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 S₂, SF₆, SF₅, SO, SO₂, SO₃, SH, H₂S, D₂S, H₂SO₃, CS, CS₂, COS, CH₂SH, C₂H₂SH, C₃H₇SH, C₆H₅SH, C₆H₅SH, CH₃SCH₃, cy-CH₃SCH₃, cy-CH₂CH₂SCH₂, CH₃SSCH₃, SCS₂, SCCl₂, and cy-CF₂SCF₂S. With one exception, the liquid phase reaction O(^3P) + H₂SO₃ → 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 hydrocarbons¹. As pointed out there, these evaluations represent a part of a larger effort directed towards the development of a comprehensive general evaluated chemical kinetic database. More specifically, they are a part of the broader database 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 evaluation¹, 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*(P) atoms this may be sometimes spin forbidden and not likely to occur (although it is not spin forbidden for O*(D) atoms reacting with hydrocarbons and occurs readily).

Rapid addition of O*(P) atoms to the CC double bond is the main and perhaps frequently the exclusive initial process in their reactions with alkenes. Similarly, in the O*(P) reactions with a number of sulfur containing compounds rapid addition of O*(P) 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*(P) atoms not electronically excited ("hot"), abstraction cannot compete effectively with the very rapid O*(P) addition to the double bond. However, at sufficiently high temperature, or with sufficiently "hot" O*(P) atoms, abstraction of H atoms may be expected to become more important.

Kinetic behavior of methyl sulfide and dimethyl disulfide of alkenes in their reactions with O*(P) 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*(P) with methyl sulfide and dimethyl disulfide is O*(P) 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 H₂S. 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 of such mechanistic ambiguity is the reaction O + H₂S → 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 has been also in the earlier evaluation of the related series of O*(P) reactions with unsaturated hydrocarbons. 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, 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 of the from 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. As was done previously, 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 lognormally distributed). The uncertainties assigned to the Arrhenius B, expressed as additive (±) deviations, are also approximate estimates.

The evaluation covers the investigated (and documented in the literature) O*(P) 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 location of the detailed tabulations of the kinetic data for the listed reactions. Section 4 contains the data sheets for O(3P) 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(3P) 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^3 mol^-1 s^-1 and cm^6 mol^-2 s^-1, respectively. The values are given in exponential form, written as (1.00±0.10)x10^11, which signifies 1.00±0.10x10^11.

Columns 4 ("n") and 5 ("B") contain, if applicable, the n and B parameters in the extended Arrhenius Eq. k = A(T/298)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/3600(ref), A, A/3600(ref)") is k (or k/3600(ref)) at that temperature; if it contains a temperature range, e.g., 200–500, the value in Column 4 is the Arrhenius 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)exp(-B/T).

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


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),
KL (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.),
SF (selected in the literature as probable "best"
value),
RE (currently recommended value).

Unit Codes for $k$, $k/k$(ref), $A$, $A/A$(ref):
1 (s$^{-1}$)
2 (cm$^3$ mol$^{-1}$ s$^{-1}$)
3 (cm$^6$ mol$^{-2}$ s$^{-1}$)
1/1, 2/2 etc. (dimensionless)
2/1 (cm$^3$ mol$^{-1}$), etc.

Type of excitation:
(EXV) (vibrationally excited)
(EXT) (translationally excited)
(EXE) (electronically excited)
(EXEV) (electronically and vibrationally excited), etc.

Units for $B$, $B-B$(ref): kelvins (K). (Arrhenius
parameter $E=R\times B$).

$T/298$ and $n$ (the exponent of $T$) are dimensionless.

Decadic exponent notation:
1.2(11) (stands for $1.2\times10^{11}$)

Temperature ($T$): in kelvins (K).

$k$ (ref), $A$ (ref) and $B$(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 nec-
eressarily lognormally distributed.

Arrhenius parameters are defined by

$$k=A(T/298)^n\exp(-B/T)$$
### CHEMICAL KINETIC DATA FOR REACTIONS OF OXYGEN WITH SULFUR COMPOUNDS

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T/K</th>
<th>( k_A ) cm(^3)mol(^{-1})s(^{-1})</th>
<th>( n )</th>
<th>B</th>
<th>( k ) err. factor</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O + S_2 \rightarrow \text{products} )</td>
<td>409</td>
<td>7(12)</td>
<td>1.2</td>
<td></td>
<td></td>
<td>1384</td>
</tr>
<tr>
<td>( O + \text{Sulfur dimer} )</td>
<td>288</td>
<td>1(13)</td>
<td>4</td>
<td></td>
<td></td>
<td>1384</td>
</tr>
<tr>
<td>(Tentative suggestion for 288K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( O + SF_2 \rightarrow \text{products} )</td>
<td>298</td>
<td>6.5(13)</td>
<td>1.3</td>
<td></td>
<td></td>
<td>1385</td>
</tr>
<tr>
<td>( O + \text{Sulfur fluoride (SF}_2\text{)} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( O + SF_3 \rightarrow \text{products} )</td>
<td>298</td>
<td>1.2(13)</td>
<td>1.3</td>
<td></td>
<td></td>
<td>1385</td>
</tr>
<tr>
<td>( O + \text{Sulfur fluoride (SF}_3\text{)} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( O + SO \rightarrow \text{products} )</td>
<td>298</td>
<td>4.8(13)</td>
<td>2</td>
<td></td>
<td></td>
<td>1386</td>
</tr>
<tr>
<td>( O + \text{Sulfur fluoride oxide} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( O + SO_2 \rightarrow \text{products} )</td>
<td>298</td>
<td>9.3(11)</td>
<td>1.3</td>
<td></td>
<td></td>
<td>1386</td>
</tr>
<tr>
<td>( O + \text{Sulfur oxide (SO}_2\text{)} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( O + SO + M \rightarrow \text{SO}_2 + M ) ((k=))</td>
<td>298</td>
<td>3.2(13)</td>
<td>1.5</td>
<td></td>
<td></td>
<td>1387</td>
</tr>
<tr>
<td>( O + \text{Sulfur monoxide (M=Ar)} )</td>
<td>298</td>
<td>1.85(17) cm(^6)mol(^{-2})s(^{-1})</td>
<td>1.2</td>
<td></td>
<td></td>
<td>1387</td>
</tr>
<tr>
<td>( k ) relative to ( k(M=Ar) ) at 298K:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Ar=1.0, Ne=0.88, Kr=1.18, He=1.25, )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Xe=1.28, N_2=1.51, CF_4=7.84, )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( CO_2=8.22, CH_4=8.65, SF_6=92, )</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>( C_3F_8=12.2, B_2=13.7, D_2=13.7. )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( O + SO \rightarrow \text{SO}_2 + \hbar )</td>
<td>298</td>
<td>2(8)</td>
<td>3</td>
<td></td>
<td></td>
<td>1389</td>
</tr>
<tr>
<td>( O + \text{Sulfur monoxide} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( O + SO_2 + M \rightarrow \text{SO}_2 + M )((M=Ar))</td>
<td>299</td>
<td>3.7(14) cm(^6)mol(^{-2})s(^{-1})</td>
<td>1.3</td>
<td></td>
<td></td>
<td>1390</td>
</tr>
<tr>
<td>( O + \text{Sulfur dioxide} )</td>
<td>((M=Ar))</td>
<td>1.1(16) cm(^6)mol(^{-2})s(^{-1})</td>
<td>1.5</td>
<td>1010±200</td>
<td></td>
<td>1390</td>
</tr>
<tr>
<td>((M=Ar))</td>
<td>1700-2500</td>
<td>1.08(13) cm(^6)mol(^{-2})s(^{-1})</td>
<td></td>
<td>-7870</td>
<td>2</td>
<td>1390</td>
</tr>
<tr>
<td>((M=Ne))</td>
<td>298</td>
<td>4.0(10) cm(^6)mol(^{-2})s(^{-1})</td>
<td></td>
<td>1400±200</td>
<td>1.5</td>
<td>1390</td>
</tr>
</tbody>
</table>

\( k \) relative to \( k(M=Ar) \) at 298K:

\( Ar=1.0, Ne=0.9, \) \( N_2=1.3, O_2=1.3, \)

\( N_2=3, SO_2=10, \) within about 30%, within about 30%,

for \( SO_2 \) up to a factor of 3.

