL	961	0.16			2/2
65 FEN/JON Microprobe sampling of H <sub>2</sub> S/H <sub>2</sub> /O <sub>2</sub> flame. Mass spec. analyses. Reference rn. O+SO <sub>2</sub> +M→SO <sub>3</sub> +M. k <sub>ref</sub> taken as 3(16) cm <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup> . The k values are undefined "averages" for O+SO <sub>3</sub> and H+SO <sub>3</sub> rns. P=60-200 Torr.	RL RN	1600 1600	5(-5) 1(12)			2/2 2
71 MER/LEV Microprobe sampling of COS/O <sub>2</sub> /N <sub>2</sub> flames. Monitored [SO <sub>3</sub> ] by wet analyses; other stable species by mass spec. Reference rn. is O+SO <sub>2</sub> +M→SO <sub>3</sub> +M (A=2.4(17)cm <sup>6</sup> mole <sup>-2</sup> s <sup>-1</sup> , B=1258 K).	RN	1480-1550	2.8(14)		6039	2
71 MER/LEV Microprobe sampling of H <sub>2</sub> S/O <sub>2</sub> /N <sub>2</sub> flames, using the same procedure as in preceding data entry. Slightly larger k values are obtained than from the COS flame, possibly due to additional loss of SO <sub>3</sub> by reaction with H.	RN	1240-1340	6.5(14)		5435	2
72 JAC/WIN Discharge flow. O formed by microwave discharge in N <sub>2</sub> followed by N+NO→O+N <sub>2</sub> . Reaction is "cold quenched". k is based on SO <sub>2</sub> yield and measured [O] and [SO <sub>3</sub> ]. P=2 Torr. (A is recalculated).	EX	300-500	1.3(8)		500	2
73 SCH Evaluation was based on only one set of data, 71 MER/LEV, which was considered questionable.	SE	1480-1550	2.8(14)		6039	2
<p>Recommendation is not warranted. Reaction order is not certain: 75 WES/DEH1 found more recently that reaction may be third order (see data sheet for rn. O+SO<sub>3</sub>+M). Also, their second order k(298) at 2 Torr is several thousand times larger than that of 72 JAC/WIN. Furthermore, 75 WES/DEH1 find that B=-785, while 72 JAC/WIN find that B=500. 76 BAU/DRY found also that no recommendation was possible. Further study is needed.</p>						

References for reaction  $O + SO_3 \rightarrow$  products

- 58 KAU Kaufman, F., "The air afterglow and its use in the study of some reactions of atomic oxygen," Proc. Roy. Soc. A 247, 123 (1958).
- 62 REU/LIN Reuben, B.G., Linnett, J.W., and Barber, M., "A new method of examining the reactions of oxygen atoms," Eighth Symposium (International) on Combustion, p. 97, The Combustion Institute (1962).
- 65 FEN/JON Fenimore, C.P., and Jones, G.W., "Sulfur in the burnt gas of hydrogen-oxygen flames," J. Phys. Chem. 69, 3593 (1965).
- 71 MER/LEV Merryman, E.L., and Levy, A., "Sulfur trioxide flame chemistry -  $H_2S$  and COS flames," Thirteenth Symposium (International) on Combustion, p. 427, The Combustion Institute (1971).
- 72 JAC/WIN Jacob, A., and Winkler, C.A., "Kinetics of the reactions of oxygen atoms and nitrogen atoms with sulphur trioxide," J. Chem. Soc. Faraday 1 68, 2077 (1972).
- 73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).
- 75 WES/DEH1 Westenberg, A.A., and deHaas, N., "Rate of the  $O + SO_3$  reaction," J. Chem. Phys. 62, 725 (1975).

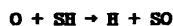
 $O +$  Sulfur trioxide

Reference Code, Notes	Data type	T/K	$k, k/k(\text{ref}), A, A/A(\text{ref})$	n	B, B-B(ref)	k, A k err. units factor
75 WES/DEH1 (M=He P=0.75-5.8 Torr)	EX	298-507	5.0(16)		-785	3
(M= $N_2$ )	EX	298	1.0(18)			3
(M= $SO_3$ $k_{\text{rel}} = k/k(\text{M=He})$ )	RL	298	<10			3/3
Discharge flow reactor with ESR detection of O.						
Recommendation: For reasons given for the previous rxn. ( $O+SO_3 \rightarrow$ products) no recommendation is warranted. Additional experimental data are required.						

Reference for reaction  $O + SO_3 + M \rightarrow SO_2 + O_2 + M$ 

- 75 WES/DEH1 Westenberg, A.A., and deHaas, N., "Rate of the  $O + SO_3$  reaction," J. Chem. Phys. 62, 725 (1975).

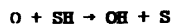


O + Mercapto

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
69 FAI/THR	RL	298	12			2/2
	RN	298	1.8(14)			2
Reference rn. $\text{H} + \text{SH} \rightarrow \text{H}_2 + \text{S}$ . $P = 0.9$ Torr. Discharge flow. $\text{H} + \text{H}_2\text{S}$ rn. in presence of $\text{O}_2$ . $\text{O}$ formed by the secondary reaction $\text{S} + \text{O}_2 \rightarrow \text{SO} + \text{O}$ . Rate constant is based on the $[\text{O}]$ and $[\text{SO}]$ , determined from $\text{O} + \text{NO}$ and $\text{O} + \text{SO}$ chemiluminescences. To calculate RN used $k_{\text{ref}} = 1.5(13)$ (76 BAU/DRY).						
73 SCH	SE	295	1.2(14)			2
Only one reported value (private communication, published subsequently in 75 CUP/GLA).						
75 CUP/GLA	RL	295	$6.5 \pm 0.7$			2/2
	RN	295	$(9.6 \pm 3)(13)$			2
Reference rn. $\text{H} + \text{SH} \rightarrow$ products. Discharge flow. ESR detection of $\text{H}$ , $\text{O}$ and $\text{OH}$ . Based on an assumed rn. mechanism, the ratio $[\text{H}]/[\text{O}]$ was identified with $k(\text{O} + \text{SH})/k(\text{H} + \text{SH})$ . In separate experiments found $k_{\text{ref}} = (1.5 \pm 0.5)(13)$ .						
85 DEM/MAR	SE	298	9.6(13)			2 5.0
Accepted RN (the Normalized k) of 75 CUP/GLA.						
Recommended value of k	RE	298	1.4(14)			2 3
Obtained as the average of the RN (the Normalized k) values of FAI/THR and 75 CUP/GLA.						

References for reaction  $\text{O} + \text{SH} \rightarrow \text{H} + \text{SO}$ 

- 69 FAI/THR Fair, R.W., and Thrush, B.A., "Reaction of hydrogen atoms with hydrogen sulphide in the presence of molecular oxygen," *Trans. Faraday Soc.* 65, 1557 (1969).
- 73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," *J. Phys. Chem. Ref. Data* 2, 25 (1973).
- 75 CUP/GLA Cupitt, L.T., and Glass, G.P., "Reactions of SH with atomic oxygen and hydrogen," *Int. J. Chem. Kinet. Symp.* 1, 39 (1975).
- 76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the  $\text{O}_2\text{-O}_3$  system, the  $\text{CO-O}_2\text{-H}_2$  system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).
- 85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," *J.P.L. Publ.* 85-37 (1985).

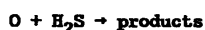
O + Mercapto

Reference Code, Notes	Data type	T/K	k,k(k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
68 MAY/SCH Used Bond Energy-Bond Order (BEBO) technique.	TH	298-2500	1.0(13)	0.67	956	2
73 SCH Based on the theoretical estimate of Mayer and Schieler (see 68 MAY/SCH, the preceding entry).	SE	298-2500	1.0(13)	0.67	956	2

Recommendation: No k values are recommended because the only available rate data have been obtained by a BEBO calculation. Until experimental values are obtained, the theoretical BEBO values of 68 MAY/SCH may be provisionally used, possibly with an uncertainty of an order of magnitude.

References for reaction  $\text{O} + \text{SH} \rightarrow \text{OH} + \text{S}$ 

- 68 MAY/SCH Mayer, S.W., and Schieler, L., "Computed activation energies and rate constants for forward and reverse transfers of hydrogen atoms," J. Phys. Chem. 72, 236 (1968).
- 73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).

O + Hydrogen sulfide

The rn. product usually assumed is OH+SH. Two alternative products (SO+H<sub>2</sub> and HSO+H) are discussed further below (see the data sheets for rns. O+H<sub>2</sub>S→SO+H<sub>2</sub> and O+H<sub>2</sub>S→HSO+H).

Reference Code, Notes	Data type	T/K	k,k(k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
65 LEV/MER  Microprobe study of H <sub>2</sub> S/O <sub>2</sub> /N <sub>2</sub> or of H <sub>2</sub> S/O <sub>2</sub> /Ar flames. Used mass spec. to analyze for O <sub>2</sub> , H <sub>2</sub> S, H <sub>2</sub> O, H <sub>2</sub> , and SO <sub>2</sub> , and wet analysis for SO + SO <sub>2</sub> and SO <sub>3</sub> . Rate constants calculated from rates of H <sub>2</sub> S consumption.	EX	1260	2.3(14)			2
	EX	1350	1.3(15)			2
66 LIU/DON *) Room temperature. P=0.38-0.53 Torr. Discharge flow. Mass spec. detection of O, H <sub>2</sub> S, and products. k calculated from the loss of H <sub>2</sub> S and the chain length of 5±1.5 for loss of H <sub>2</sub> S.	EX	*)	(2.4±1.2)(10)			2

O + H<sub>2</sub>S → products -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A units	k err. factor
67 MER/LEV Microprobe sampling of H <sub>2</sub> S/O <sub>2</sub> /N <sub>2</sub> flames using mass spec. Rate constant calculated from rates of formation of H <sub>2</sub> S, H <sub>2</sub> O and H <sub>2</sub> , and the calculated equilibrium O concentration. P=76 Torr.	EX	1055	2.8(13)			2	
70 CUP/GLA Discharge flow. ESR detection of O, SO, and H. Rate constant derived by adjusting it and three other k values to obtain the best fit of a 7 rn. mechanism to the experimental data. Revised k to 9.09(9) in 75 CUP/GLA.	DE	295	8.25(9)			2	
70 HOL/KUR Discharge flow. Monitored O atoms by ESR. Allowance was made for the assumed stoichiometry d[O]/d[H <sub>2</sub> S]=3.5±0.5. P=1.38-2.25 Torr at 300 K.	EX	205-300	(1.74±0.40)(11)		755±50	2	
70 TAK Discharge flow. Monitored the afterglow of SO, SO <sub>2</sub> , and O <sub>2</sub> . Evaluated k from consumption of H <sub>2</sub> S, correcting for stoichiometry (d[O]/d[H <sub>2</sub> S] = 1.2) and the chain decomposition of H <sub>2</sub> S.	EX	293	2.12(10)			2	
73 SCH	SE	200-350	3.8(11)		921±126	2	<2
75 CUP/GLA Revised k of 70 CUP/GLA.	DE	295	9.09(9)			2	
76 WHY/TIM Flash photolysis of Ar/H <sub>2</sub> S/O <sub>2</sub> mixtures. O monitored by resonance fluorescence. P=10-400 Torr.	EX	263-495	(4.36±0.64)(12)		1661±50	2	
78 HAM/GAR	SE	263-495	4.36(12)		1660	2	1.25
78 SLA/BAI P=0.7-2.1 Torr at 496 K. Discharge flow. Photoionization mass spec. Decay of H <sub>2</sub> S monitored in excess O atoms. A and B (not reported by the authors) were calculated (87 SIN/CVE) from the 19 k values listed in the supplementary material of 78 SLA/BAI.	EX	280-497	(1.96±0.20)(13)		2019±39	2	

O + H<sub>2</sub>S → products -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
79 SIN/IRW Phase shift technique, with modulated [O] measured by O+NO chemiluminescence. O generated by Hg-photosensitized decomposition of N <sub>2</sub> O.	EX	297-502	(1.56±0.83)(13)		2171±202	2
84 BAU/COX  For discussion see 82 BAU/COX.	SE	298	1.3(10)			2 2
	SE	290-500	8.4(12)		1920±750	2
85 DEM/MAR  Selection based on 79 SIN/IRW and 76 WHY/TIM.	SE	298	1.3(10)			2 1.7
	SE		6.0(12)		1810±550	2
Recommended value of k	RE	298	1.5(10)			2 1.3
Recommended values of Arrhenius A and B 82 BAU/COX and 85 DEM/MAR reviews give the least squares fit of the preferred data of 76 WHY/TIM and 79 SIN/IRW, which give the same values within experimental error for 330<T<500K, but those of 79 SIN/IRW are lower at lower T. Higher T data (>1000K) of other workers, considered less reliable, are scattered and lie significantly above the fitted line. The present recommended values have been derived by fitting the Arrhenius equation to the data of 76 WHY/TIM and 79 SIN/IRW.	RE	263-502	6.0(12)		1789±200	2 1.8
Arrhenius plots for the reaction O+H <sub>2</sub> S→products are shown in Fig. 2.						