\( O + SO_2 \rightarrow SO + O_2 \)

\( O + \text{Sulfur dioxide} \)

\( O + \text{Sulfur trioxide} \)

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T/K</th>
<th>(k A) cm(^3) mol(^{-1}) s(^{-1})</th>
<th>n</th>
<th>S</th>
<th>k err. factor</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O + SO_3 + M \rightarrow SO_2 + O_2 + M)</td>
<td>298</td>
<td>1.4(14)</td>
<td>3</td>
<td>1400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O + S + H \rightarrow H + SO)</td>
<td>1401</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(O + S + H \rightarrow OH + S)</td>
<td>1401</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(O + SO_2 \rightarrow \text{products})</td>
<td>288</td>
<td>1.0(10)</td>
<td>1.0</td>
<td>1401</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O + \text{Hydrogen sulfide})</td>
<td>1406</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>(O + \text{Deuterium sulfide})</td>
<td>2144±200</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O + \text{Hydrogen sulfide})</td>
<td>1406</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(O + \text{Hydrogen sulfide})</td>
<td>0.2</td>
<td>1.1</td>
<td>1406</td>
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<td></td>
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</tr>
<tr>
<td>(O + H_2SO_4 \rightarrow \text{products})</td>
<td>298</td>
<td>0</td>
<td>1407</td>
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<td></td>
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<tr>
<td>(O + \text{Sulfuric acid})</td>
<td>1408</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(O + \text{Carbon monosulfide})</td>
<td>156-305</td>
<td>1.5(14)</td>
<td>751±100</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O + \text{Carbon disulfide})</td>
<td>218-920</td>
<td>3.55(13)</td>
<td>821±100</td>
<td>1.5</td>
<td></td>
<td></td>
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<tr>
<td>(O + \text{Carbon disulfide})</td>
<td>298</td>
<td>2.1(11)</td>
<td>1.3</td>
<td>1415</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O + \text{Carbon disulfide})</td>
<td>298</td>
<td>2.2(12)</td>
<td>701±100</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O + \text{Carbon disulfide})</td>
<td>298</td>
<td>1.4(-21)</td>
<td>1.2</td>
<td>1416</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O + \text{Carbon disulfide})</td>
<td>298</td>
<td>3.5(10)</td>
<td>1.3</td>
<td>1417</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O + \text{Carbon oxide sulfide})</td>
<td>239-523</td>
<td>1.6(13)</td>
<td>2257±200</td>
<td>1.3</td>
<td></td>
<td></td>
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<tr>
<td>(O + \text{Carbon oxide sulfide})</td>
<td>239-1900</td>
<td>4.7(13)</td>
<td>2821±200</td>
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<tr>
<td>(O + \text{Carbon oxide sulfide})</td>
<td>1200</td>
<td>5(11)</td>
<td>3</td>
<td>1422</td>
<td></td>
<td></td>
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<tr>
<td>(O + \text{Carbon oxide sulfide})</td>
<td>1200-1900</td>
<td>5(13)</td>
<td>5530±1000</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>T/K</td>
<td>k.A (cm³mol⁻¹s⁻¹)</td>
<td>n</td>
<td>B</td>
<td>k err. factor</td>
<td>Page</td>
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<td>----------</td>
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<td>------</td>
</tr>
<tr>
<td>O + CH₃SH → products</td>
<td>288</td>
<td>1.21(12)</td>
<td>1.2</td>
<td>1422</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + Methanethiol</td>
<td>252-661 *)</td>
<td>*)</td>
<td>*)</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*) Strongly curved Arrhenius plot: k=A1+A2exp(-B/T) with A1=0.0(11), A2=1.0(13), B=1261.</td>
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</tr>
<tr>
<td>O + C₂H₅SH → products</td>
<td>298</td>
<td>1.71(12)</td>
<td>1.2</td>
<td>1424</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + Ethanol</td>
<td>256-574 *)</td>
<td>*)</td>
<td>*)</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*) Strongly curved Arrhenius plot: k=A1+A2exp(-B/T) with A1=1.6(12), A2=1.0(14), B=2198.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + C₃H₇SH → products</td>
<td>298</td>
<td>1.61(12)</td>
<td>1.3</td>
<td>1427</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + 1-Propanethiol</td>
<td>303-421</td>
<td>8.3(12)</td>
<td>494±50</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + C₄H₉SH → products</td>
<td>298</td>
<td>2.0(12)</td>
<td>1.3</td>
<td>1427</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + 1-Butanethiol</td>
<td>306-419</td>
<td>5.8(12)</td>
<td>321±50</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + C₅H₁₁SH → products</td>
<td>298</td>
<td>2.1(12)</td>
<td>1.3</td>
<td>1428</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + 1-Pentanethiol</td>
<td>302-409</td>
<td>6.2(12)</td>
<td>328±50</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + CH₃SCH₃ → products</td>
<td>298</td>
<td>3.1(13)</td>
<td>1.2</td>
<td>1429</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + Methane, thiobis-</td>
<td>252-557</td>
<td>8.2(12)</td>
<td>-397±100</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + cy-CH₂SCH₂ → products</td>
<td>298</td>
<td>7.6(12)</td>
<td>1.3</td>
<td>1431</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + Ethylenes episulfide</td>
<td>268-624</td>
<td>8.1(12)</td>
<td>18±50</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + cy-C6H₅SCH₂ → products</td>
<td>1432</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + CH₃SSCH₃ → products</td>
<td>298</td>
<td>6.0(13)</td>
<td>1.2</td>
<td>1433</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + Butylsulfide, dimethyl-</td>
<td>298-570</td>
<td>2.6(13)</td>
<td>-250±100</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + SCF₂ → products</td>
<td>298</td>
<td>2.1(12)</td>
<td>1.5</td>
<td>1435</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + Carbomethoxylic dihydroxide</td>
<td>298-445</td>
<td>7.4(12)</td>
<td>376±100</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + SOCl₂ → products</td>
<td>298</td>
<td>2.3(13)</td>
<td>1.3</td>
<td>1436</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + Carbomethoxylic dichloride</td>
<td>298-445</td>
<td>1.9(13)</td>
<td>-62±100</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + cy-C₆H₅SCF₂S → products</td>
<td>298</td>
<td>8.1(11)</td>
<td>1.3</td>
<td>1437</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + 1,3-dithiobenzene, 2,2,4,4-tetrafluoro-</td>
<td>233-493</td>
<td>1.4(13)</td>
<td>855±100</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4. Reaction Data Sheets

O + S₂ → products
O + Sulfur dimer

The assumed reaction product is SO₂ (88 EOM/KRO, 87 HIL/CIC).

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>k,k/(k(ref), A, A/A(ref))</th>
<th>n</th>
<th>B, k,A k err.</th>
<th>B-B(ref)</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>88 EOM/KRO</td>
<td>EX 1050</td>
<td>4(12)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge flow, O formed by microwave discharge in N₂/Ar, followed by NH₂+O₂H₂. SO formation monitored by mass spec. Excess [S₂] over [O]. P=2 Torr. Uncertainty is an order of magnitude.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>73 SCH</td>
<td>SE 1050</td>
<td>4(12)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Only one reported value (88 EOM/KRO).</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>87 HIL/CIC</td>
<td>EX 409</td>
<td>(6.62±0.78)(12)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge flow. Decay of S₂ in excess O monitored by mass spec. O formed by microwave discharge in O₂. For absolute k measurement, [O] was determined by titration with excess NO₂. For relative rate measurement, O + NO₂ was used as the reference reac. (taking k₁/₈=5.6(12) from 83 EOM/HAR). Decay of NO₂ was measured in excess O. P = 0.89-1.60 Torr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RN 409</td>
<td>(7.17±1.02)(12)</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Recommended value of k

<table>
<thead>
<tr>
<th>Data Type</th>
<th>k,A k err.</th>
<th>B-B(ref)</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE 409</td>
<td>7(12)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Suggested tentative value of k at 298 K

<table>
<thead>
<tr>
<th>Data Type</th>
<th>k,A k err.</th>
<th>B-B(ref)</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE 298</td>
<td>1(13)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Recommended value of k, and potential estimates of 88 EOM/KRO. More determinations are needed.

References for reaction O + S₂ → products


### CHEMICAL KINETIC DATA FOR REACTIONS OF OXYGEN WITH SULFUR COMPOUNDS

#### O + SF$_{2}$ → products

**O + Sulfur fluoride (SF$_{2}$)**

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data T/K type</th>
<th>$k,k/k$(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, B-S(ref) units factor</th>
<th>k,A k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>86 PLU/RYA</td>
<td>EX 295</td>
<td>(6.5±1.2)(13)</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

**Recommended value of k**

| RE 298 | 6.5(13) | 2 | 1.3 |

Based on the only data available (86 PLU/RYA). Additional determinations would be useful.

---

#### Reference for reaction O + SF$_{2}$ → products


---

### O + SF$_{5}$ → products

**O + Sulfur fluoride (SF$_{5}$)**

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data T/K type</th>
<th>$k,k/k$(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, B-S(ref) units factor</th>
<th>k,A k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>86 PLU/RYA</td>
<td>EX 295</td>
<td>(1.2±0.3)(13)</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

**Recommended value of k**

| RE 298 | 1.2(13) | 2 | 1.3 |

Based on the only data available (86 PLU/RYA). Additional determinations would be useful.

---

#### Reference for reaction O + SF$_{5}$ → products

D. L. Singleton and R. J. Cveticanovic

O + SOF \rightarrow products

O + Sulfur fluoride oxide

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data</th>
<th>k/kk(ref), n</th>
<th>B, kA k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>86 PLU/KYA</td>
<td>EX 295</td>
<td>((4.8 \pm 1.2)(13))</td>
<td>2</td>
</tr>
</tbody>
</table>

Discharge flow-mass spec. Analysis of the formation and decay of SOF in the rm. O+SF\(_2\), O and SF\(_2\) formed by microwave discharge in O\(_2\)/He and in SF\(_6\)/He.

Recommended value of k

Based on the only data available (86 PLU/KYA). Additional determinations would be useful.

Reference for reaction O + SOF \rightarrow products


O + S\(_2\)O \rightarrow products

O + Sulfur oxide (S\(_2\)O)

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data</th>
<th>k/kk(ref), n</th>
<th>B, kA k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>74 STE/ALV</td>
<td>RL 298</td>
<td>0.17 \pm 0.02</td>
<td>2/2</td>
</tr>
<tr>
<td></td>
<td>RN 298</td>
<td>((9.3 \pm 1.2)(11))</td>
<td>2</td>
</tr>
</tbody>
</table>

Reference rm. is O\(^{16}\)NO\(_2\)-NO+O\(_2\). Discharge flow. O formed by microwave discharge of O\(_2\)/Ar or by H\(^{16}\)NO. The RL value obtained by comparing the O\(^{16}\)SO and O\(^{16}\)NO chemiluminescences for different flow rates of S\(_2\)O and NO\(_2\). [RN value has been updated using k\(^{ref}=3.0(12)\) (83 DEM/Year)]. S\(_2\)O observed as a product.

Recommended value of k

Based on the only data available (74 STE/ALV). Additional determinations would be useful.

References for reaction O + S\(_2\)O \rightarrow products

### Chemical Kinetic Data for Reactions of Oxygen with Sulfur Compounds

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


\[
O + SO + M \rightarrow SO_2 + M
\]

**O + Sulfur monoxide**

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>$T/K$</th>
<th>$k, k/k(\text{ref})$, units</th>
<th>$n$</th>
<th>$B$, $B-B(\text{ref})$, units</th>
</tr>
</thead>
<tbody>
<tr>
<td>66 HAL/THR</td>
<td>EX</td>
<td>300</td>
<td>(3.2±0.4)(17)</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

Discharge flow. $O$ and $SO$ formed by microwave discharge in $SO_2$/Ar. [O] and [SO] monitored by $O+NO$ and $O+SO$ chemiluminescences.

| 67 SHA/PAD             | EN *)       | 8.0(16) |                               | 3  |                               |

*) Room T. $M$=Ar. $P$=0.8 Torr. Obtained SO in the rm. $O+COS$. Rate of light emission measured relative to the reaction $O+NO$+$NO_2$+$hv$. The second order rate constant was derived using $k(O+NO$+$NO_2$+$hv)$, $k(O+COS+COS+SO)$, and relative emission intensities of the $O+NO$+$NO_2$+$hv$ and $O+SO$+$SO_2$+$hv$ rms. The listed termolecular $k$ was obtained by dividing the second order constant by $F$. (See also 67 SHA/PAD in the next data sheet).

| 70 TAK                 | EX          | 293  | 5.8(16)                      | 3  |                               |

$M$=Ar. $P(Ar)$=4.2 Torr.

Discharge flow. $O$ formed by microwave discharge of $H_2O$/Ar. [O] monitored by chemiluminescence $E_r(OM$, $O+NO$ and $O+NO$ rms). SO formed by reaction of excess $O$ with $H_2S$, and its decay monitored by chemiluminescence from $O+SO$ reaction.

| 71 MIV/TAK             | EX *)       | 7.3(16) |                               | 3  |                               |

*) Room temperature. $M$=Ar. $P$=3.8 Torr. Discharge flow. $O$ formed by microwave discharge of $H_2O$/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].

| 73 SCH                 | SE          | 300  | 3.2(17)                      | 3  |                               |

Based on only one measurement (66 HAL/THR).
D. L. SINGLETON AND R. J. CVETANOVIĆ

O + SO + M → SO2 + M -- Continued

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k(k(ref.), A/A(ref))</th>
<th>n</th>
<th>B</th>
<th>k, A k err. units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>76 BAU/DRY</td>
<td>SE</td>
<td>298</td>
<td>(6.7±2.0)(18)</td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>M=Ar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>78 HAM/UK</td>
<td>SE</td>
<td>298</td>
<td>6.7(18)</td>
<td></td>
<td></td>
<td>3 1.3</td>
</tr>
<tr>
<td>M=Ar. Accepted...</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85 CUB/HEL</td>
<td>EX</td>
<td>300</td>
<td>1.85(17)</td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>(M=Ar P=0.2-200 bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(M=N2 P=0.2-200 bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(M=C3F8 P=0.2-3 bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(M=CF3 H=0.2-25 bar)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(M=Kr P=0.5-5 bar)</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(M=Ar H=0.5-5 bar)</td>
<td>LA</td>
<td>300</td>
<td>4.20(17)</td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>(M=N2 P=0.5-5 bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(M=Ar P=0.5-5 bar)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(M=CO2 P=0.2-3 bar)</td>
<td>EA</td>
<td>300</td>
<td>1.24(18)</td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>(M=CF4 P=0.5-5 bar)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(M=SOF2 P=0.2-3 bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k0, high P limit)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

O and SO formed by laser photolysis of SO2 at 180nm. k values obtained from 2nd order plots of uv absorption, used to monitor SO2 reforma-
tion. Pressure of third body ranged from 0.2 to 200 bar. k0 (high pressure limit) is based on data for M=Ar, N2, and C3F8. Used broadening
factors (F0) of 0.55, 0.58 and 0.76 to fit the data for N2, Ar and C3F8, respectively.

Recommended value of k0 (high P limit) | RE | 298 | 3.2(13) |

Recommended value of k(M=Ar) | NS | 298 | 1.05(17) |

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, N2=1.51, CF4=7.84, CO2=8.22, CH4=8.65, SF6=9.62, C3F8=12.2, H2=2.0=13.7

The recommended values are based on the extensive data of 05 CUB/HEL. (The average of the listed k(M=Ar) values, excluding the value of 67 SHE/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 → SO2 + M

65 HAL/THR


67 SHE/PAD

CHEMICAL KINETIC DATA FOR REACTIONS OF OXYGEN WITH SULFUR COMPOUNDS

References for reaction O + SO + M -> SO2 + M -- Continued


O + SO + M -> SO2 + hν
O + Sulfur monoxide

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data type</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, B-B(ref)</th>
<th>k,A k err. units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>65 ROL/REE *) Room temperature. P &lt; 0.02 Torr. Rate constant for light emission. Discharge flow. Excess O, formed by discharge in O2. SO obtained from OH+O2. Reaction determined relative to light emission from OH+NO.</td>
<td>RN *</td>
<td>4.2(8)</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>78 HAL/THN Reaction constant for light emission. Discharge flow. Excess O, formed by discharge in O2/Ar. SO obtained from OH+O2. Reaction determined relative to light emission from OH+NO. Intensity was independent of Ar pressure, at P=0.2-1.6 Torr.</td>
<td>RN 298</td>
<td>1.5(8)</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>87 SHA/PAD *) Room T. Discharge flow in O2 or O2/Ar. OH+O2 gives SO, measured light emission at 0.8 Torr relative to OH+NO2+hv. Listed k derived using k(OH+O2+hv), k(OH+O2+CO+SO), and relative emission intensities of various O2+SO2+hv and OH+O2+SO2 +hv 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).</td>
<td>RN *</td>
<td>3.4(8)</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

O + SO → SO₂ + hv — Continued

<table>
<thead>
<tr>
<th>Data</th>
<th>T/K</th>
<th>k,k/k(ref), n</th>
<th>B, k,A k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>type</td>
<td>A/A(A(ref)</td>
<td>B-B(ref) units factor</td>
<td></td>
</tr>
</tbody>
</table>

68 FLE/LEV

Shock tube study of SO₂/Ar mixtures. Calibrated the optical system with tungsten and hydrogen lamps. [O] and [SO] calculated assuming equilibrium for the species SO₂, Ar, O, O₂, and SO₃. Adopting k=1.5(5) at 286 K (66 MAL/THR), the authors calculate A=1.5(8), n=1.0, B=0. Total P = 0.5 atm.

Recommended value of k

Additional experimental work is desirable.

References for reaction O + SO → SO₂ + hv


O + SO₂ + M → SO₃ + M

O + Sulfur dioxide

<table>
<thead>
<tr>
<th>Data</th>
<th>T/K</th>
<th>k,k/k(ref), n</th>
<th>B, k,A k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>type</td>
<td>A/A(A(ref)</td>
<td>B-B(ref) units factor</td>
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58 KAU EX *) 3(18) 3

*) Room temperature. M=O₂.