References for reaction O + H<sub>2</sub>S → products

- 65 LEV/MER Levy, A., and Merryman, E. L., "The microstructure of hydrogen sulphide flames," *Combustion and Flame* 9, 229 (1965).
- 66 LIU/DON Liuti, G., Dondes, S., and Harteck, P., "The reaction of hydrogen sulfide and atomic oxygen," *J. Am. Chem. Soc.* 88, 3212 (1966).
- 67 MER/LEV Merryman, E. L., and Levy, A., "Kinetics of sulfur-oxide formation in flames: II. Low pressure H<sub>2</sub>S flames," *J. Air Pollution Control Association* 17, 800 (1967).
- 70 CUP/GLA Cupitt, L.T., and Glass, G.P., "Reaction of atomic oxygen with hydrogen sulfide," *Trans. Faraday Soc.* 66, 3007 (1970).
- 70 HOL/KUR Hollinden, G.A., Kurylo, M.J., and Timmons, R.B., "Electron spin resonance study of the reaction of O(<sup>3</sup>P) atoms with H<sub>2</sub>S," *J. Phys. Chem.* 74, 988 (1970).
- 70 TAK Takahashi, S., "The study of the reaction of hydrogen sulphide with atomic oxygen using emission spectrum," *Mem. Nat. Def. Acad. Japan* 10, 369 (1970).
- 73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," *J. Phys. Chem. Ref. Data* 2, 25 (1973).
- 75 CUP/GLA Cupitt, L.T., and Glass, G.P., "Reactions of SH with atomic oxygen and hydrogen," *Int. J. Chem. Kinet. Symp.* 1, 39 (1975).
- 76 WHY/TIM Whytock, D.A., Timmons, R.B., Lee, J.H., Michael, J.V., Payne, W.A., and Stief, L.J., "Absolute rate of the reaction of O(<sup>3</sup>P) with hydrogen sulfide over the temperature range 263 to 495K," *J. Chem. Phys.* 65, 2052 (1976).

References for reaction  $O + H_2S \rightarrow$  products -- Continued

- 78 HAM/GAR Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," Nat. Bur. Stand. Spec. Publ. 513 (1978).
- 78 SLA/BAI Slagle, I.R., Baiocchi, F., and Gutman, D., "Study of the reactions of oxygen atoms with hydrogen sulfide, methanethiol, ethanethiol, and methyl sulfide," J. Phys. Chem. 82, 1333 (1978).
- 79 SIN/IRW Singleton, D.L., Irwin, R.S., Nip, W.S., and Cvetanovic, R.J., "Kinetics and mechanism of the reaction of oxygen atoms with hydrogen sulfide," J. Phys. Chem. 83, 2195 (1979).
- 82 BAU/COX Baulch, D.L., Cox, R.A., Crutzen, P.J., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement 1," J. Phys. Chem. Ref. Data 11, 327 (1982).
- 84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data 13, 1259 (1984).
- 85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).
- 87 SIN/CVE Singleton, D.L., and Cvetanovic, R.J., The present evaluation.

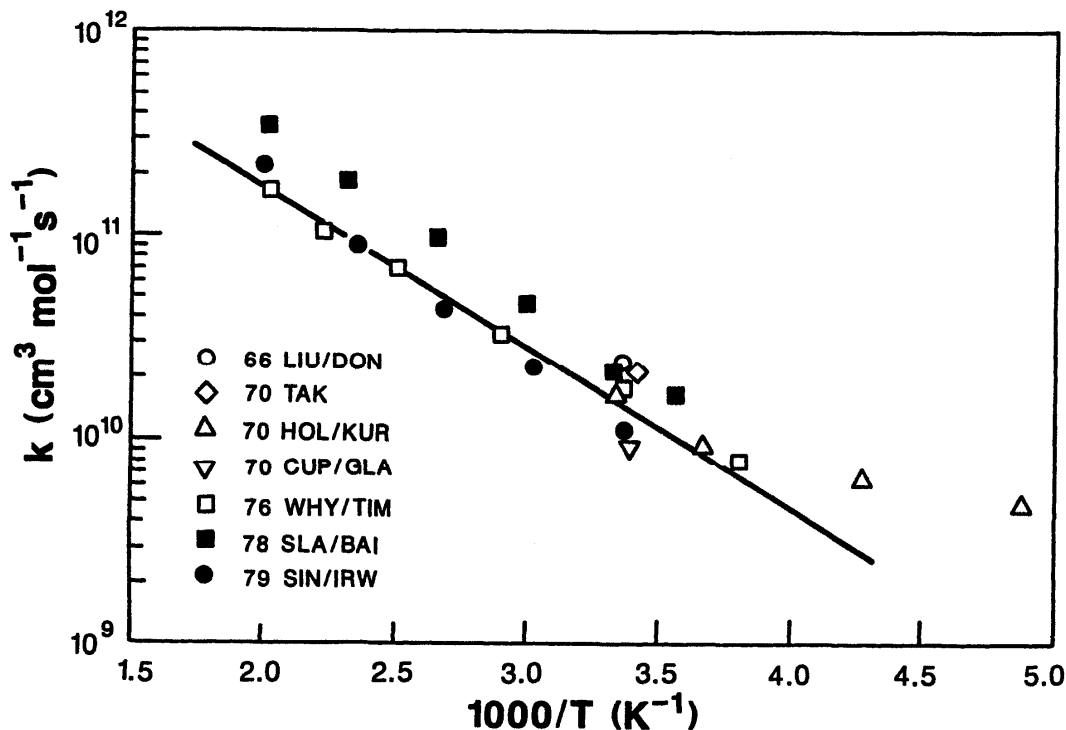
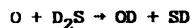


Fig. 2. Arrhenius plots for the reaction  $O + H_2S \rightarrow$  products.  
The line is calculated using the recommended A and B values.

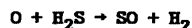


O + Deuterium sulfide

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
76 WHY/TIM Flash photolysis of Ar, D <sub>2</sub> S, O <sub>2</sub> mixtures with time-resolved resonance fluorescence detection of O atoms. P=10-200 Torr.	EX	298-450	(6.32±3.4)(12)		2144±156	2
Recommended value of k	RE	298	4.7(9)			2 1.4
Recommended values of Arrhenius A and B	RE	298-450	6.3(12)		2144±200	2 2
Based on the only data available (76 WHY/TIM). Additional determinations would be useful.						

Reference for reaction  $\text{O} + \text{D}_2\text{S} \rightarrow \text{OD} + \text{SD}$

76 WHY/TIM Whytock, D.A., Timmons, R.B., Lee, J.H., Michael, J.V., Payne, W.A., and Stief, L.J., "Absolute rate of the reaction of O(<sup>3</sup>P) with hydrogen sulfide over the temperature range 263 to 495K," J. Chem. Phys. 65, 2052 (1976).



O + Hydrogen sulfide

A higher temperature channel in the rn. O+H<sub>2</sub>S→products. See also the rn. O+H<sub>2</sub>S→HSO+H.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
67 BRA/DOB *) Reference rn. O+H <sub>2</sub> S → products. Arrh. A not given. Shock tube-Absorption spec. H <sub>2</sub> S/O <sub>2</sub> /Ar mixtures. This channel is proposed to account for increased SO <sub>2</sub> at high T. Based on the difference in the induction times of OH and SO <sub>2</sub> at low and high T, a value of E-E <sub>ref</sub> = 8 kcal/mole (B=4026 K) is proposed.	RL	1350-2450	*)		4026	2/2
81 FRE/LEE Reflected shock waves, measurement of induction time modeling of 57 reactions. Identical k values are derived for another rn. channel (see 81 FRE/LEE in the following rn.).	DE	1050-2000	1.0(13)		5032	2

Recommendation: This is evidently an insignificant pathway at room temp. There are no direct determinations on which to base a recommended value. The two reported values are indirectly derived in studies of complex systems at high temperatures (1050-2450K). More data are needed.

References for reaction  $O + H_2S \rightarrow SO + H_2$ 

- 67 BRA/DOB Bradley, J.N., and Dobson, D.C., "Oxidation of hydrogen sulfide in shock waves. I. Absorption studies of OH and SO<sub>2</sub> in H<sub>2</sub>S-O<sub>2</sub>-Ar mixtures," J. Chem. Phys. 46, 2865 (1967).
- 81 FRE/LEE Frenklach, M., Lee, J.H., White, J.N., and Gardiner, W.C., Jr., "Oxidation of hydrogen sulfide," Combustion and Flame 41, 1 (1981).

 $O + H_2S \rightarrow HSO + H$ O + Hydrogen sulfide

A potential minor channel in the rn.  $O+H_2S \rightarrow$ products. See also the rn.  $O+H_2S \rightarrow SO+H_2$ .

A channel in the rn.  $O+H_2S \rightarrow$ products due to attack on S rather than on H. Quantitative determination of the "branching ratio" for O addition to S as opposed to H abstraction is difficult (79 SIN/IRW; 82 SIN/PAR) because rates of some potentially involved elementary reactions are not known.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
79 SIN/IRW *) Room temperature. O generated by Hg-photo-sensitized decomposition of N <sub>2</sub> O. Reference rn. $O+H_2S \rightarrow$ products. Relative k based on collection of noncondensable gases formed (H <sub>2</sub> and N <sub>2</sub> ) and their GC analysis. The upper limit may be as high as 0.2 (82 SIN/PAR).	RL	*)	<0.11			2/2
81 FRE/LEE Reflected shock waves, measurement of induction time modeling of 57 reactions. Identical k values are derived for another rn. channel (see 81 FRE/LEE in the preceding rn.).	DE	1050-2000	1.0(13)		5032	2
81 CLE/DAV Crossed molecular beam method, with angular resolved mass spec. Reaction cross section for HSO formation as function of translational energy of the reactants. Value given for B is the threshold translational energy, not the Arrhenius activation energy. (See 82 DAV/CLE).	EX				1683±240	2
82 DAV/CLE Crossed molecular beam method, with angular resolved mass spec. Reaction cross section for HSO formation as function of translational energy of the reactants. Value given for B is the threshold translational energy, not the Arrhenius activation energy. (See 81 CLE/DAV).	EX				1683±240	2

+  $\text{H}_2\text{S} \rightarrow \text{HSO} + \text{H}$  -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
82 SIN/PAR An upper-limit value for the branching ratio $k/k(\text{O}+\text{H}_2\text{S} \rightarrow \text{products})$ .	RL	298	<0.2			2/2 1.1
Recommended branching ratio $k/k(\text{O}+\text{H}_2\text{S} \rightarrow \text{products})$ Based on the upper-limit value of 82 SIN/PAR.	RE	298	<0.2			2/2 1.1

References for reaction  $\text{O} + \text{H}_2\text{S} \rightarrow \text{HSO} + \text{H}$ 

- 79 SIN/IRW Singleton, D.L., Irwin, R.S., Nip, W.S., and Cvetanovic, R.J., "Kinetics and mechanism of the reaction of oxygen atoms with hydrogen sulfide," J. Phys. Chem. 83, 2195 (1979).
- 81 CLE/DAV Clemo, A.R., Davidson, F.E., Duncan, G.L., and Grice, R., "Translational energy threshold functions for oxygen atom reactions," Chem. Phys. Lett. 84, 509 (1981).
- 81 FRE/LEE Frenklach, M., Lee, J.H., White, J.N., and Gardiner, W.C., Jr., "Oxidation of hydrogen sulfide," Combustion and Flame 41, 1 (1981).
- 82 DAV/CLE Davidson, F.E., Clemo, A.R., Duncan, G.L., Browett, R.J., Hobson, J.H., and Grice, R., "Reactive scattering of a supersonic oxygen atom beam:  $\text{O} + \text{H}_2\text{S}$ ," Molec. Phys. 46, 33 (1982).
- 82 SIN/PAR Singleton, D.L., Paraskevopoulos, G., and Irwin, R.S., "Mechanism of the  $\text{O}(^3\text{P}) + \text{H}_2\text{S}$  Reaction. Abstraction or Addition?," J. Phys. Chem. 86, 2605 (1986).

+  $\text{H}_2\text{SO}_4 \rightarrow \text{products}$ 

+ Sulfuric acid

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
80 BAL/GOL *) Room temperature; $\text{H}_2\text{SO}_4$ liquid. #) Reaction probability per collision < $1.0(-6)$ . Discharge flow with Knudsen cell reactor. Mass spec. detection of O. No measureable reaction, no detectable products.	EX	*)	#)			2/2
Recommended value of k #) Reaction probability per collision < $1.0(-6)$ . Based on the only data available (80 BAL/GOL). Additional experimental work is desirable.	RE	298	#)			2/2



Reference for reaction  $O + H_2SO_4 \rightarrow$  products

80 BAL/GOL Baldwin, A.C., and Golden, D.M., "Heterogeneous atmospheric reactions. 2. Atom and radical reactions with sulfuric acid," J. Geophys. Res. 85, 2888 (1980).

 $O + CS \rightarrow$  products $O +$  Carbon monosulfide

The main and probably exclusive rn. channel is  $O + CS \rightarrow CO + S$ .