Discharge flow. O formed by microwave discharge in O₂. Decay of O in excess SO₂ determined from intensity of the O₃NO chemiluminescence. Detailed experimental conditions not reported.
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<tr>
<td>65 LEV/MEK</td>
<td>DE 300-1300 (2.2-22)(15)</td>
<td>3019</td>
<td>3</td>
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<tr>
<td>Microprobe study of ( \text{H}_2\text{S}/\text{O}_2/\text{N}_2 ) or of ( \text{H}_2\text{S}/\text{O}_2/\text{Ar} ) flames. Mass spec. analyses for ( \text{O}_2, \text{H}_2\text{S}, \text{H}_2\text{O}, \text{H}_2 ), and ( \text{SO}_2 ); wet analyses for ( \text{SO} + \text{SO}_2 ) and ( \text{SO}_3 ). Calculated equilibrium concentrations of atoms and radicals. ( k )'s derived from observed ( [\text{SO}_2] ) and ( [\text{SO}_3] ) profiles. The value for ( B ) is assumed.</td>
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<td>65 WEB/WAL</td>
<td>RN 784</td>
<td>1.1(18)</td>
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<tr>
<td>( \text{N}=\text{H}_2+\text{O}_2 ). ( P=27.9 ) Torr. Reference run. ( \text{O}+\text{H}_2\rightarrow\text{OH}+\text{H} ) (used ( k=2.0(10) )). Determined second explosion limits for ( \text{H}_2/\text{O}_2 ) mixtures with and without ( \text{SO}_2 ).</td>
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<tr>
<td>66 CAD/FOW</td>
<td>EX 300</td>
<td>4.7(15)</td>
<td>3</td>
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<tr>
<td>( \text{M}+\text{N}_2 ). Discharge flow. ( \text{O} ) from microwave discharge in ( \text{O}_2 ) or in ( \text{N}_2 ) followed by ( \text{N}+\text{NO} \rightarrow \text{O}+\text{N}_2 ). ( k ) determined from initial decrease in [( \text{O} )] (measured by ( \text{O}+\text{NO} ) chemiluminescence) and [( \text{SO}_2 )] decrease (measured by gas chromatography). Activation energy reported as near 0. ( \text{N}_2 ) and ( \text{O}_2 ) are equally efficient as third bodies.</td>
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<td>66 HAL/THB</td>
<td>EX 293</td>
<td>(4.7±0.8)(15)</td>
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<tr>
<td>( \text{M}+\text{Ar} ). Discharge flow. ( \text{O} ) formed by microwave discharge in ( \text{O}_2/\text{Ar} ) mixture. Monitored ( \text{O} ) in excess ( \text{SO}_2 ) by ( \text{O}+\text{NO} ) chemiluminescence. The efficiency of ( \text{Ar} ) relative to ( \text{O}_2 ) is 1.0±0.2. Pressure range was not reported.</td>
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<td>66 JAF/KLE</td>
<td>DE 297</td>
<td>1.4(18)</td>
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<td>( \text{M} = \text{SO}_2 ). Photoysis of ( \text{NO}_2 ) in presence of ( \text{SO}_2 ). ( k ) derived from quantum yield of ( \text{NO}_2 ) consumption. ( _{18}\text{O} _{16} \text{O} ) isotope exchange, and rate constant for the ( \text{O}+\text{NO}_2 ) run. The ( k ) value is for ( P=2 ) Torr.</td>
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<tr>
<td>67 MUL/STE</td>
<td>EX 289</td>
<td>(1.6±0.4)(18)</td>
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<tr>
<td>( \text{M}+\text{SO}_2 \ P=0.7-3 ) Torr</td>
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<tr>
<td>( \text{M}+\text{Ar} \ P=\ldots ) Torr</td>
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<tr>
<td>( \text{M}+\text{O}_2 \ P=0.7-3 ) Torr</td>
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<td>Stirred flow - ESR detection of ( \text{O} ). Excess ( \text{SO}_2 ). Allowance was made for influence of ( \text{SO}_2 ) on the wall recombination of ( \text{O} ) atoms (see 69 MUL/STE).</td>
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<td>69 MUL/STE</td>
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<td>300</td>
<td>(1.1e0, 3)(15)</td>
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<td>Supersedes 67 MUL/STE for M=Ar. P( Ar)=2-6 Torr. Stirred flow. O formed by microwave discharge in O₂ in excess Ar and monitored by O+NO chemiluminescence and ESR. Allowance made for influence of SO₃ on the wall recombination of O.</td>
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<td>69 NET/STI</td>
<td>DE</td>
<td>2150</td>
<td>2(15)</td>
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<td>M=H₂. Sampled with an alumina tube the flames composed of either CH₄ or CO with O₂, SO₂, and H₂. Determined CO, CO₂, O₂, SO₃, and SO₂. Rate constant is based on the SO₃ production, the calculated equilibrium concentrations of O, and the value k=1(12) for O+SO₃ → SO₂+O₂ m. The authors suggest that the value of k is a lower limit.</td>
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<tr>
<td>71 BEI/MDO</td>
<td>RL</td>
<td>*)</td>
<td>3.6(6)</td>
<td></td>
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<td>*) Room temperature. M=H₂O. O formed by Hg-photosensitized decomposition of H₂O in the presence of COS. SO₂ produced in secondary reactions. Rate constant determined relative to O+COS, based on yields of N₂ and CO. The authors indicate a large experimental uncertainty.</td>
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<td>71 TIM/LEF</td>
<td>EX</td>
<td>298</td>
<td>4.10(18)</td>
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<td>(M=SO₂)</td>
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<tr>
<td>(M=Ar)</td>
<td>EX</td>
<td>298</td>
<td>1.0(15)</td>
<td></td>
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<tr>
<td>(M=He)</td>
<td>EX</td>
<td>298</td>
<td>8(14)</td>
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<td>Discharge flow DMR detection of O. Excess SO₂. Allowance is made for the third body effect of SO₂. An Arrhenius plot is given for M=SO₂ at 308K→-309K (-values of A and B are not quoted).</td>
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<tr>
<td>73 SCH</td>
<td>SE</td>
<td>250-1000</td>
<td>3.6(14)</td>
<td>-503</td>
<td>3</td>
<td></td>
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<tr>
<td>M=Ar. Estimated a factor of 5 error at 500 K, greater at other temperatures. Third body efficiencies taken to be about the same for Ar, O₂, N₂, He, and from 6 to 40 times greater for SO₂, NO₂, N₂O.</td>
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<td>k error</td>
<td>B-B/(ref)</td>
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<tr>
<td>74 ATK/PIT</td>
<td>EX</td>
<td>299-392 3.32(16)</td>
<td>1006±200</td>
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<td>N₂O₂. P(N₂O₂)=54-135 Torr.</td>
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<td></td>
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<td>Phase shift technique. 0 atoms generated by the</td>
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<td>N₂ photolysed decomposition of N₂O. O monitored by the O+NO chemiluminescence. An upper</td>
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<tr>
<td></td>
<td></td>
<td>limit of k(SO₃)/k(N₂O₂) = 5 assessed for SO₂ and</td>
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<tr>
<td></td>
<td></td>
<td>N₂O as third bodies (see also 74 ATK/PIT).</td>
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<tr>
<td>74 DAV</td>
<td>EX</td>
<td>220-353 1.2(16)</td>
<td>1120</td>
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<tr>
<td>N₂</td>
<td></td>
<td>Flash photolysis-resonance fluorescence.</td>
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<tr>
<td>Relative third body efficiencies N₂:He:Ar:SO₂=1.0:0.45:0.87:50. Few details. Reference to unpublished data of D.D. Davis, R. Schiff, and S. Fischer.</td>
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<td>75 WES/DEH2</td>
<td>EX</td>
<td>248-415 (3.9±0.9)(16)</td>
<td>1400±50</td>
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<tr>
<td>(N²He P=0.7-6.7 Torr)</td>
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<tr>
<td>(N²H₂ P=0.7-6.7 Torr)</td>
<td>EX</td>
<td>297 (7.2±0.3)(14)</td>
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<tr>
<td>(N²SO₂ kₚ/kₚ(k(N²He))</td>
<td>RL</td>
<td>297 9.5±2.7</td>
<td>3/3</td>
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<td>Discharge flow-ESR detection of O. Excess SO₂. Allowance is made for third body effect of SO₂.</td>
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<tr>
<td>76 BAU/DRY</td>
<td>SE</td>
<td>*</td>
<td>3</td>
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<tr>
<td>*) No new recommendation. Suggest using Davis's data (see entry for 74 DAV).</td>
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<tr>
<td>78 ATK/PIT</td>
<td>EX</td>
<td>299-440 1.12(16)</td>
<td>1008±151</td>
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<tr>
<td>N²Ar. P(Ar)=25-50 Torr. Flash photolysis - NO₂ chemiluminescence. O formed by photolyzing SO₂ and NO. [O] was followed by the O+NO chemiluminescence. The effect of SO₂ as third body was taken into account. Relative k values for different Ar at 300 K are Ar:N₂:N₂O:SO₂ = 1.0:1.3:9.0:0.0.</td>
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<td>78 RAM/GAR</td>
<td>SE</td>
<td>220-353 1.2(16)</td>
<td>1130</td>
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<tr>
<td>N²/N²He. Relative k values for different N²Ar:</td>
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<td>N₂:He:Ar:SO₂=1.0:0.45:0.87:58.</td>
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<tr>
<td>78 TRO</td>
<td>DE</td>
<td>250-2500 4.9(16)</td>
<td>-4</td>
<td>2846</td>
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<tr>
<td>M²Ar. Derived by fitting a modified Arrhenius expression to the experimental data of 75 WES/</td>
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<tr>
<td>DEH and 70 AST/GLA.</td>
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\[
O + \text{SO}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M}
\]

--- Continued

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<td>79 AST/GLA</td>
<td>EX</td>
<td>1700-2500</td>
<td>1.08(13)</td>
<td>-7870</td>
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<td>(\text{M=Ar} ) Shock wave decomposition of (\text{SO}_3). Monitor(\text{ed SO}_2) formed by uv absorption. Calculated (k) for the reverse (\text{rn. (O+SO}_2+\text{M=SO}_3+\text{M)}) using the equilibrium constant.</td>
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<td>80 BAU/COX</td>
<td>SE</td>
<td>200-2500</td>
<td>2.8(19)</td>
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<td>*) (\text{M=Ar} ) Estimated error factor: 3 for 200-500K, 2 for 300K.</td>
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<td>4.9(14)</td>
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<tr>
<td>(\text{M=H}_2) and (\text{M=O}_2)</td>
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<td>1.5(16)</td>
<td>1009</td>
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<td>The third body efficiencies of (\text{H}_2) and (\text{O}_2) are assumed equal.</td>
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<td>84 BAU/COX</td>
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<td>5.1(14)</td>
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<tr>
<td>(\text{M=H}_2) and (\text{M=O}_2)</td>
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<tr>
<td>(\text{M=H}_2) and (\text{M=O}_2)</td>
<td>SE 200-400</td>
<td>1.5(16)</td>
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<td>Recommended value of (k) for (\text{M=Ar})</td>
<td>RE 298</td>
<td>3.7(14)</td>
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<td>Recommended values of Arrhenius A and B for (\text{M=Ar})</td>
<td>RE 298-440</td>
<td>1.1(16)</td>
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<td>Recommended values of Arrhenius A and B for (\text{M=Ar})</td>
<td>RE 1700-2500</td>
<td>1.06(13)</td>
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<td>Recommended value of (k) for (\text{M=He})</td>
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<td>1.3</td>
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<tr>
<td>Recommended values of Arrhenius A and B for (\text{M=He})</td>
<td>RE 248-415</td>
<td>4.0(16)</td>
<td>1400x200</td>
<td>3</td>
<td>1.5</td>
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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 \(\text{Ar:He:H}_2:O_2:N_2:O:SO}_2\) = 1.0:0.81:3:1.3:13:10, within about 30% and, for \(\text{SO}_2\), up to a factor of 3.

Arrhenius plots for \(\text{O+SO}_2+\text{M=products}\) are shown in Fig. 1 (1a for \(\text{M=He}\) and 1b for \(\text{M=Ar}\) at 298-440K).

References for reaction \(O + \text{SO}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M}\)


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


74 ATK/FIT Atkinson, R., and Pitts, J.N., Jr., "Rate constants for the reaction of \( O^{(3P)} \) atoms with \( SO_2 \) (\( M=H_2O \)) over the temperature range 299-392K," Chem. Phys. Lett. 29, 26 (1974).


Fig. 1. Arrhenius plots for $O+SO_2 \rightarrow NO+O_2$ (a) and $N+Ar$ at 298-440 K (b).

The lines are calculated using the recommended A and B values.

$$O + SO_2 \rightarrow NO + O_2$$

$O +$ Sulfur dioxide

<table>
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<tr>
<th>Reference Code, Notes</th>
<th>Data T/K</th>
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<th>B, k err.</th>
<th>k, A, k err.</th>
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<tr>
<td>73 WAG</td>
<td>DE 5(12)</td>
<td>9813</td>
<td>2</td>
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<td>Derived from the rate parameters ($A=1.3(12)$, $B=3986$) for the reverse reaction and the equilibrium constant.</td>
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<td>76 BAU/DRY</td>
<td>SE 440-2100</td>
<td>6.80(12)</td>
<td>-0.511</td>
<td>9980</td>
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<tr>
<td>Based on the recommended rate constant expression for the reverse reaction (76 BAU/DRY) and the equilibrium constant expression of 73 SCH.</td>
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<tr>
<td>78 BAM/GAR</td>
<td>SE 440-2100</td>
<td>7.3(12)</td>
<td>-0.5</td>
<td>9980 2.0</td>
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<td>Accepted recommendation of 76 BAU/DRY.</td>
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### Chemical Kinetic Data for Reactions of Oxygen with Sulfur Compounds

(i) \( \text{SO}_2 \rightarrow \text{SO} + \text{O}_2 \) -- Continued

<table>
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<th>Reference Code, Notes</th>
<th>Data T/K</th>
<th>( k,k/(\text{ref}) ), ( A,A/(\text{ref}) )</th>
<th>n</th>
<th>( B ), ( k,A ) k err.</th>
<th>B-B(\text{ref})</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 SLA/GRI</td>
<td>EX 3320-3760</td>
<td>(3.8±0.5)(11)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reflected shock waves in mixture of \( \text{SO}_2/\text{H}_2\text{O}/\text{Ar} \).
P=2-5 atm. Monitored decay of \( \text{SO}_2 \) by IR emission at 7.347 microns. \([\text{O}]\), used to calculate \( k \) values, computed from a model of 8 reactions.

Recommended values of Arrhenius A and B

| RE | 440-3000 | 5(12) | 9800 | 2 | 3 |

Based on the indirectly derived parameters of 73 WAG and 76 BAI/DRY. Additional experimental work is needed.

---

### References for reaction \( \text{O} + \text{SO}_3 \rightarrow \text{SO} + \text{O}_2 \)

73 WAG  

76 BAI/DRY  

78 HAM/GAR  

80 SLA/GRI  
Slack, M., and Grillo, A., "Rate coefficient measurements for \( \text{SO}_2 + \text{O} = \text{SO} + \text{O}_2 \)," J. Chem. Phys. 73, 987 (1980).

---

### \( \text{O} + \text{SO}_3 \rightarrow \) products

#### \( \text{O} + \text{Sulfur trioxide} \)

The product is always assumed to be \( \text{SO}_2+\text{O}_2 \). (See 75 WES/DEH1 for suggestion that \( \text{nn} \) is third order, i.e. \( \text{O}+\text{SO}_3+\text{H} \rightarrow \text{SO}_2+\text{O}_2+\text{H} \)).

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data T/K</th>
<th>( k,k/(\text{ref}) ), ( A,A/(\text{ref}) )</th>
<th>n</th>
<th>( B ), ( k,A ) k err.</th>
<th>B-B(\text{ref})</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>58 KAU</td>
<td>EX 300</td>
<td>( 3500 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Discharge flow. \( \text{O} \) formed by microwave discharge in \( \text{O}_2 \) and monitored by \( \text{O}+\text{NO} \) chemiluminescence. No reaction was detectable between \( \text{O} \) and \( \text{SO}_3 \) in the gas phase, and the estimate of \( B \) is a lower limit. \( \text{SO}_2 \) was observed to change the rate of recombination of \( \text{O} \) on the reactor walls.

---

D. L. SINGLETION AND R. J. CVETANOVIĆ

0 + SO₃ → products — Continued

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data type</th>
<th>Z/k</th>
<th>k, k(ref), A, A/Å(ref)</th>
<th>n</th>
<th>B</th>
<th>k, A</th>
<th>k err. B-B(ref) units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>62 NEU/LIN</td>
<td>RL 961</td>
<td>0.16</td>
<td>2/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reference ran. O+SO₃→SO₃ (assumed to be binocular). Thermal decomposition of H₂O mixed with SO₂ and either Ar, He, or CO₂. [SO₂] determined by uv absorption. Monitored total pressure (up to about 500 Torr).

| 65 FEN/JON            | RL 1600   | 5(-5) | 2/2                    |   |   |     |                           |


| 71 MER/LEV            | RN 1240   | 2.9(14)  | 2/2                    |   |   |     |                           |

Microprobe sampling of COS/O₂/N₂ flames. Monitored (SO₃) by wet analyses; other stable species by mass spect. Reference ran. is O+SO₂/H→SO₃/H (A=2.4(17)cm³mole⁻²s⁻¹, B=1258 K).

| 71 MER/LEV            | RN 1450   | 5405  | 2/2                    |   |   |     |                           |

Microprobe sampling of H₂S/O₂/N₂ 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 SO₃ by reaction with H.

| 72 JAC/WIN            | EX 300    | 1.3(8)  | 2/2                    |   |   |     |                           |

Discharge flow. O formed by microwave discharge in N₂ followed by N₂+N=O+N=O→N₂. Reaction is "cold" quenched. k is based on SO₂ yield and measured [0] and [SO₃]. P=2 Torr. (A is recalculated).

| 73 SCH                | CE 1480   | 2.0(14)  | 2/2                    |   |   |     |                           |

Evaluation was based on only one set of data, 71 MER/LEV, which was considered questionable.

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 ran. O+SO₂/H). Also, their second order k(298) at 2 Torr is several thousand times larger than that of 72 JAC/WIN. Furthermore, 74 WES/DEH1 find that B=785, while 72 JAC/WIN find that B=500. 76 BAE/DRE found also that no recommendation was possible. Further study is needed.
References for reaction O + SO₃ → products


\[
O + SO₃ + M → SO₂ + O₂ + M
\]

**DISULFUR TRIOXIDE**

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>(k/k_{\text{ref}}), n,n/n_{\text{ref}}</th>
<th>n</th>
<th>B, (k_{\text{err}})</th>
<th>k, A, k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 WES/DEH1</td>
<td>EX</td>
<td>298-507</td>
<td>5.0(10)</td>
<td>-785</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EX</td>
<td>206</td>
<td>1.0(10)</td>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RL</td>
<td>298</td>
<td>&lt;10</td>
<td></td>
<td>3/3</td>
<td></td>
</tr>
</tbody>
</table>

Discharge flow reactor with ESR detection of O.

Recommendation: For reasons given for the previous rm. (O+SO₃-products) no recommendation is warranted. Additional experimental data are required.

Reference for reaction O + SO₃ + M → SO₂ + O₂ + M

D. L. Singleton and R. J. Cvetanović

$O + SH \rightarrow H + SO$

$O + Merzanto$

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data type</th>
<th>T/K</th>
<th>$k_A/k_B$</th>
<th>$B_A/B_B$</th>
<th>$B$</th>
<th>$k_A$</th>
<th>$k_B$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>69 FAI/THR</td>
<td>RL</td>
<td>298</td>
<td>12</td>
<td>2/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>RN</td>
<td>298</td>
<td>1.8(14)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reference: H + SH $\rightarrow$ H$_2$ + S. $P = 0.9$ Torr.
Discharge flow. H + H$_2$S in presence of O$_2$.
O formed by the secondary reaction S+O$_2$ $\rightarrow$ SO+O.
Rate constant is based on the (O) and (SO) determined from CHNO and O+SO chemiluminescences.
To calculate RN used $k_{ref} = 1.5(13)$ (76 BAU/DRY).

73 SCH

Only one reported value (private communication, published subsequently in 73 CUP/GLA).