Reference Code, Notes	Data type	T/K	k, k(k(ref), A, A(A(ref))	n	B, B-B(ref)	k, A k err. units factor
68 HCM/KRO An order of magnitude estimate of k quoted in the Abstract of the paper.	ES	1100	~1(14)			2
71 HAN/SMI Reference rn. $O+NO_2 \rightarrow NO+O_2$ . Measured the effect of $NO_2$ on the vibrational emission intensities of CO. [RN value has been updated using $k_{ref} = 5.6(12)$ (85 DEM/MAR)].	RL RN	298 298	2.3 1.3(13)			2/2 2
73 SCH Based on the data (without a recommendation) of 71 HAN/SMI.	SE	298	8.4(12)			2
75 SLA/GRA Discharge flow. CS formed by a dc discharge in $CS_2$ , and O by microwave discharge in $O_2$ (or in $N_2$ followed by $N+NO$ rn.). Decay of CS in excess O followed by photoionization mass spec.	EX	305	(1.24±0.08)(13)			2
76 BAU/DRY *) No new recommendation. Suggest using Hancock and Smith's data (see 71 HAN/SMI).	SE		*)			2
76 BID/ERE Flow tube technique. CS, produced by microwave discharge in a dilute $CS_2/Ar$ stream, monitored by multipath uv absorption. Small [O] (<< [CS]) is maintained by rapid regeneration in the rn. $S + O_2 \rightarrow O + SO$ . (See also 78 KOL).	EX	300	(1.35±0.22)(13)			2

O + CS → products -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
77 LIL/RIC	EX	150-300	(1.6±0.2)(14)		758±144	2
	EX	298	1.26(13)			2
Discharge flow. Mass spec. measurement of CO formation in excess CS and of CS disappearance in excess O. Also monitored S and O by ESR. CS made by a dc discharge (CS <sub>2</sub> ), and O by a microwave discharge (NO or O <sub>2</sub> ). [k(298K) calculated from the Arrhenius eqn.].						
78 HAM/GAR	SE	300	1.3(13)			2 1.6
Accepted recommendation of 76 BAU/DRY.						
78 KOL	EX	300	(1.35±0.22)(13)			2
Flow tube technique. CS, produced by microwave discharge in a dilute CS <sub>2</sub> /Ar stream, monitored by multipath uv absorption. Small [O] (<< [CS]) is maintained by rapid regeneration in the rn. S + O <sub>2</sub> → O + SO. (See also 76 BID/BRE).						
78 TAL/BUT	EX	298	(1.3±0.13)(13)			2
Diffusion cloud ("diffusion flame") technique. O atoms formed by N+NO rn. CS consumption monitored by mass spec. P(He)=20 Torr.						
84 BAU/COX	SE	298	1.3(13)			2 1.25
	SE	150-300	1.6(14)		760±250	2
For discussion see 80 BAU/COX.						
Recommended value of k	RE	298	1.2(13)			2 1.2
Recommended values of Arrhenius A and B	RE	156-305	1.5(14)		751±100	2 1.5
Based on the least squares fit of all the data in 156-305K range assuming linear Arrhenius plot.						

Arrhenius plot for O+CS→products is shown in Fig. 3.

## References for reaction O + CS → products

- 68 HOM/KRO Homann, K.H., Krome, G., and Wagner, H.Gg., "Schwefelkohlenstoff-oxydation, geschwindigkeit von elementarreaktionen. Teil 1," Ber. Bunsenges. Phys. Chem. 72, 998 (1968).
- 71 HAN/SMI Hancock, G., and Smith, I.W.M., "Infra-red chemiluminescence from vibrationally excited CO. Part 1. The reaction of atomic oxygen with carbon disulphide," Trans. Faraday Soc. 67, 2586 (1971).
- 73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).
- 75 SLA/GRA Slagle, I.R., Graham, R.E., Gilbert, J.R., and Gutman, D., "Direct determination of the rate constant for the reaction of oxygen atoms with carbon monosulphide," Chem. Phys. Lett. 32, 184 (1975).

References for reaction  $O + CS \rightarrow$  products -- Continued

- 76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the  $O_2$ - $O_3$  system, the  $CO$ - $O_2$ - $H_2$  system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).
- 76 BID/BRE Bida, G.T., Breckenridge, W.E., and Kolln, W.S., "A kinetic study of the very fast reaction:  $O(^3P)+CS \rightarrow CO+S(^3P)$ ," J. Chem. Phys. 64, 3296 (1976).
- 77 LIL/RIC Lilenfeld, H.V., and Richardson, R.J., "Temperature dependence of the rate constant for the reaction between carbon monosulfide and atomic oxygen," J. Chem. Phys. 67, 3991 (1977).
- 78 HAM/GAR Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," Nat. Bur. Stand. Spec. Publ. 513 (1978).
- 78 KOL Kolln, W.S., "Gas Phase Reactions of Carbon Monosulfide Studied by the Fast Flow Technique," Diss. Abst. Int. B 39, 771 (1978).
- 78 TAL/BUT V.L. Tal'roze, Butkovskaya, N.I., Larichev, M.N., Leipunskii, I.O., Morozov, I.I., Dodonov, A.F., Kudrov, B.V., Zelenov, V.V., and Raznikov, V.V., (Daly, N.R., editor) "Advances in the mass spectrometry of free radicals," Advances in Mass Spectrometry 7A, 693 (1978).
- 80 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and Photochemical Data for Atmospheric Chemistry," J. Phys. Chem. Ref. Data 9, 295 (1980).
- 84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data 13, 1259 (1984).
- 85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).

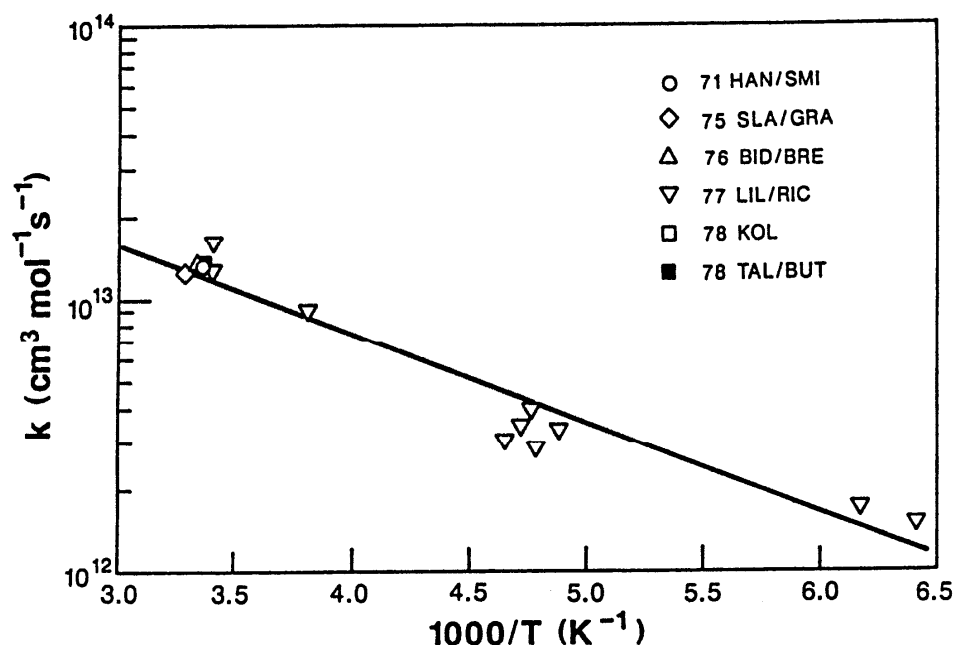


Fig. 3. Arrhenius plots for the reaction  $O+CS \rightarrow$  products.  
The line is calculated using the recommended A and B values.

O + CS<sub>2</sub> → products

## O + Carbon disulfide

The main rxn. product is CS+SO. For minor channels see rxns. O+CS<sub>2</sub>→COS+S and O+CS<sub>2</sub>→CO+S<sub>2</sub>.

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A units	k err. factor
67 CAL/SMI Flash photolysis-kinetic spectroscopy. O formed by photolysis of NO <sub>2</sub> . The product CS monitored by uv spec. [The same values and some relative determinations reported also in 68 SMI].	EX	305-410	(6.3±1.3)(12)		302±151	2	
67 SMI Flash photolysis-kinetic spectroscopy. O formed by photolysis of NO <sub>2</sub> . The reaction product CS monitored and SO detected by uv spec. 8% and 16% of rxn. exothermicity goes into vibrational excitation of CS and SO, respectively. [See also 67 CAL/SMI and 68 SMI].	EX	305-410	(6.3±1.3)(12)		302±151	2	
68 HOM/KRO Discharge flow. Excess O formed by a microwave discharge in O <sub>2</sub> or in N <sub>2</sub> (followed by N+NO rxn.). Decay of CS <sub>2</sub> and formation of SO followed by mass spec. P=3-6 Torr.	EX	300-920	5(13)		956	2	
68 SMI (Ref. rxn. O + isobutene)	EX	305-410	(6.3±1.3)(12)		302±151	2	
(Ref. rxn. O + isobutene)	RL	298	0.32±0.03			2/2	
(Ref. rxn. O + isobutene)	RL	410	0.40±0.05			2/2	
(Ref. rxn. O + 1-butene)	RL	298	1.3±0.1			2/2	
(Ref. rxn. O + 1-butene)	RL	410	1.2±0.1			2/2	
(Ref. rxn. O + NO <sub>2</sub> )	RL	298	0.71±0.2			2/2	
(Ref. rxn. O + NO <sub>2</sub> )	RL	410	0.65±0.2			2/2	
(Ref. rxn. O + isobutene)	RN	298	3.26(12)			2	
(Ref. rxn. O + 1-butene)	RN	298	3.25(12)			2	
(Ref. rxn. O + NO <sub>2</sub> )	RN	298	4.0(12)			2	
Flash photolysis-kinetic spectroscopy. O formed by photolysis of NO <sub>2</sub> . The product CS monitored by uv spec. [See also 67 SMI and 67 CAL/SMI]. [The normalized (RN) values have been calculated (87 SIN/CVE) using the following k <sub>ref</sub> values at 298 K: isobutene 1.02(13) (87 CVE), 1-butene 2.50(12) (87 CVE), NO <sub>2</sub> 5.6(12) (85 DEM/MAR)].							

O + CS<sub>2</sub> → products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
69 WES/DEH Discharge flow. O formed by microwave discharge in O <sub>2</sub> or in N <sub>2</sub> (followed by N+NO rn.). Decay of O followed by ESR. Results were divided by a stoichiometric factor of 2. The reported A and B values were calculated by including the results of 68 SMI. P=1.93-2.10 Torr at 297 K. SO detected as a product by ESR.	EX	227-538	(1.2±0.2)(13)		528±50	2	
70 CAL/HED Flash Hg-photosensitized decomposition of N <sub>2</sub> O in the presence of CS <sub>2</sub> to form O. Time dependence of CS determined by uv absorption. P=678 Torr.	EX	298	(2.2±0.2)(12)			2	
73 SCH Suggested error limits of ± 20% for 200-1000K.	SE	200-1000	1.2(13)		518±40	2	
74 SLA/GIL Discharge flow. O formed by microwave discharge in O <sub>2</sub> or in N <sub>2</sub> followed by N+NO rn. Decay of CS <sub>2</sub> in the presence of excess O followed by photoionization mass spec. P=1.4 Torr.	EX	302	(2.4±0.2)(12)			2	
75 WEI/TIM Discharge flow. O formed by microwave discharge of O <sub>2</sub> or of N <sub>2</sub> (followed by N+NO rn.). Decay of O in excess CS <sub>2</sub> followed by ESR. Results divided by the stoichiometric factor of 2.	EX	218-293	(1.66±0.23)(13)		644±35	2	
76 BAU/DRY Estimated uncertainty is 30% below 350 K, increasing to 100% at 1000 K.	SE	200-1000	2.2(13)		700	2	
77 GRA/GUT Discharge flow. O formed by microwave discharge in N <sub>2</sub> followed by N+NO rn. The decay of CS <sub>2</sub> in excess O followed by photoionization mass spec. The authors suggest that their data do not follow Arrhenius behavior. The values of A and B given above were calculated (87 SIN/CVE) assuming linear Arrhenius plots.	EX	249-500	(2.23±0.33)(13)		659±48	2	
78 HAM/GAR *) Accepted recommendation of 76 BAU/DRY. Suggested error factor of 1.4 for T<360K.	SE	200-1000	2.2(13)		700	2	*)

O + CS<sub>2</sub> → products -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
78 TAL/BUT Diffusion cloud ("diffusion flame") technique. O atoms formed by N+NO rn. CS <sub>2</sub> consumption monitored by mass spec. P(He)=20 Torr.	EX	298	(1.4±0.14)(12)			2
84 BAU/COX  Accepted the NASA evaluation (83 DEM/MOL). For k(O+CS <sub>2</sub> →SO+CS)/k(O+CS <sub>2</sub> →products), i.e. for branching ratio, recommend a value ≥0.90.	SE	298	2.2(12)			2 1.6
	SE	200-500	1.9(13)		650±100	2
85 DEM/MAR  Averaged the room temp. data of 75 WEI/TIM, 69 WES/DEH, 74 SLA/GIL, 67 CAL/SMI, 70 CAL/HED, 68 HOM/KRO, and 77 GRA/GUT; averaged the B values of 75 WEI/TIM and 77 GRA/GUT; set the error in B to encompass the value of B of 69 WES/DEH.	SE	298	2.2(12)			2 1.2
	SE		1.9(13)		650±150	2
Recommended value of k	RE	298	2.3(12)			2 1.2
Recommended values of Arrhenius A and B	RE	218-920	3.55(13)		821±100	2 1.5
Based on the least squares fit of all data in the data sheet assuming linear Arrhenius plot.						
Arrhenius plot for O+CS <sub>2</sub> →products is shown in Fig. 4.						