75 CUP/GLA

<table>
<thead>
<tr>
<th>Data type</th>
<th>T/K</th>
<th>$k_A/k_B$</th>
<th>$B_A/B_B$</th>
<th>$B$</th>
<th>$k_A$</th>
<th>$k_B$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>RL</td>
<td>285</td>
<td>6.5±0.7</td>
<td>2/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RN</td>
<td>285</td>
<td>(9.0±3)(15)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reference: H + SH $\rightarrow$ products.
Discharge flow. ESR detection of H, O and OH.
Based on an assumed mechanism, the ratio [H]/[O] was identified with $k_3$.$k_{3H}$/$k(3H+SH)$. In separate experiments found $k_{ref} = (1.5±0.5)(13)$.

85 DEM/MAR

Accepted RN (the Normalized $k$) of 75 CUP/GLA.

Recommended value of $k$

<table>
<thead>
<tr>
<th>Data type</th>
<th>T/K</th>
<th>$k_A/k_B$</th>
<th>$B_A/B_B$</th>
<th>$B$</th>
<th>$k_A$</th>
<th>$k_B$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE</td>
<td>288</td>
<td>9.6(13)</td>
<td>2</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Obtained as the average of the RN (the Normalized $k$) values of FAI/THR and 75 CUP/GLA.

References for reaction $O + SH \rightarrow H + SO$


### Reference Code, Notes

<table>
<thead>
<tr>
<th>Data T/K type</th>
<th>k,k/ka(ref), units factor</th>
<th>n</th>
<th>B, units factor</th>
<th>k,A k err. units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O + SH → OH + S</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>68 MAY/SCH</td>
<td>TH 298-2500 1.0(13)</td>
<td>0.67</td>
<td>956</td>
<td>2</td>
</tr>
<tr>
<td>Used Bond Energy-Bond Order (BEBO) technique.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>73 SCH</td>
<td>SE 298-2500 1.0(13)</td>
<td>0.67</td>
<td>956</td>
<td>2</td>
</tr>
<tr>
<td>Based on the theoretical estimate of Mayer and Schieler (see 68 MAY/SCH, the preceding entry).</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 O + SH → OH + S


### O + H₂S → products

**O + Hydrogen sulfide**

The reaction product usually assumed is OH+SH. Two alternative products (SO+H₂ and HSO+H) are discussed further below (see the data sheets for rns. O+H₂S=SO+H₂ and O+H₂S=HSO+H).

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data T/K type</th>
<th>k,k/ka(ref), units factor</th>
<th>n</th>
<th>B, units factor</th>
<th>k,A k err. units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>65 LEV/MER</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EX 1260</td>
<td>2.3(14)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EX 1350</td>
<td>1.3(15)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Homogeneous analysis of H₂S/0₂/H₂ or O₂ H₂S/0₂/Ar flames. Used mass spec. to analyze for O₂, H₂S, H₂O, H₂, and SO₂, and wet analysis for SO + SO₂ and CO₂. Rate constants calculated from rates of H₂S consumption.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

66 LIU/DON |

*) Room temperature. P=0.38-0.53 Torr. |
Discharge flow. Mass spec. detection of O, H₂S, and products. k calculated from the loss of H₂S and the chain length of 5±1.5 for loss of H₂S.
<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>n</th>
<th>B</th>
<th>k, A</th>
<th>k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>67 MER/LEV</td>
<td>EX 1055</td>
<td>2.8(13)</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Microprobe sampling of H₂S/O₂/N₂ flames using mass spec. Rate constant calculated from rates of formation of H₂S, H₂O and N₂, and the calculated equilibrium O concentration. P=76 Torr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 CUP/GLA</td>
<td>DE 295</td>
<td>8.25(9)</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>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 rm. mechanism to the experimental data. Revised k to 8.09(9) in 75 CUP/GLA.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 BOI/KUR</td>
<td>EX 205-300</td>
<td>(1.74±0.40)(11)</td>
<td>755±50</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Discharge flow. Monitored O atoms by ESR. Allowance was made for the assumed stoichiometry d(O)/d(H₂S)=3.5±0.5. P=1.38-2.25 Torr at 300 K.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 TAK</td>
<td>EX 293</td>
<td>2.12(10)</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Discharge flow. Monitored the afterflow of SO, SO₂, and O₂. Evaluated k from consumption of H₂S, correcting for stoichiometry (d(O)/d(H₂S) = 1.2) and the chain decomposition of H₂S.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>73 SCK</td>
<td>SE 200-350</td>
<td>3.8(11)</td>
<td>82±1±25</td>
<td></td>
<td>2 &lt;2</td>
</tr>
<tr>
<td>75 CUP/GLA</td>
<td>DE 285</td>
<td>9.09(9)</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Revised k of 70 CUP/GLA.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>78 WHY/TIM</td>
<td>EX 283-495</td>
<td>(4.36±0.64)(12)</td>
<td>166±50</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>78 SAG/BAI</td>
<td>SE 800</td>
<td>4.00(12)</td>
<td>1000</td>
<td></td>
<td>1.83</td>
</tr>
<tr>
<td>P=0.7-2.1 Torr at 400 K. Discharge flow. The ionization mass spec. Decay of H₂S monitored in excess O atoms. A and B (not reported by the authors) were calculated (87 SAG/BAI) from the 19 k values listed in the supplementary material of 78 SAG/BAI.</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
CHEMICAL KINETIC DATA FOR REACTIONS OF OXYGEN WITH SULFUR COMPOUNDS

0 + \text{H}_2\text{S} \rightarrow \text{products} \quad \text{Continued}

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k/(ref), A,A/(ref)</th>
<th>n</th>
<th>B</th>
<th>k,A</th>
<th>k err.</th>
<th>B-B/(ref)</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>79 SIN/IRW</td>
<td>EX</td>
<td>297-502</td>
<td>(1.56±0.83)(13)</td>
<td>2171±202</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase shift technique, with modulated [O] measured by O/HO chemiluminescence. O generated by Hg-photosensitized decomposition of HgO.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>84 BAU/COX</td>
<td>SE</td>
<td>298</td>
<td>1.3(10)</td>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SE 290-500</td>
<td></td>
<td>8.4(12)</td>
<td></td>
<td>1920±750</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For discussion see 82 BAU/COX.</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85 DEM/MAR</td>
<td>SE</td>
<td>298</td>
<td>1.3(10)</td>
<td>2</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SE 6.0(12)</td>
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<td></td>
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<td>1810±550</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selection based on 79 SIN/IRW and 76 WHY/TIM.</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
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</table>

Recommended value of k

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k/(ref), A,A/(ref)</th>
<th>n</th>
<th>B</th>
<th>k,A</th>
<th>k err.</th>
<th>B-B/(ref)</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>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&lt;T&lt;500K, but those of 79 SIN/IRW are lower at lower T. Higher T data (&gt;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.</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Arrhenius plots for the reaction O+H,S products are shown in Fig. 2.

References for reaction O + H,S \rightarrow products

Fig. 2. Arrhenius plots for the reaction $\text{OH}_2\text{S}$-products. The line is calculated using the recommended $A$ and $B$ values.
### O + D₂S → OD + SD

#### O + Deuterium sulfide

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k(k(ref), A,A(A(ref))</th>
<th>n</th>
<th>B</th>
<th>k,A k err. B=B(ref) units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>76 WHY/TIM</td>
<td>EX</td>
<td>298-450</td>
<td>(6.3±0.3)(12)</td>
<td>2144±156</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

**Recommended value of k**

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k(k(ref), A,A(A(ref))</th>
<th>n</th>
<th>B</th>
<th>k,A k err. B=B(ref) units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>76 WHY/TIM</td>
<td>RE</td>
<td>298</td>
<td>4.7(9)</td>
<td>2</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td><strong>Recommended values of Arrhenius A and B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RE 298-450</td>
<td>6.3(12)</td>
<td>2144±200</td>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Based on the only data available (76 WHY/TIM). Additional determinations would be useful.

### Reference for reaction O + D₂S → OD + SD


### O + H₂S → SO + H₂

#### U + HYDROGEN SULFIDE

A higher temperature channel in the rm. OHS⁻S-products. See also the rm. OHS⁻HS⁺H⁺.

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k(k(ref), A,A(A(ref))</th>
<th>n</th>
<th>B</th>
<th>k,A k err. B=B(ref) units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>07 DMA/DAC</td>
<td>NL</td>
<td>2250-2430</td>
<td>*)</td>
<td>9960</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

*) Reference rm. OHS⁻S-products. Arrh. A not given. Shock tube-Absorption spec. H₂S/O₂/Ar mixtures. This channel is proposed to account for increased SO² at high T. Based on the difference in the induction times of OH and SO² at low and high T, a value of E=E_ref - 0 kcal/mole (B=4026 K) is proposed.

81 FRE/LEE

Reflected shock waves, measurement of induction time modeling of 57 reactions. Identical k values are derived for another rm. channel (see 81 FRE/LEE in the following rm.).

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.
D. L. Singleton AND R. J. Cvetanović

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


$\text{O + H}_2\text{S} \rightarrow \text{SO + H}_2$

O + Hydrogen sulfide

A potential minor channel in the r.n. O$^+$H$_2$S$^-$products. See also the r.n. O$^+$H$_2$S$^-$SO+H$_2$.

A channel in the r.n. O$^+$H$_2$O products due to attack on O rather than on H. Quantitative determination of the "branching ratio" for O addition to S as opposed to H abstraction is difficult (79 SIN/IRB; 82 SIN/PAR) because rates of some potentially involved elementary reactions are not known.