References for reaction O + CS<sub>2</sub> → products

- 67 CAL/SMI Callear, A.B., and Smith, I.W.M., "Measurement of the rate parameters for reaction of O(2<sup>3</sup>P) with carbon disulphide and olefines, by flash spectroscopy," *Nature* **213**, 382 (1967).
- 67 SMI Smith, I.W.M., "Experimental and computer studies of the kinetics and distribution of vibrational energy in both products of the reaction: O(2<sup>3</sup>P) + CS<sub>2</sub> → SO + CS," *Disc. Faraday Soc.* **44**, 194 (1967).
- 68 HOM/KRO Homann, K.H., Krome, G., and Wagner, H.G., "Schwefelkohlenstoff-oxydation, geschwindigkeit von elementarreaktionen. Teil 1," *Ber. Bunsenges. Phys. Chem.* **72**, 998 (1968).
- 68 SMI Smith, I.W.M., "Rate parameters for reactions of O(2<sup>3</sup>P) with CS<sub>2</sub>, NO<sub>2</sub>, and olefins," *Trans. Faraday Soc.* **64**, 378 (1968).
- 69 WES/DEH Westenberg, A.A., and deHaas, N., "Atom-molecule kinetics using ESR detection. V. Results for O + OCS, O + CS<sub>2</sub>, O + NO<sub>2</sub>, and H + C<sub>2</sub>H<sub>4</sub>," *J. Chem. Phys.* **50**, 707 (1969).
- 70 CAL/HED Callear, A.B., and Hedges, R.E.M., "Flash spectroscopy with mercury resonance radiation. Part 1. An experimental method with microwave-pulse excitation," *Trans. Faraday Soc.* **66**, 605 (1970).
- 73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," *J. Phys. Chem. Ref. Data* **2**, 25 (1973).

References for reaction  $O + CS_2 \rightarrow$  products -- Continued

- 74 SLA/GIL Slagle, I.R., Gilbert, J.R., and Gutman, D., "Kinetics of the reaction between oxygen atoms and carbon disulfide," J. Chem. Phys. 61, 704 (1974).
- 75 WEI/TIM Wei, C.-N., and Timmons, R.B., "ESR study of the kinetics of the reactions of  $O(^3P)$  atoms with  $CS_2$  and  $OCS$ ," J. Chem. Phys. 62, 3240 (1975).
- 76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the  $O_2$ - $O_3$  system, the  $CO$ - $O_2$ - $H_2$  system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).
- 77 GRA/GUT Graham, R.E., and Gutman, D., "Temperature dependence of rate constants and branching ratios for the reaction of oxygen atoms with carbon disulfide," J. Phys. Chem. 81, 207 (1977).
- 78 HAM/GAR Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," Nat. Bur. Stand. Spec. Publ. 513 (1978).
- 78 TAL/BUT V.L. Tal'roze, Butkovskaya, N.I., Larichev, M.N., Leipunskii, I.O., Morozov, I.I., Dodonov, A.F., Kudrov, B.V., Zelenov, V.V., and Raznikov, V.V., (Daly, N.R., editor) "Advances in the mass spectrometry of free radicals," Advances in Mass Spectrometry 7A, 593 (1978).
- 84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data 13, 1259 (1984).
- 85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).
- 87 CVE Cveticanovic, R.J., "Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen  $O(^3P)$  with Unsaturated Hydrocarbons," J. Phys. Chem. Ref. Data 16, 261 (1987).
- 87 SIN/CVE Singleton, D.L., and Cveticanovic, R.J., The present evaluation.

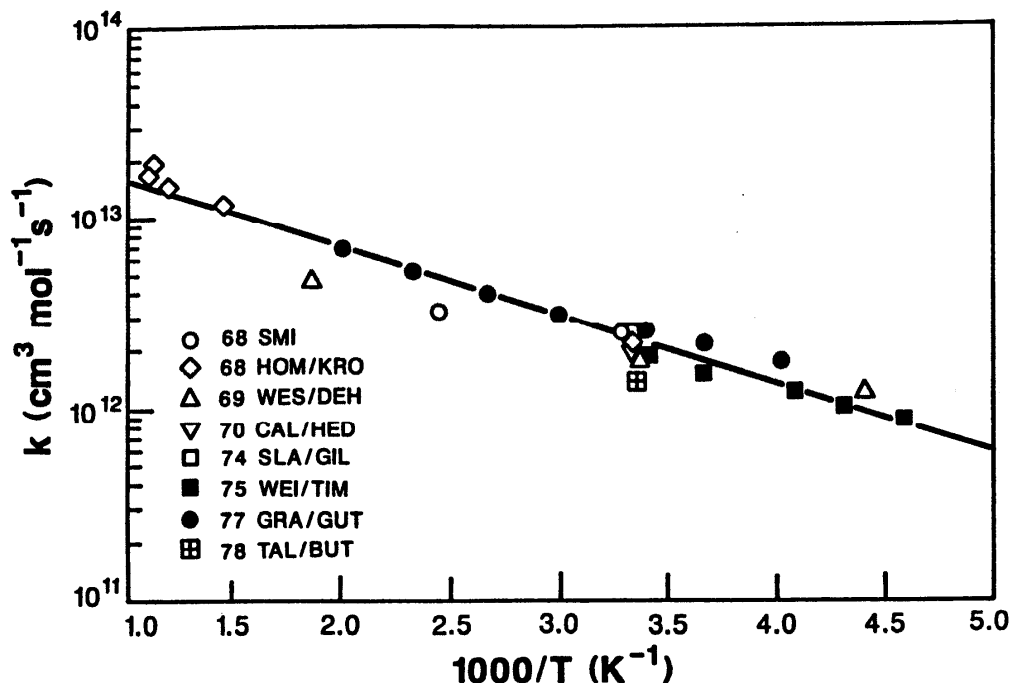
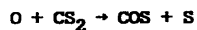


Fig. 4. Arrhenius plot for the reaction  $O + CS_2 \rightarrow$  products.  
The line is calculated using the recommended A and B values.

O + Carbon disulfideA channel in the rn.  $\text{O} + \text{CS}_2 \rightarrow \text{products}$ .

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
68 HOM/KRO Discharge flow. Excess O formed by a microwave discharge in $\text{O}_2$ or in $\text{N}_2$ (followed by $\text{N} + \text{NO}$ rn.). k value, based on rate of formation of COS, is approximate. The authors suggest that the branching ratio of the channel giving COS is 0.05 at 1100 K. P=3-6 Torr.	EX	1100	1(12)			2
73 SCH Only one reported value (68 HOM/KRO). An estimated value at 298 K is given as 2.4(10).	SE	1100	1(12)			2
74 SLA/GIL Discharge flow. O formed by microwave discharge in $\text{N}_2$ followed by $\text{N} + \text{NO}$ rn. Decay of $\text{CS}_2$ and formation of COS followed by photoionization mass spec. P=1.4 Torr.	RL	302	0.093±0.008			2/2
76 BAU/DRY The selected k value is based on the branching ratio reported by 74 SLA/GIL and the selected overall k value by 76 BAU/DRY.	SE	302	(2.2±1.1)(11)			2
77 GRA/GUT *) k/k(overall) = (0.098±0.004) - (0.081±0.007). Discharge flow. O formed by microwave discharge in $\text{N}_2$ followed by $\text{N} + \text{NO}$ rn. Decay of $\text{CS}_2$ and formation of COS followed by photoionization mass spec.	RL	249-500	*)			2/2
Recommended value of k	RE	298	2.1(11)			2 1.3
Recommended values of Arrhenius A and B	RE	249-500	2.2(12)		701±100	2 2
Based on the data of 77 GRA/GUT for the branching ratio and the recommended Arrhenius parameters for the overall reaction of 87 SIN/CVE.						

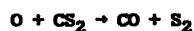
References for reaction  $\text{O} + \text{CS}_2 \rightarrow \text{COS} + \text{S}$ 

- 68 HOM/KRO Homann, K.H., Krome, G., and Wagner, H.Gg., "Schwefelkohlenstoff-oxydation, geschwindigkeit von elementarreaktionen. Teil 1," Ber. Bunsenges. Phys. Chem. 72, 998 (1968).
- 73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).



References for reaction  $O + CS_2 \rightarrow COS + S$  -- Continued

- 74 SLA/GIL Slagle, I.R., Gilbert, J.R., and Gutman, D., "Kinetics of the reaction between oxygen atoms and carbon disulfide," J. Chem. Phys. 61, 704 (1974).
- 76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the  $O_2$ - $O_3$  system, the  $CO$ - $O_2$ - $H_2$  system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).
- 77 GRA/GUT Graham, R.E., and Gutman, D., "Temperature dependence of rate constants and branching ratios for the reaction of oxygen atoms with carbon disulfide," J. Phys. Chem. 81, 207 (1977).

O + Carbon disulfide

A minor channel in the rx.  $O+CS_2 \rightarrow$  products.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
79 HSU/SHA	RL	298	0.014±0.002			2/2
	RN	298	(3.51±0.45)(10)			2
Flash photolysis-CO laser absorption technique. The listed RL k is the branching ratio for the channel $O+CS_2 \rightarrow CO+S_2$ . The normalized (RN) k is based on the ratio of 0.373 measured for the CO formed in the $O+CS_2$ and $O+C_2H_2$ rxns. The RN value was obtained using $k(O+C_2H_2 \rightarrow CO+CH_2)=9.4(10)$ (73 HER/HUI) and the branching ratio (the RL value) and $k(O+CS_2 \rightarrow \text{products})=2.53(12)$ (77 GRA/GUT).						
Recommended branching ratio $k/k(O+CS_2 \rightarrow \text{products})$	RE	298	1.4(-2)			2/2 1.2
Recommended value of k	RE	298	3.5(10)			2 1.3
Based on the only data available (79 HSU/SHA). Additional determinations would be useful.						

References for reaction  $O + CS_2 \rightarrow CO + S_2$ 

- 73 HER/HUI Herron, J.T., and Huie, R.E., "Rate Constants for the Reactions of Atomic Oxygen  $O(^3P)$  with Organic Compounds in the Gas Phase," J. Phys. Chem. Ref. Data 2, 467 (1973).
- 77 GRA/GUT Graham, R.E., and Gutman, D., "Temperature dependence of rate constants and branching ratios for the reaction of oxygen atoms with carbon disulfide," J. Phys. Chem. 81, 207 (1977).
- 79 HSU/SHA Hsu, D.S.Y., Shaub, W.M., Burks, T.L., and Lin, M.C., "Dynamics of reactions of  $O(^3P)$  atoms with  $CS$ ,  $CS_2$ , and  $OCS$ ," Chem. Phys. 44, 143 (1979).

## O + COS → products

## O + Carbon oxide sulfide

At lower T the only observed product is SO+CO. See rn. O+COS+CO<sub>2</sub>+S for a higher T rn. channel.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
65 ROL/REE O produced by discharge in O <sub>2</sub> . Measured O+SO chemiluminescence. k is approximate, with no details given. No CO <sub>2</sub> observed by mass spec. A reference is made to the channel forming CO <sub>2</sub> and S, as being less than 0.001 of the channel forming CO and SO.	EX	298	6(9)			2
65 SUL/WAR T not specified: presumably room temperature. Discharge flow. O formed by microwave discharge of O <sub>2</sub> . Consumption of COS determined by mass spec. Consumption of O matched the formation of CO. P=0.3-1.3 Torr.	EX	*)	(5.5±0.8)(9)			2
67 HOY/WAG Discharge flow. O formed by microwave discharge of N <sub>2</sub> (followed by the N+NO rn.). With excess COS, rate of decay of O measured by ESR and of formation of SO by molecular beam mass spec. Products CO, SO <sub>2</sub> , S <sub>2</sub> O, and S were detected by mass spec. P=0.5-5 Torr.	EX	290-465	1.2(14)		2919±50	2
68 HOM/KRO Discharge flow. O formed by microwave discharge of O <sub>2</sub> or N <sub>2</sub> (followed by N+NO rn.). Decay of COS and formation of SO followed by molecular beam mass spec. in excess O. Measurements at 880-1150 K were combined with the earlier data (67 HOY/WAG) to obtain the listed Arrhenius parameters. Small amounts of CO <sub>2</sub> , but not of SO <sub>2</sub> , were observed as products.	EX	300-1150	6.5(13)		2768	2
69 WES/DEH Discharge flow. O formed by microwave discharge of O <sub>2</sub> in He or Ar, or of N <sub>2</sub> (followed by N+NO rn.) and detected by ESR in excess COS. P=0.7-2.34 Torr at 297 K. SO detected as product; its yield, obtained using an adjusted value for final [SO], equalled consumption of O at 297 K. CO (but not CO <sub>2</sub> ) was detected as a product by mass spectrometry.	EX	273-808	(1.9±0.7)(13)		2280±126	2

O + COS → products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
71 KRE/SIM Ref. rn. O + 2-trifluoromethylpropene (TMP). O formed by Hg-photosensitized decomposition of N <sub>2</sub> O. Monitored CO yield as a function of the ratio of TMP to COS. The normalized (RN) values were obtained using A <sub>ref</sub> =9.09(12), B <sub>ref</sub> =1117. P(N <sub>2</sub> O)=490-657 Torr at 298 K.	RN	298-523	9.76(12)		2264	2	
72 BRE/MIL Discharge flow. O formed by microwave discharge of O <sub>2</sub> in He and monitored in excess COS by ESR. Details are not given. SO detected as product.	EX	297	(7.2±0.4)(9)			2	
73 SCH Suggested error limits of ± 35%.	SE	270-1500	4.1(13)		2556±70	2	
74 KLE/STI Flash photolysis - resonance fluorescence. O formed by flash photolysis of O <sub>2</sub> ; its decay was measured by resonance fluorescence in excess COS and 50 Torr He or 40-200 Torr Ar.	EX	263-503	(9.94±0.78)(12)		2166±28	2	
75 WEI/TIM Discharge flow. O formed by microwave discharge in O <sub>2</sub> or N <sub>2</sub> (followed by N+NO rn.) diluted with He, was monitored in excess COS by ESR. P=0.69-1.49 at 295 K.	EX	239-404	(1.2±0.2)(13)		2149±35	2	
76 BAU/DRY Estimated uncertainty is 50% below 600 K and a factor of 3 above 600 K.	SE	180-1200	1.6(13)		2250	2	
76 MAN/BRA Flash photolysis-resonance fluorescence. Photolysed mixtures of COS, O <sub>2</sub> , Ar, and either CH <sub>3</sub> F or CH <sub>2</sub> F <sub>2</sub> . Resonance fluorescence detection of O decay in excess COS. Rate was not significantly increased by vibrational excitation of COS.	EX	296	(8.37±0.84)(9)			2	

## O + COS → products -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
78 YOS/SAI Discharge flow. O formed by microwave discharge in O <sub>2</sub> . Excess COS. Formation of SO monitored by microwave absorption. Ratio of consumption of O to formation of SO was found to be unity. P=0.13 Torr.	EX	297	(7.1±0.7)(9)			2
79 HSU/SHA *) Vibrational distribution of CO product measured by CO laser resonance absorption method. Vibrational distribution was independent of the O isotope (16 or 18), indicating direct stripping of S by O (i.e., O in CO arises from COS).	EX		*)			
80 ROB/SMI Laser photolysis-chemiluminescence. O formed by laser photolysis of O <sub>3</sub> at 275nm. k was obtained by least squares fit of a reaction mechanism to the measured time dependence of the SO+O <sub>3</sub> chemiluminescence. P(N <sub>2</sub> )=100 Torr.	EX	296	(1.0±0.1)(10)			2
81 KRU/WAG  Shock tube. O generated by decomposition of N <sub>2</sub> O in Ar and monitored by resonance absorption. The two alternative T-dependence expressions were derived by combining the data with other results in the literature (67 HOY/WAG and 68 HOM/KRO).	EX 1900 DE 298-1900 DE 298-1900		1.8(13) 7.5(13) 7.4(12)			2 2 2
				0 1.0	2754 2057	
84 BAU/COX  For discussion see 80 BAU/COX. Note that only data for T<600 K are considered and that the data above 600 K are significantly higher than the fitted line.	SE 298 SE 220-600		8.4(9) 1.6(13)			2 1.6 2250±150 2
85 DEM/MAR  Averaged the room temp. data of 69 WES/DEH, 74 KLE/STI, 75 WEI/TIM, 76 MAN/BRA, 72 BRE/MIL; averaged the B values of 69 WES/DEH, 74 KLE/STI, 75 WEI/TIM.	SE 298 SE		7.8(9) 1.3(13)			2 1.2 2200±150 2

O + COS → products -- Continued

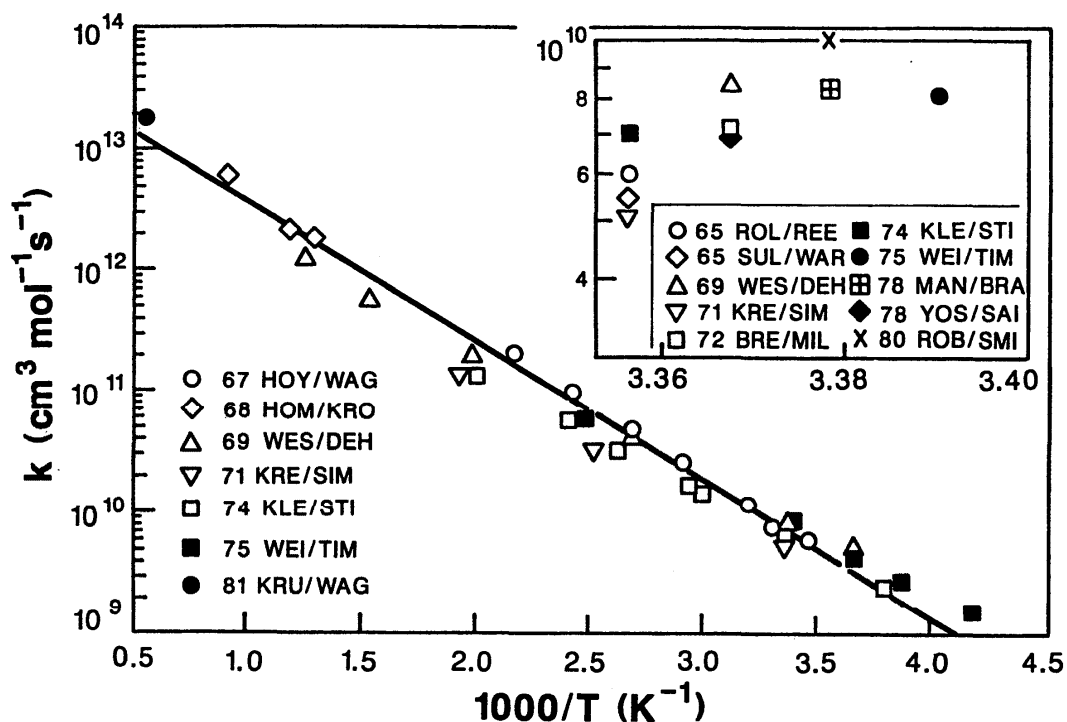
Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
Recommended value of k	RE	298	8.0(9)			2 1.2
Recommended values of Arrhenius A and B	RE	239-523	1.6(13)		2257±200	2 1.3
Recommended values of Arrhenius A and B	RE	239-1900	4.7(13)		2621±200	2 1.5
Based on least squares fitting of all data in the data sheet for (a) 239-523 and (b) 239-1900 K temp. ranges.						
Arrhenius plot for O+COS→products is shown in Fig. 5. The insert in Fig. 5 shows an enlarged area (for greater clarity) with several additional k values (those reported at room temperature only).						

## References for reaction O + COS → products

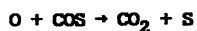
- 65 ROL/REE Rolfe, T.R., Reeves, R.R., Jr., and Harteck, P., "The chemiluminescent reaction of oxygen atoms with sulfur monoxide at low pressures," J. Phys. Chem. 69, 849 (1965).
- 65 SUL/WAR Sullivan, J.O., and Warneck, P., "Mass spectrometric investigation of the reaction between oxygen atoms and carbonyl sulfide," Ber. Bunsenges. Phys. Chem. 69, 7 (1965).
- 67 HOY/WAG Hoyermann, K., Wagner, H.G., and Wolfrum, J., "Bestimmung der Geschwindigkeit der Reaktion O + COS → CO + SO," Ber. Bunsenges. Phys. Chem. 71, 603 (1967).
- 68 HOM/KRO Homann, K.H., Krome, G., and Wagner, H.G., "Schwefelkohlenstoff-oxydation, geschwindigkeit von elementarreaktionen. Teil 1," Ber. Bunsenges. Phys. Chem. 72, 998 (1968).
- 69 WES/DEH Westenberg, A.A., and deHaas, N., "Atom-molecule kinetics using ESR detection. V. Results for O + OCS, O + CS<sub>2</sub>, O + NO<sub>2</sub>, and H + C<sub>2</sub>H<sub>4</sub>," J. Chem. Phys. 50, 707 (1969).
- 71 KRE/SIM Krezenski, D.C., Simonaitis, R., and Heicklen, J., "The reactions of O(<sup>3</sup>P) with ozone and carbonyl sulfide," Int. J. Chem. Kinet. 3, 467 (1971).
- 72 BRE/MIL Breckenridge, W.H., and Miller, T.A., "Kinetic study by EPR of the production and decay of SO(<sup>1</sup>Δ) in the reaction of O<sub>2</sub> (<sup>1</sup>Δ<sub>g</sub>) with SO(<sup>3</sup>Σ<sup>-</sup>)," J. Chem. Phys. 56, 465 (1972).
- 73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).
- 74 KLE/STI Klemm, R.B., and Stief, L.J., "Absolute rate parameters for the reaction of ground state atomic oxygen with carbonyl sulfide," J. Chem. Phys. 61, 4900 (1974).
- 75 WEI/TIM Wei, C.-N., and Timmons, R.B., "ESR study of the kinetics of the reactions of O(<sup>3</sup>P) atoms with CS<sub>2</sub> and OCS," J. Chem. Phys. 62, 3240 (1975).
- 76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the O<sub>2</sub>-O<sub>3</sub> system, the CO-O<sub>2</sub>-H<sub>2</sub> system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).
- 76 MAN/BRA Manning, R.G., Braun, W., and Kurylo, M.J., "The effect of infrared laser excitation on reaction dynamics: O + C<sub>2</sub>H<sub>4</sub>\* and O + OCS\*," J. Chem. Phys. 65, 2609 (1976).
- 78 YOS/SAI Yoshida, N., and Saito, S., "Application of microwave spectroscopy to kinetic study of the reaction of carbonyl sulfide with atomic oxygen," Bull. Chem. Soc. Japan 51, 1635 (1978).

References for reaction  $O + COS \rightarrow$  products -- Continued

- 79 HSU/SHA Hsu, D.S.Y., Shaub, W.M., Burks, T.L., and Lin, M.C., "Dynamics of reactions of  $O(^3P)$  atoms with CS,  $CS_2$ , and OCS," Chem. Phys. 44, 143 (1979).
- 80 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry," J. Phys. Chem. Ref. Data 9, 295 (1980).
- 80 ROB/SMI Robertshaw, J. S., and Smith, I. W. M., "Rate data for  $O + OCS \rightarrow SO + CO$  and  $SO + O_3 \rightarrow SO_2 + O_2$  by a new time-resolved technique," Int. J. Chem. Kinet. 12, 729 (1980).
- 81 KRU/WAG Kruger, B., and Wagner, H.G., "Shock tube study of the rate constant of the reaction of oxygen atoms with carbonyl sulfide," Z. Phys. Chem. Neue Folge 126, 1 (1981).
- 84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data 13, 1259 (1984).
- 85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).

Fig. 5. Arrhenius plot for the reaction  $O+COS \rightarrow$  products.

The line is calculated using the recommended A and B values at 239-1900K.



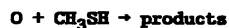
O + Carbon oxide sulfide

A higher temperature path in the rn.  $\text{O} + \text{COS} \rightarrow \text{products}$

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
82 TOP Shock tube oxidation of COS. Monitored COS, O <sub>2</sub> , CO, CO <sub>2</sub> , SO <sub>2</sub> and total pressure. The relative rates of CO <sub>2</sub> and CO production at the beginning of the COS conversion phase were interpreted to estimate k for the rn. path $\text{O} + \text{COS} \rightarrow \text{CO}_2 + \text{S}$ .	EX	1200-1900	5.0(13)		5527±636	2
Recommended value of k	RE	1200	5(11)			2 3
Recommended values of Arrhenius A and B	RE	1200-1900	5(13)		5530±1000	2 3
Based on the single determination (82 TOP). Additional data would be useful.						