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, B-B(ref)</th>
<th>k, A</th>
<th>k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>79 SIN/IRB</td>
<td>RL *)</td>
<td>&lt;0.11</td>
<td>2/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>*) Room temperature. O generated by Hg-photo-sensitized decomposition of H$_2$O. Reference r.n. O$^+$H$_2$S$^-$products. Relative k based on collection of noncondensible gases formed (H$_2$ and H$_2$O) and their GC analysis. The upper limit may be as high as 0.2 (82 SIN/PAR).</td>
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</tr>
<tr>
<td>81 FRE/LEE</td>
<td>DK 1250-2000 1.0(13)</td>
<td>5032</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reflected shock waves, measurement of induction time modeling of 57 reactions. Identical k values are derived for another r.n. channel (see 81 FRE/LEE in the preceding r.n.).</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>81 CLE/DAV</td>
<td>FX 1683$\pm$240</td>
<td>2</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Crossed molecular beam method, with angular resolved mass spec. Reaction cross section for HSO formation as function of translational energy of the reactants. Value given for B is the threshold translational energy, not the Arrhenius activation energy. (See 82 DAV/CLE).</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>82 DAV/CLE</td>
<td>EX 1683$\pm$240</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>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).</td>
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</tbody>
</table>

CHEMICAL KINETIC DATA FOR REACTIONS OF OXYGEN WITH SULFUR COMPOUNDS

+ H₂S → HSO + H -- Continued

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k/κ(ref), A,k/A(ref)</th>
<th>n</th>
<th>B,</th>
<th>k,A</th>
<th>k err.</th>
<th>B-S(ref)</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>82 SIN/PAR</td>
<td>RL 298</td>
<td>&lt;0.2</td>
<td></td>
<td></td>
<td></td>
<td>2/2</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

An upper-limit value for the branching ratio k/k(O+H₂S=products).

Recommended branching ratio k/k(O+H₂S=products) RE 298 <0.2 2/2 1.1

Based on the upper-limit value of 82 SIN/PAR.

References for reaction O + H₂S → HSO + H

79 SIN/IIBW

81 CLE/DAV

81 FEE/LEE

82 DAV/CLE

82 SIN/PAR

+ H₂SO₄ → products
+ Sulfuric acid

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k/κ(ref), A,k/A(ref)</th>
<th>n</th>
<th>B,</th>
<th>k,A</th>
<th>k err.</th>
<th>B-S(ref)</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 BAL/GOL</td>
<td>EX *)</td>
<td>#)</td>
<td></td>
<td></td>
<td></td>
<td>2/2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*) Room temperature, H₂SO₄ liquid.
#) Reaction probability per collision < 1.0(-6).

Discharge flow with Knudsen cell reactor. Mass spec. detection of O. No measurable reaction, no detectable products.

Recommended value of k RE 288 #) 2/2

#) Reaction probability per collision < 1.0(-6).

Based on the only data available (80 BAL/GOL). Additional experimental work is desirable.
Reference for reaction \( O + \text{H}_2\text{SO}_4 \rightarrow \text{products} \)


\( O + \text{CS} \rightarrow \text{products} \)

\( O + \text{Carbon monosulfide} \)
The main and probably exclusive reaction channel is \( O + \text{CS} \rightarrow \text{CO} + S \).

| Reference Code, Notes | Data T/K | k/k(k(ref)), n B, k, A k err. B=B(ref) units factor |
|-----------------------|----------|-------------------------------------------------|-------------------------------------------------|
|                       | type     | A/A(A(ref))                                    |                                                 |
| 68 BDM/KRO            | ES 1100  | -1(14)                                          | 2                                               |
| An order of magnitude estimate of \( k \) quoted in the Abstract of the paper. |
| 71 BAN/SMI            | RL 298   | 2.3                                             | 2/2                                             |
| BN 298                | 1.3(13)                                         | 2                                               |
| Reference run \( \text{OHNO}_2 + \text{NO} + \text{O}_2 \). Measured the effect of \( \text{NO}_2 \) on the vibrational emission intensities of \( \text{CO} \). [BN value has been updated using \( k_{\text{ref}} = 5.6(12) \) (85 DEM/MAR)]. |
| 73 SCH                | SE 298   | 8.4(12)                                         | 2                                               |
| Based on the data (without a recommendation) of 71 BAN/SMI. |
| 75 SLA/GRA            | EX 305   | (1.24±0.08)(13)                                 | 2                                               |
| Discharge flow. \( \text{CS} \) formed by a dc discharge in \( \text{CS}_2 \), and \( \text{O} \) by microwave discharge in \( \text{O}_2 \) (or in \( \text{N}_2 \) followed by \( \text{NO} \) run). Decay of \( \text{CS} \) in excess \( \text{O} \) followed by photoionization mass spec. |
| 76 BAU/DRY            | SE       | *)                                               | 2                                               |
| *) No new recommendation. Suggest using Hancock and Smith's data (see 71 BAN/SMI). |
| 76 BID/BRE            | EX 300   | (1.35±0.22)(13)                                 | 2                                               |
| Flow tube technique. \( \text{CS} \), produced by microwave discharge in a dilute \( \text{CS}_2/\text{Ar} \) stream, monitored by multipath uv absorption. Small \( \text{O} \) (<< \( \text{CS} \)) is maintained by rapid regeneration in the run. \( \text{S} + \text{O}_2 \rightarrow \text{O} + \text{SO} \). (See also 78 XOL). |
### Chemical Kinetic Data for Reactions of Oxygen with Sulfur Compounds

#### O + CS → products -- Continued

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, B±B(ref)</th>
<th>k, A, k err.</th>
<th>Units Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>77 LIL/RIC</td>
<td>EX</td>
<td>150-300</td>
<td>(1.6±0.2)(14)</td>
<td></td>
<td>758±144</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EX</td>
<td>288</td>
<td>1.26(13)</td>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

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 (CS₂), and O by a microwave discharge (NO or O₂). [k(298K) calculated from the Arrhenius eqn.].

78 BAI/VAK

Accepted recommendation of 76 BAI/DRY.

79 TAL/BUT

Flow tube technique. CS, produced by microwave discharge in a dilute CS₂/Ar stream, monitored by multipath uv absorption. Small [O] (~ CS) is maintained by rapid regeneration in the rm. S + O₂ → O + SO. (See also 76 BID/BRE).

84 BAI/COX

Diffusion cloud ("diffusion flame") technique. O atoms formed by N/NO rm. CS consumption monitored by mass spec. P(Re)=20 Torr.

For discussion see 80 BAI/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) | 2 | 1.5 |

Based on the least squares fit of all the data in 150-305K 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**  

- **71 HAN/SMI**  

- **73 SCH**  

- **75 SLA/GRA**  

---

References for reaction O + CS → products -- Continued

76 BAU/DRY

76 BID/NE

77 LIL/RIC

78 RAS/GAR

78 KOL

77 TAL/BUT

80 BAU/COX

84 BAU/COX

85 DEM/MAR

Fig. 3. Arrhenius plots for the reaction OCS → products.
The line is calculated using the recommended A and B values.
CHEMICAL KINETIC DATA FOR REACTIONS OF OXYGEN WITH SULFUR COMPOUNDS

O + CS₂ → products
O + Carbon disulfide

The main rm. product is CS+SO. For minor channels see rns. O+CS₂→COS+S and O+CS₂→CO+S₂.

| Reference Code, Notes | Data type | T/K | k,k(ref), A, A(ref) | n | B, k.A k err. B-B(ref) units factor |
|-----------------------|-----------|-----|---------------------|---|------------------|------------------|
| 67 CAL/SMI            | EX        | 305-410 | (6.3±1.3)(12)                           | 302±151 | 2 |

Flash photolysis-kinetic spectroscopy. O formed by photolysis of NO₂. The product CS monitored by uv spec. [The same values and some relative determinations reported also in 68 SMI].

| Reference Code, Notes | Data type | T/K | k,k(ref), A, A(ref) | n | B, k.A k err. B-B(ref) units factor |
|-----------------------|-----------|-----|---------------------|---|------------------|------------------|
| 87 SMI                | EX        | 305-410 | (6.3±1.3)(12)                           | 302±151 | 2 |

Flash photolysis-kinetic spectroscopy. O formed by photolysis of NO₂. The reaction product CS monitored and SO detected by uv spec. 8% and 10% or rm. exotermicity goes into vibrational excitation of CS and SO, respectively. [See also 67 CAL/SMI and 68 SMI].

| Reference Code, Notes | Data type | T/K | k,k(ref), A, A(ref) | n | B, k.A k err. B-B(ref) units factor |
|-----------------------|-----------|-----|---------------------|---|------------------|------------------|
| 68 EDE/KRO            | EX        | 300-920 | 5(13)                           | 956 | 2 |

Discharge flow. Excess O formed by a microwave discharge in O₂ or in N₂ (followed by N+NO rm.). Decay of CS₂ and formation of SO followed by mass spec. P=3-6 Torr.

| Reference Code, Notes | Data type | T/K | k,k(ref), A, A(ref) | n | B, k.A k err. B-B(ref) units factor |
|-----------------------|-----------|-----|---------------------|---|------------------|------------------|
| 68 SMI                | EX        | 305-410 | (6.3±1.3)(12)                           | 302±151 | 2 |

Flash photolysis-kinetic spectroscopy. O formed by photolysis of NO₂. The product CS monitored by uv spec. [See also 67 SMI and 67 CAL/SMI].