Reference for reaction  $\text{O} + \text{COS} \rightarrow \text{CO}_2 + \text{S}$

82 TOP Topaloglu, T., "A shock tube study of carbonyl sulfide oxidation," Diss. Abst. Int. B 42, 4134 (1982).



O + Methanethiol

For potential rn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
76 SLA/GRA Discharge flow. Photoionization mass spec. Monitored decay of CH <sub>3</sub> SH in excess O atoms. P=0.64-2.0 Torr.	EX	300	1.1(12)			2 1.2
78 KIR/VET Discharge flow. High resolution mass spec. Monitored decay of thiol in excess O atoms. P≈1 Torr. Rate constant measurements at 302 K based on thiol decay agree with those based on O atom decay when thiol was in sufficient excess (100 fold), but were otherwise larger.	EX	300-661	(8.5±1.0)(12)		625±36	2

O + CH<sub>3</sub>SH → products -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
78 SLA/BAI *) n=4.53±0.49 Discharge flow. Photoionization mass spec. Monitored decay of CH <sub>3</sub> SH in excess O atoms. P=0.745-2.25 Torr. [A, n, and B values were calculated (87 SIN/CVE) from the supplementary data of 78 SLA BAI].	EX	252-496	(2.65±1.52)(10)	*)	-1135±169	2
81 NIP/SIN *) n=3.65±0.61. P=22-61 Torr. Phase shift technique with modulated [O] monitored by O+NO chemiluminescence. O atoms generated by Hg-photosensitized decomposition of N <sub>2</sub> O. 81 NIP/SIN report the rate expression k = (9.16±1.02)(11) + (3.85±2.41)(13) × exp(-(1673±322)/T). [A, n, and B values listed here were calculated (87 SIN/CVE) from the data of 81 NIP/SIN].	EX	297-537	(6.58±5.05)(10)	*)	-829±234	2
Recommended value of k	RE	298	1.2(12)			2 1.2
Recommended values of Arrhenius parameters	RE	252-661	*)	*)	*)	2 1.3
*) Strongly curved Arrhenius plot: fitted all data to k=A1+A2exp(-B/T) with A1=9.0(11), A2=1.8(13), B=1261. Although the agreement between the reported studies is reasonable, they differ in finer details. The Arrhenius plot is reported to be curved according to 78 SLA/BAI and 81 NIP/SIN, although the data of 78 SLA/BAI are consistently about 15% higher than those of 81 NIP/SIN. However, there was no evidence in 78 KIR/VET of an Arrhenius plot curvature in the same temp. interval. The present recommended Arrhenius parameters, A1, A2 and B, have been obtained by a least squares fit of all data in the data sheet to the composite Arrhenius expression. The data of 81 NIP/SIN fall below the fitted line; for example the fitted k(298) value is 1.17(12), which is about 10% greater than the value 1.06(12) of 81 NIP/SIN.  Arrhenius plot for O+CH <sub>3</sub> SH→products is shown in Fig. 6.						

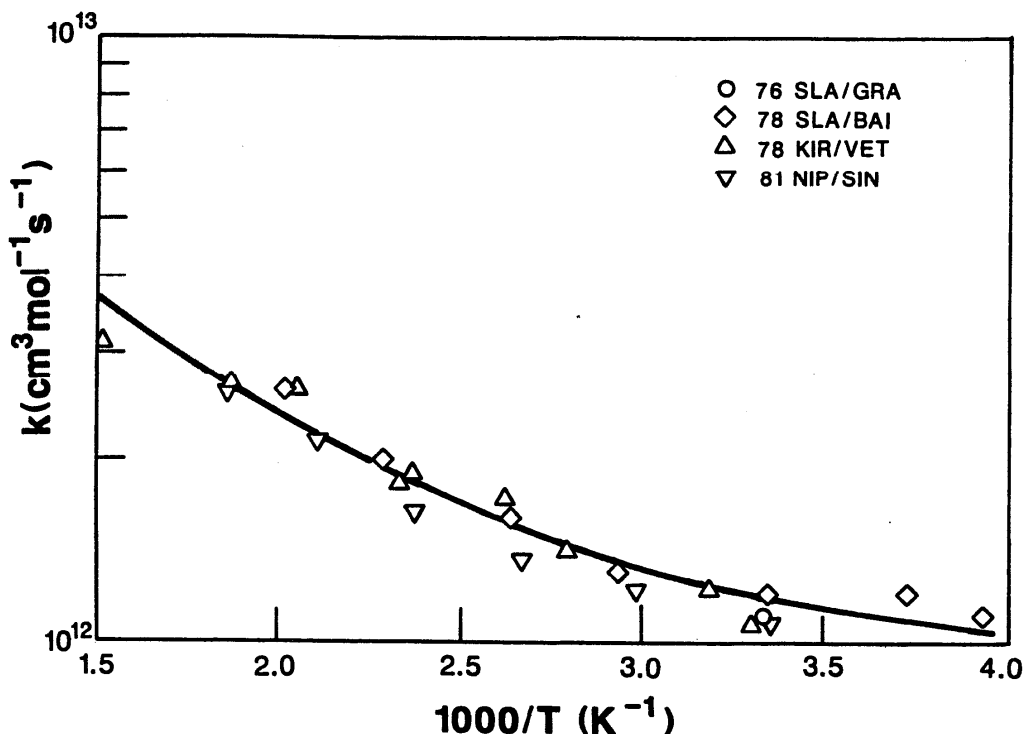
References for reaction O + CH<sub>3</sub>SH → products

- 76 SLA/GRA Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reactions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," Int. J. Chem. Kinet. 8, 451 (1976).
- 78 KIR/VET Kirchmer, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with O(<sup>3</sup>P) under consideration of the influence of molecular oxygen," Ber. Bunsenges. Phys. Chem. 82, 1223 (1978).
- 78 SLA/BAI Slagle, I.R., Baiocchi, F., and Gutman, D., "Study of the reactions of oxygen atoms with hydrogen sulfide, methanethiol, ethanethiol, and methyl sulfide," J. Phys. Chem. 82, 1333 (1978).



References for reaction  $O + CH_3SH \rightarrow$  products -- Continued

- 81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S., "Gas-Phase Reactions of  $O(^3P)$  Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," J. Am. Chem. Soc. 103, 3530 (1981).
- 81 NIP/SIN Nip, W.S., Singleton, D.L., and Cvetanovic, R.J., "Gas-phase reactions of  $O(^3P)$  atoms with methanethiol, ethanethiol, methyl sulfide, and dimethyl disulfide. 1. Rate constants and Arrhenius parameters," J. Am. Chem. Soc. 103, 3526 (1981).
- 87 SIN/CVE Singleton, D.L., and Cvetanovic, R.J., The present evaluation.

Fig. 6. Arrhenius plot for the reaction  $O + CH_3SH \rightarrow$  products.

The line is calculated using the modified Arrhenius Eqn.  $k = A_1 + A_2 \exp(-B/T)$  and the recommended values:  $A_1 = 0.0(11) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $A_2 = 1.8(13) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $B = 1261 \text{ K}$ .

 $O + C_2H_5SH \rightarrow$  products $O +$  Ethanethiol

For potential rn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k, k(k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
76 SLA/GRA	EX	300	1.7(12)			2 1.2
Discharge flow. Photoionization mass spec. Monitored decay of $C_2H_5SH$ in excess O atoms. P=0.64-2.0 Torr.						

O + C<sub>2</sub>H<sub>5</sub>SH → products -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
78 KIR/VET Discharge flow. High resolution mass spec. Monitored decay of thiol in excess O atoms. P=1 Torr. Rate constant measurements at 302 K based on thiol decay agree with those based on O atom decay when thiol was in sufficient excess (100 fold), but were otherwise larger.	EX	304-421	(5.75±0.3)(12)		391±18	2
78 SLA/BAI *) n=6.13±1.04 Discharge flow. Photoionization mass spec. Monitored decay of C <sub>2</sub> H <sub>5</sub> SH in excess O atoms. P=0.719-2.16 Torr. [A, n, and B values were calculated (87 SIN/CVE) from the supplementary data of 78 SLA BAI].	EX	256-496	(3.17±3.84)(9)	*)	-1882±356	2
81 NIP/SIN *) n=4.66±0.31. P=21-50 Torr. Phase shift technique with modulated [O] monitored by O+NO chemiluminescence. O atoms generated by Hg-photosensitized decomposition of N <sub>2</sub> O. 81 NIP/SIN report the rate expression k = (1.37±0.66)(12) + (8.73±4.46)(13)x exp(-(2075±268)/T). [A, n, and B values listed here were calculated (87 SIN/CVE) from the data of 81 NIP/SIN].	EX	300-574	(1.78±0.71)(10)	*)	-1313±122	2
Recommended value of k	RE	298	1.7(12)			2 1.2
Recommended values of Arrhenius parameters	RE	256-574	*)	*)	*)	2 1.4
*) Strongly curved Arrhenius plot: fitted all data to k=A1+A2exp(-B/T) with A1=1.6(12), A2=1.0(14), B=2198. As for O+CH <sub>3</sub> SH, the reported data are in reasonable agreement, although they differ in finer details. A curved Arrhenius plot is reported in 78 SLA/BAI and 81 NIP/SIN, although the value of 78 SLA/BAI is as much as 20% greater than that of 81 NIP/SIN at room temp. However, there was no evidence of an Arrhenius plot curvature in 78 KIR/VET.						
The present recommended Arrhenius parameters, A1, A2 and B, have been obtained by a least squares fit of all data in the data sheet to the composite Arrhenius expression. The data of 81 NIP/SIN lie below the fitted line; for example the fitted k(298) value is 1.70(12), which is about 15% greater than the value 1.47(12) of 81 NIP/SIN.						
Arrhenius plot for O+C <sub>2</sub> H <sub>5</sub> SH+products is shown in Fig. 7.						

References for reaction  $O + C_2H_5SH \rightarrow \text{products}$ 

- 76 SLA/GRA Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reactions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," *Int. J. Chem. Kinet.* **8**, 451 (1976).
- 78 KIR/VET Kirchner, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with  $O(^3P)$  under consideration of the influence of molecular oxygen," *Ber. Bunsenges. Phys. Chem.* **82**, 1223 (1978).
- 78 SLA/BAI Slagle, I.R., Baiocchi, F., and Gutman, D., "Study of the reactions of oxygen atoms with hydrogen sulfide, methanethiol, ethanethiol, and methyl sulfide," *J. Phys. Chem.* **82**, 1333 (1978).
- 81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S., "Gas-Phase Reactions of  $O(^3P)$  Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," *J. Am. Chem. Soc.* **103**, 3530 (1981).
- 81 NIP/SIN Nip, W.S., Singleton, D.L., and Cvetanovic, R.J., "Gas-Phase Reactions of  $O(^3P)$  Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 1. Rate Constants and Arrhenius Parameters," *J. Am. Chem. Soc.* **103**, 3526 (1981).
- 87 SIN/CVE Singleton, D.L., and Cvetanovic, R.J., The present evaluation.

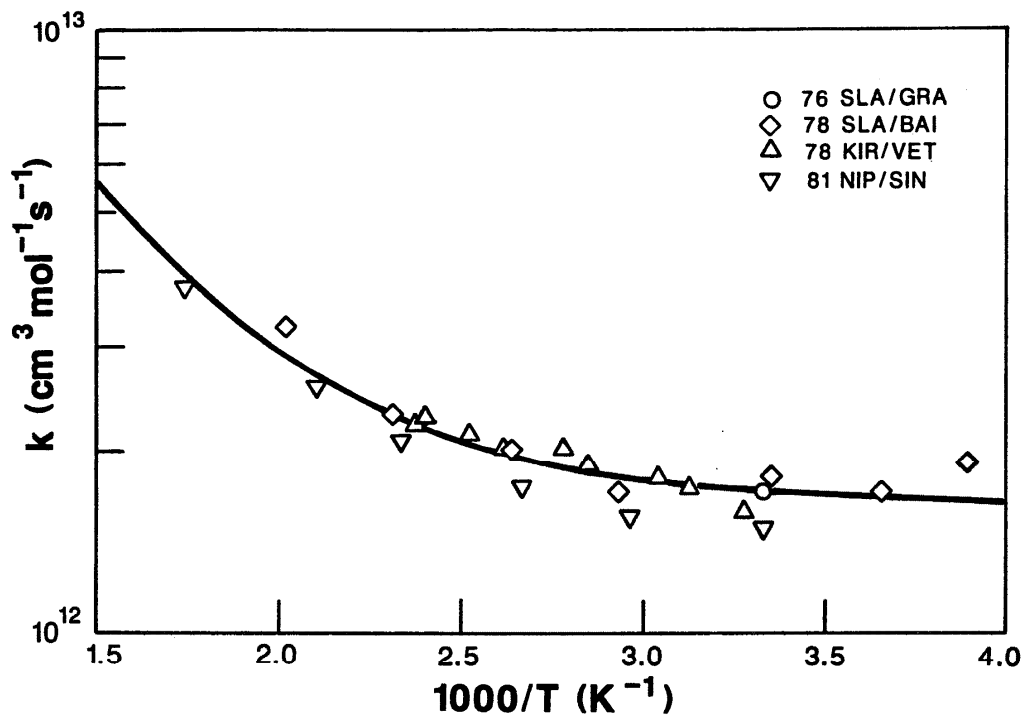


Fig. 7. Arrhenius plot for the reaction  $O + C_2H_5SH \rightarrow \text{products}$ .

The line is calculated using the modified Arrhenius Eqn.  $k = A_1 + A_2 \exp(-B/T)$  and the recommended values:  $A_1 = 1.6(12) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $A_2 = 1.0(14) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $B = 2198 \text{ K}$ .

$O + C_3H_7SH \rightarrow$  products $O + 1$ -Propanethiol

For potential rn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
78 KIR/VET Discharge flow. High resolution mass spec. Monitored decay of thiol in excess O atoms. $P \sim 1$ Torr.	EX	303-421	(8.33 $\pm$ 0.54)(12)		494 $\pm$ 22	2
Recommended value of k	RE	298	1.6(12)			2 1.3
Recommended values of Arrhenius A and B Based on the only data available (78 KIR/VET). Additional determinations would be useful.	RE	303-421	8.3(12)		494 $\pm$ 50	2 1.5

References for reaction  $O + C_3H_7SH \rightarrow$  products

- 76 SLA/GRA Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reactions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," *Int. J. Chem. Kinet.* **8**, 451 (1976).
- 78 KIR/VET Kirchner, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with  $O(^3P)$  under consideration of the influence of molecular oxygen," *Ber. Bunsenges. Phys. Chem.* **82**, 1223 (1978).
- 81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S., "Gas-Phase Reactions of  $O(^3P)$  Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," *J. Am. Chem. Soc.* **103**, 3530 (1981).

 $O + C_4H_9SH \rightarrow$  products $O + 1$ -Butanethiol

For potential rn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
78 KIR/VET Discharge flow. High resolution mass spec. Monitored decay of thiol in excess O atoms. $P \sim 1$ Torr.	EX	306-419	(5.78 $\pm$ 0.33)(12)		321 $\pm$ 19	2
Recommended value of k	RE	298	2.0(12)			2 1.3
Recommended values of Arrhenius A and B Based on the only data available (78 KIR/VET). Additional determinations would be useful.	RE	306-419	5.8(12)		321 $\pm$ 50	2 1.5

References for reaction  $O + C_4H_9SH \rightarrow$  products

- 76 SLA/GRA Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reactions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," *Int. J. Chem. Kinet.* **8**, 451 (1976).
- 78 KIR/VET Kirchner, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with  $O(^3P)$  under consideration of the influence of molecular oxygen," *Ber. Bunsenges. Phys. Chem.* **82**, 1223 (1978).
- 81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S., "Gas-Phase Reactions of  $O(^3P)$  Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," *J. Am. Chem. Soc.* **103**, 3530 (1981).

 $O + C_5H_{11}SH \rightarrow$  products $O + 1$ -Pentanethiol

For potential rxn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
78 KIR/VET Discharge flow. High resolution mass spec. Monitored decay of thiol in excess O atoms. P $\approx$ 1 Torr.	EX	302-409	(6.18 $\pm$ 0.35)(12)		328 $\pm$ 19	2
Recommended value of k	RE	298	2.1(12)			2 1.3
Recommended values of Arrhenius A and B Based on the only data available (78 KIR/VET). Additional determinations would be useful.	RE	302-409	6.2(12)		328 $\pm$ 50	2 1.5

References for reaction  $O + C_5H_{11}SH \rightarrow$  products

- 76 SLA/GRA Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reactions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," *Int. J. Chem. Kinet.* **8**, 451 (1976).
- 78 KIR/VET Kirchner, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with  $O(^3P)$  under consideration of the influence of molecular oxygen," *Ber. Bunsenges. Phys. Chem.* **82**, 1223 (1978).
- 81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S., "Gas-Phase Reactions of  $O(^3P)$  Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," *J. Am. Chem. Soc.* **103**, 3530 (1981).

O + CH<sub>3</sub>SCH<sub>3</sub> → products

O + Methane, thiobis-

Presumably O + CH<sub>3</sub>SCH<sub>3</sub> → CH<sub>3</sub>SO + CH<sub>3</sub>. For potential rn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
74 CAD/WIC Discharge flow. Excess CH <sub>3</sub> SCH <sub>3</sub> . [O] monitored by O+NO chemiluminescence.	EX	300	3.3(11)			2
76 LEE/TIM Flash photolysis. [O] monitored by resonance fluorescence in excess CH <sub>3</sub> SCH <sub>3</sub> . O <sub>2</sub> used as source of O atoms. P=40-100 Torr (Ar).	EX	268-424	(8.56±0.42)(12)		-366±16	2
76 SLA/GRA Discharge flow. Photoionization mass spec. Monitored decay of CH <sub>3</sub> SCH <sub>3</sub> in excess O atoms. P=0.6-1.9 Torr.	EX	300	3.8(13)			2 1.2
78 SLA/BAI Discharge flow. Photoionization mass spec. Monitored decay of CH <sub>3</sub> SCH <sub>3</sub> in excess O atoms. P=0.7-1.2 Torr. [A and B values were calculated (87 SIN/CVE) from the supplementary data of 78 SLA/BAI].	EX	252-493	(1.16±0.08)(13)		-300±22	2
80 LEE/TAN1 Discharge flow. [O] monitored by resonance fluorescence in excess sulfide. P = 1.1-2.8 Torr.	EX	272-472	(7.71±0.72)(12)		-404±30	2
81 NIP/SIN Phase shift technique with modulated [O] monitored by O+NO chemiluminescence. O atoms generated by Hg-photosensitized decomposition of N <sub>2</sub> O. P=22-56 Torr at 297 K.	EX	296-557	(6.69±0.72)(12)		-460±41	2
81 NIP/SIN	RL	300	13.8±0.9			2/2
	RN	300	(3.32±0.25)(13)			2
Reference rn. O + 1-Butene → products						
O formed by Hg-photosensitized decomposition of N <sub>2</sub> O. Monitored the rate of formation of butene oxide and n-butanal as a function of the ratio of reactants. The above RN k value was calculated (81 NIP/SIN) using k <sub>ref</sub> =2.42(12) cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> .						

O + CH<sub>3</sub>SCCH<sub>3</sub> → products -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
84 BAU/COX	SE	298	3.0(13)			2 1.25
	SE	270-560	7.8(12)		-408±100	2

Fitted by least squares the data of 76 LEE/TIM, 80

LEE/TAN, 81 NIP/SIN, and excluded the data of 76

SLA/GRA, 78 SLA/BAI.

Recommended value of k	RE	298	3.1(13)			2 1.2
Recommended values of Arrhenius A and B	RE	252-557	8.2(12)		-397±100	2 1.3

Assigned zero weight to the very low k of 74 CAD/WIC. (If the treatment is restricted to the same data as used in 84 BAU/COX and 74 CAD/WIC is excluded, the values would be only slightly altered: for T=268-557 K k(298)=3.0(13), A=7.4(12), B=-416±100, and k err. factor=1.3).

Arrhenius plots for the reaction O+CH<sub>3</sub>SCCH<sub>3</sub>→products are shown in Fig. 8.References for reaction O + CH<sub>3</sub>SCCH<sub>3</sub> → products

- 74 CAD/WIC Cadle, R.D., Wickman, H.H., Hall, C.B., and Eberle, K.M., "The reaction of atomic oxygen with formaldehyde, crotonaldehyde, and dimethyl sulfide," *Chemosphere* 3, 115 (1974).
- 76 LEE/TIM Lee, J.H., Timmons, R.B., and Stief, L.J., "Absolute rate parameters for the reaction of ground state atomic oxygen with dimethyl sulfide and episulfide," *J. Chem. Phys.* 64, 300 (1976).
- 76 SLA/GRA Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reactions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," *Int. J. Chem. Kinet.* 8, 451 (1976).
- 78 KIR/VET Kirchner, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with O(<sup>3</sup>P) under consideration of the influence of molecular oxygen," *Ber. Bunsenges. Phys. Chem.* 82, 1223 (1978).
- 78 SLA/BAI Slagle, I.R., Baiocchi, F., and Gutman, D., "Study of the reactions of oxygen atoms with hydrogen sulfide, methanethiol, ethanethiol, and methyl sulfide," *J. Phys. Chem.* 82, 1333 (1978).
- 80 LEE/TAN1 Lee, J.H., Tang, I.N., and Klemm, R.B., "Absolute rate constant for the reaction of O(<sup>3</sup>P) with CH<sub>3</sub>SCCH<sub>3</sub> from 272 to 472K," *J. Chem. Phys.* 72, 1793 (1980).
- 81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S., "Gas-Phase Reactions of O(<sup>3</sup>P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," *J. Am. Chem. Soc.* 103, 3530 (1981).
- 81 NIP/SIN Nip, W.S., Singleton, D.L., and Cvetanovic, R.J., "Gas-Phase Reactions of O(<sup>3</sup>P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 1. Rate Constants and Arrhenius Parameters," *J. Am. Chem. Soc.* 103, 3526 (1981).
- 84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," *J. Phys. Chem. Ref. Data* 13, 1259 (1984).
- 87 SIN/CVE Singleton, D.L., and Cvetanovic, R.J., The present evaluation.

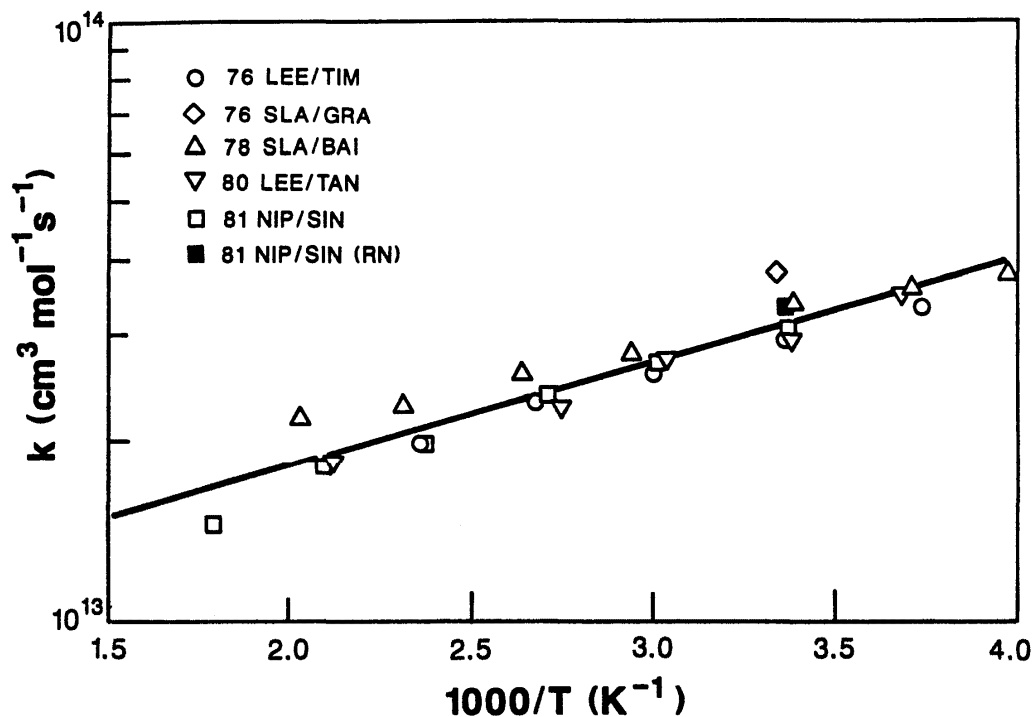


Fig. 8. Arrhenius plots for the reaction  $\text{O} + \text{CH}_3\text{SCH}_3 \rightarrow \text{products}$ .  
The line is calculated using the recommended A and B values.

**$\text{O} + \text{cy-CH}_2\text{SCH}_2 \rightarrow \text{products}$**

**$\text{O} + \text{Ethylene episulfide}$**

The exclusive primary products appear to be  $\text{CH}_2=\text{CH}_2 + \text{SO}$  (76 LEE/TIM, 87 SIN).

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
76 LEE/TIM Flash photolysis. [O] monitored by resonance fluorescence in excess $\text{cy-CH}_2\text{SCH}_2$ . $\text{O}_2$ used as source of O atoms. P=40-100 Torr (Ar).	EX	268-424	(8.07±0.54)(12)		18±20	2
Recommended value of k	RE	298	7.6(12)			2 1.3
Recommended values of Arrhenius A and B	RE	268-424	8.1(12)		18±50	2 1.5
Based on the only data available (76 LEE/TIM). Additional determinations would be useful.						

**References for reaction  $\text{O} + \text{cy-CH}_2\text{SCH}_2 \rightarrow \text{products}$**

- 76 LEE/TIM Lee, J.H., Timmons, R.B., and Stief, L.J., "Absolute rate parameters for the reaction of ground state atomic oxygen with dimethyl sulfide and episulfide," J. Chem. Phys. 64, 300 (1976).
- 87 SIN Singleton, D.L., Unpublished data.



O + cy-CHCHSCHCH → products

O + Thiophene

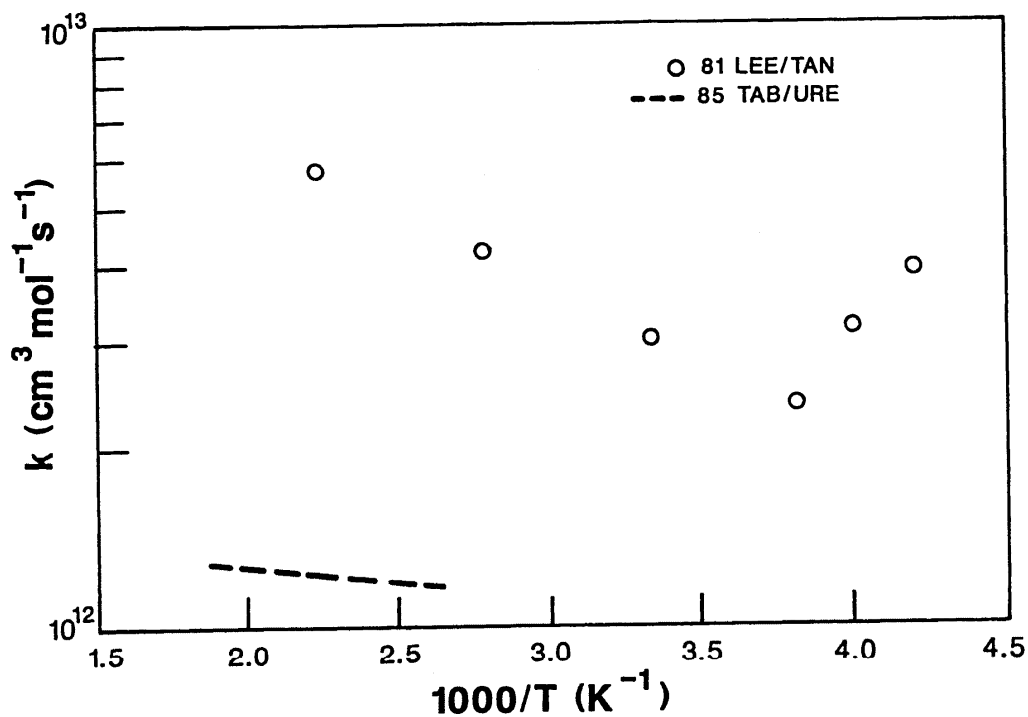
Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A k err. units factor
81 LEE/TAN Discharge flow. O formed by microwave discharge of O <sub>2</sub> in He, followed by resonance fluorescence in excess thiophene. Abrupt change in the sign of the slope of the Arrhenius plot at ~ 260 K suggested to be possibly due to O addition at two different sites in thiophene (C=C and S).	EX	262-448	(2.01±0.20)(13)		569±30	2
85 TAB/URE Discharge flow. O formed by microwave discharge in N <sub>2</sub> O and Ar. The intensity of emission from excited SO <sub>2</sub> was determined at fixed reaction time for various initial excess thiophene concentrations. P < 2 Torr.	EX	379-525	(1.6±0.2)(12)		121	2

Recommendation is not warranted: 81 LEE/TAN's data show a minimum at about 262 K and indicate a substantial positive activation energy at higher T (262-448 K). 85 TAB/URE, who only report data at higher temp. (379-525K), find essentially no temperature dependence, and their values are only 1/4 of the values at 425 K of 81 LEE/TAN. There appears a discrepancy in 85 TAB/URE between the reported Arrhenius expression and the data points plotted in their Figure 4 (the only place where rate constants at specific temperatures are presented). Additional determinations are needed.

Arrhenius plot for O+cy-CHCHSCHCH→products is shown in Fig. 9.

#### References for reaction O + cy-CHCHSCHCH → products

- 81 LEE/TAN Lee, J.H., and Tang, I.N., "Absolute rate constant for the reaction of O(<sup>3</sup>P) with thiophene from 238 to 448K," J. Chem. Phys. 75, 137 (1981).
- 85 TAB/URE Tabares, F.L., and Urena, A.G., "Chemiluminescence and kinetic studies in O(<sup>3</sup>P) + thiophene, pyrrole and furan mixtures," J. Chem. Soc. Faraday Trans. 2 81, 1305 (1985).

Fig. 9. Arrhenius plots for the reaction  $\text{O} + \text{cy-CHCHSCHCH} \rightarrow \text{products}$ .

$\text{O} + \text{CH}_3\text{SSCH}_3 \rightarrow \text{products}$

$\text{O} + \text{Disulfide, dimethyl-}$

For potential reaction channels see 81 CVE/SIN and 83 SIN/IRW.

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	E, B-B(ref)	k, A k err. units factor
80 LEE/TAN2 Discharge flow. [O] monitored by resonance fluorescence in excess sulfide. P=0.52-2.60 Torr.	EX	270-329	(1.28±0.13)(14)	0		2
81 NIP/SIN Phase shift technique with modulated [O] monitored by O+NO chemiluminescence. O atoms formed by Hg-photosensitized decomposition of N <sub>2</sub> O.	EX	298-571	(2.62±0.42)(13)		-251±61	2

O + CH<sub>3</sub>SSCH<sub>3</sub> → products -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A k err. units factor
81 NIP/SIN	RL	300	24.5±1.5			2/2
	RN	300	(5.91±0.37)(13)			2
Reference rn. O + 1-Butene → products O formed by Hg-photosensitized decomposition of N <sub>2</sub> O. Monitored the rate of formation of butene oxide and n-butanal as a function of the ratio of reactants. The above RN k value was calculated (81 NIP/SIN) using $k_{ref}=2.42(12) \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ .						
84 BAU/COX	SE	298	7.8(13)			2 2
	SE	290-570	3.3(13)		-250±100	2
Averaged the room temp. data of 80 LEE/TAN and 81 NIP/SIN, although they differ by a factor of 2. Accepted the B value of 81 NIP/SIN and adjusted A to give the k(298) value.						
Recommended value of k	RE	298	6.0(13)			2 1.2
Recommended values of Arrhenius A and B	RE	298-570	2.6(13)		-250±100	2 1.5
Based on the data of 81 NIP/SIN and assuming linear Arrhenius plot.						
Arrhenius plot for O+CH <sub>3</sub> SSCH <sub>3</sub> →products is shown in Fig. 10.						

References for reaction O + CH<sub>3</sub>SSCH<sub>3</sub> → products

- 80 LEE/TAN2 Lee, J.H., and Tang, I.N., "Absolute rate constant for the reaction of O(<sup>3</sup>P) with CH<sub>3</sub>SSCH<sub>3</sub> from 270 to 329K," J. Chem. Phys. **72**, 5718 (1980).
- 81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S., "Gas-Phase Reactions of O(<sup>3</sup>P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," J. Am. Chem. Soc. **103**, 3530 (1981).
- 81 NIP/SIN Nip, W.S., Singleton, D.L., and Cvetanovic, R.J., "Gas-Phase Reactions of O(<sup>3</sup>P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 1. Rate Constants and Arrhenius Parameters," J. Am. Chem. Soc. **103**, 3526 (1981).
- 83 SIN/IRW Singleton, D.L., Irwin, R.S., and Cvetanovic, R.J., "Mechanism of the reaction of oxygen atoms, O(<sup>3</sup>P) with dimethyl disulfide," Can. J. Chem. **61**, 968 (1983).
- 84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data **13**, 1259 (1984).

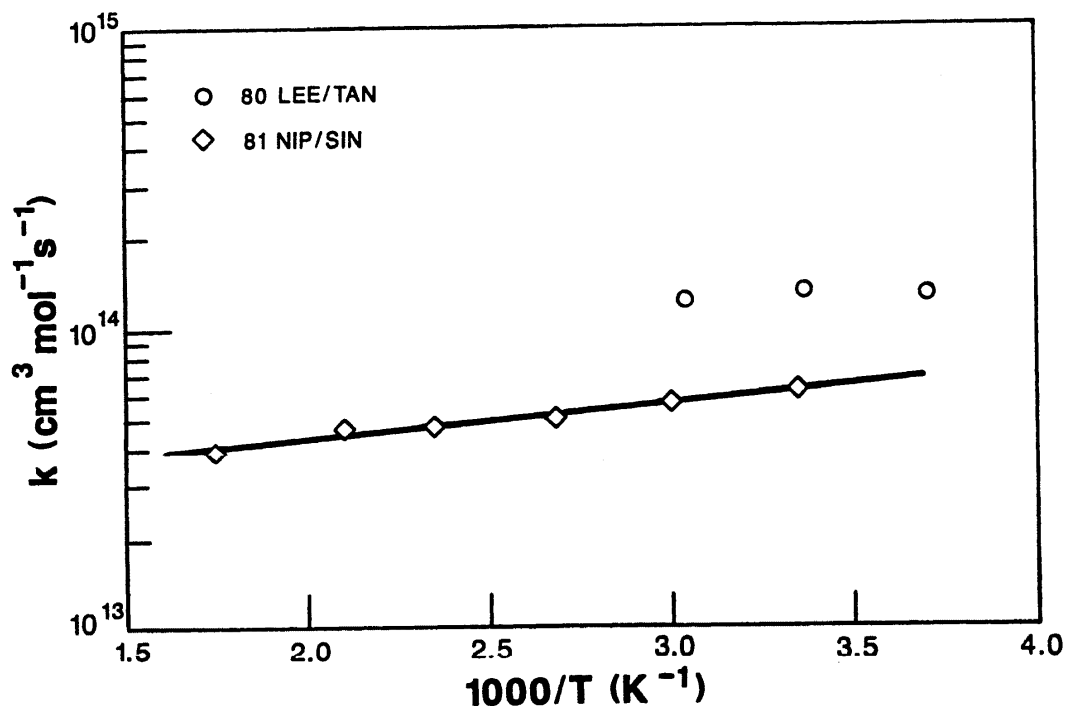


Fig. 10. Arrhenius plot for the  $O+CH_3SSCH_3 \rightarrow \text{products}$  reaction.  
 The line is calculated using the recommended A and B values.

$O + SCF_2 \rightarrow \text{products}$

O + Carbonothioic difluoride

Reference Code, Notes	Data type	T/K	k, k/k(ref). A, A/A(ref)	n	B, B-B(ref)	k.A units	k err. factor
79 SLA/GUT Discharge flow. O formed by microwave discharge of $O_2$ in He. Decay of $SCF_2$ in excess O measured by mass spec. P = 0.7-2.1 Torr at 298 K. Products identified in cross jet reactor indicated only the channel forming SO + $CF_2$ .	EX	259-493	(7.35±1.1)(12)		376±48	2	
Recommended value of k	RE	298	2.1(12)			2	1.5
Recommended values of Arrhenius A and B	RE	259-493	7.4(12)		376±100	2	1.5
Based on the only data available (79 SLA/GUT). Additional determinations would be useful.							

Reference for reaction  $O + SCF_2 \rightarrow$  products

- 79 SLA/GUT Slagle, I.R., and Gutman, D., "Study of the reactions of oxygen atoms with carbonothioicdichloride, carbonothioicdifluoride, and tetrafluoro-1,3-dithietane," Int. J. Chem. Kinet. 11, 453 (1979).

 $O + SCl_2 \rightarrow$  products $O +$  Carbonothioic dichloride

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
79 SLA/GUT Discharge flow. O formed by microwave discharge of $O_2$ in He. Decay of $SCl_2$ in excess O measured by mass spec. P = 0.7-2.1 Torr at 298 K. Products identified in cross jet reactor indicated two channels: $SO+CCl_2$ and $SCCl+ClO$ .	EX	251-493	(1.86±0.33)(13)		-58±53	2	
Recommended value of k	RE	298	2.3(13)			2	1.3
Recommended values of Arrhenius A and B	RE	251-493	1.9(13)		-60±100	2	1.5
Based on the only data available (79 SLA/GUT). Additional determinations would be useful.							

Reference for reaction  $O + SCl_2 \rightarrow$  products

- 79 SLA/GUT Slagle, I.R., and Gutman, D., "Study of the reactions of oxygen atoms with carbonothioicdichloride, carbonothioicdifluoride, and tetrafluoro-1,3-dithietane," Int. J. Chem. Kinet. 11, 453 (1979).

 $O + cy-CF_2SCF_2S \rightarrow$  products $O +$  1,3-dithietane, 2,2,4,4-tetrafluoro-

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
79 SLA/GUT Discharge flow. O formed by microwave discharge of $O_2$ in He. Monitored decay of $cy-CF_2SCF_2S$ in excess O by mass spec. P=0.7-2.1 Torr at 298 K. Products identified in cross jet reactor indicated only the channel forming $SO+CF_2+SCF_2$ .	EX	253-493	(1.42±0.31)(13)		855±64	2	

O + cy-CF<sub>2</sub>SCF<sub>2</sub>S → products -- Continued

Reference Code, Notes	Data type	T/K	k, k/k(ref), A, A/A(ref)	n	B, B-B(ref)	k, A units	k err. factor
Recommended value of k	RE	298	8.1(11)			2	1.3
Recommended values of Arrhenius A and B	RE	253-493	1.4(13)		855±100	2	1.5
Based on the only data available (79 SLA/GUT). Additional determinations would be useful.							

Reference for reaction O + cy-CF<sub>2</sub>SCF<sub>2</sub>S → products

79 SLA/GUT      Slagle, I.R., and Gutman, D., "Study of the reactions of oxygen atoms with carbonothioicdichloride, carbonothioicdifluoride, and tetrafluoro-1,3-dithietane," Int. J. Chem. Kinet. 11, 453 (1979).