(Ref. rm. O + isobutene) RL 298 0.32±0.03 2/2
(Ref. rm. O + isobutene) RL 410 0.40±0.05 2/2
(Ref. rm. O + 1-butene) RL 298 1.3±0.1 2/2
(Ref. rm. O + 1-butene) RL 410 1.2±0.1 2/2
(Ref. rm. O + NO₂) RL 298 0.71±0.2 2/2
(Ref. rm. O + NO₂) RL 410 0.65±0.2 2/2
(Ref. rm. O + isobutene) RN 298 3.25(12) 2
(Ref. rm. O + 1-butene) RN 500 0.85(12) 2
(Ref. rm. O + NO₂) RN 298 4.0(12) 2

Flash photolysis-kinetic spectroscopy. O formed by photolysis of NO₂. The product CS monitored by uv spec. [See also 67 SMI and 67 CAL/SMI].

(Ref. rm. O + isobutene) RL 298 0.32±0.03 2/2
(Ref. rm. O + isobutene) RL 410 0.40±0.05 2/2
(Ref. rm. O + 1-butene) RL 298 1.3±0.1 2/2
(Ref. rm. O + 1-butene) RL 410 1.2±0.1 2/2
(Ref. rm. O + NO₂) RL 298 0.71±0.2 2/2
(Ref. rm. O + NO₂) RL 410 0.65±0.2 2/2
(Ref. rm. O + isobutene) RN 298 3.25(12) 2
(Ref. rm. O + 1-butene) RN 500 0.85(12) 2
(Ref. rm. O + NO₂) RN 298 4.0(12) 2

The normalized (RN) values have been calculated (87 STN/CVE) using the following T° values at 298 K: isobutene 1.02(13) (87 CVE), 1-butene 2.50(12) (87 CVE), NO₂ 5.6(12) (85 DEM/MAR).
<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>( T/\text{K} )</th>
<th>( k_A/k_B(\text{ref}) )</th>
<th>( n )</th>
<th>( B )</th>
<th>( k_A )</th>
<th>( \text{err.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>69 WES/DHE</td>
<td>EX 227-538</td>
<td>(1.2±0.2)(13)</td>
<td>326±50</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge flow. O formed by microwave discharge in ( \text{O}_2 ) or in ( \text{N}_2 ) (followed by \text{NMO} \text{ mn.}). Decay of ( \text{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 ( 65 \text{ SN} ). ( P=1.93-2.10 \text{ Torr at 297 K.} )</td>
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<td></td>
</tr>
<tr>
<td>70 CAL/HED</td>
<td>EX 480</td>
<td>(0.4±0.4)(14)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Flash Hg-photosensitized decomposition of ( \text{N}_2\text{O} ) in the presence of ( \text{CS}_2 ) to form ( \text{O} ). Time dependence of ( \text{O} ) determined by uv absorption. ( P=1.4 \text{ Torr.} )</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>72 SCH</td>
<td>SE 200-1000</td>
<td>1.2(10)</td>
<td>310±40</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suggested error limits of ± 20% for 200-1000K.</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>74 SLA/GIL</td>
<td>EX 302</td>
<td>(2.4±0.2)(12)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge flow. O formed by microwave discharge in ( \text{O}_2 ) or in ( \text{N}_2 ) followed by \text{NMO} \text{ mn.}. Decay of ( \text{CS}_2 ) in the presence of excess ( \text{O} ) followed by photoionization mass spec. ( P=1.4 \text{ Torr.} )</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>75 WIT/TIM</td>
<td>EX 218-203</td>
<td>(1.86±0.20)(13)</td>
<td>644±85</td>
<td>2</td>
<td></td>
<td></td>
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<tr>
<td>Discharge flow. O formed by microwave discharge of ( \text{O}_2 ) or of ( \text{N}_2 ) (followed by \text{NMO} \text{ mn.}). Decay of ( \text{O} ) in excess ( \text{CS}_2 ) followed by ESR. Results divided by the stoichiometric factor of 2.</td>
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</tr>
<tr>
<td>76 RAN/DIV</td>
<td>EX 200-1000</td>
<td>2.2(13)</td>
<td>700</td>
<td>2</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Estimated uncertainty is 30% below 350 K, increasing to 100% at 1000 K.</td>
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<td></td>
</tr>
<tr>
<td>77 GRI/GUT</td>
<td>EX 248-500</td>
<td>(2.23±0.33)(13)</td>
<td>659±48</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge flow. O formed by microwave discharge in ( \text{N}_2 ) followed by \text{NMO} \text{ mn.}. The decay of ( \text{CS}_2 ) in excess ( \text{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.</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>78 RAM/GAR</td>
<td>SE 200-1000</td>
<td>2.2(13)</td>
<td>700</td>
<td>2 *)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*) Accepted recommendation of 78 RAN/DIV. Suggested error factor of 1.4 for ( T=360K. )</td>
<td></td>
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</tbody>
</table>
CHEMICAL KINETIC DATA FOR REACTIONS OF OXYGEN WITH SULFUR COMPOUNDS

\[ \text{O} + \text{CS}_2 \rightarrow \text{products} \]

--- Continued ---

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, B=B(ref)</th>
<th>k, A A err. units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>78 TAL/BUT</td>
<td>EX 298</td>
<td></td>
<td>(1.4±0.14)(12)</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Diffusion cloud (“diffusion flame”) technique. O atoms formed by N+NO rm. CS(_2) consumption monitored by mass spec. P(He)=20 Torr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>84 BAU/COX</td>
<td>SE 298</td>
<td></td>
<td>2.2(12)</td>
<td></td>
<td></td>
<td>2 1.6</td>
</tr>
<tr>
<td>SE 200-500</td>
<td></td>
<td></td>
<td>1.9(13)</td>
<td></td>
<td>650±100</td>
<td>2</td>
</tr>
<tr>
<td>Accepted the NASA evaluation (83 DEM/MOL). For (k(O+CS_2=SO+CS)/k(O+CS_2=products)), i.e. for branching ratio, recommend a value (20.90).</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85 DEM/MAR</td>
<td>SE 298</td>
<td></td>
<td>2.2(12)</td>
<td></td>
<td></td>
<td>2 1.2</td>
</tr>
<tr>
<td>SE 1.9(13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>650±150</td>
<td>2</td>
</tr>
<tr>
<td>Averaged the room temp. data of 75 WEI/TIM, 69 WES/DEH, 74 SLA/GIL, 67 CAL/SMI, 70 CAL/HED, 68 KOM/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.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommended value of k</td>
<td>RE 298</td>
<td></td>
<td>2.3(12)</td>
<td></td>
<td></td>
<td>2 1.2</td>
</tr>
<tr>
<td>Recommended values of Arrhenius A and B</td>
<td>RE 218-920</td>
<td></td>
<td>3.55(13)</td>
<td></td>
<td>821±100</td>
<td>2 1.5</td>
</tr>
<tr>
<td>Based on the least squares fit of all data in the data sheet assuming linear Arrhenius plot.</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Arrhenius plot for O+CS\(_2\)=products is shown in Fig. 4.

References for reaction O + CS\(_2\) = products


D. L. Singleton and R. J. Cvetanović

References for reaction O + CS₂ → products -- Continued


87 SIN/CVE Singleton, D.L., and Cvetanovic, R.J., The present evaluation.

---

![Figure 4](image)

**Fig. 4.** Arrhenius plot for the reaction O+CS₂ → products.

The line is calculated using the recommended A and B values.
CHEMICAL KINETIC DATA FOR REACTIONS OF OXYGEN WITH SULFUR COMPOUNDS

O + CS₂ → COS + S

O + Carbon disulfide
A channel in the rm. O+CS₂-products.

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data T/K type</th>
<th>k,k(k(ref), A/A(A(ref))</th>
<th>n</th>
<th>B, B-B(ref)</th>
<th>k, A k err. units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>68 HOM/KRO</td>
<td>EX 1100</td>
<td>1(12)</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Discharge flow. Excess O formed by a microwave discharge in O₂ or in N₂ (followed by N₂O rm.). 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.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>73 SCH</td>
<td>SE 1100</td>
<td>1(12)</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Only one reported value (68 HOM/KRO). An estimated value at 298 K is given as 2.4(10).</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>74 SLA/GIL</td>
<td>RL 302</td>
<td>0.093±0.008</td>
<td></td>
<td></td>
<td>2/2</td>
</tr>
<tr>
<td>Discharge flow. O formed by microwave discharge in N₂ followed by N₂O rm. Decay of CS₂ and formation of COS followed by photolization mass spec. P=1.4 Torr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>76 BAI/DRY</td>
<td>SE 302</td>
<td>(2.2±1.1)(11)</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>The selected k value is based on the branching ratio reported by 74 SLA/GIL and the selected overall k value by 76 BAI/DRY.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>77 GRA/GUT</td>
<td>RL 249-500</td>
<td>*)</td>
<td></td>
<td></td>
<td>2/2</td>
</tr>
<tr>
<td>*) k/k(overall) = (0.088±0.004) - (0.081±0.007). Discharge flow. O formed by microwave discharge in N₂ followed by N₂O rm. Decay of CS₂ and formation of COS followed by photolization mass spec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommended value of k</td>
<td>RE 298</td>
<td>2.1(11)</td>
<td></td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>Recommended values of Arrhenius A and B</td>
<td>RE 249-500</td>
<td>2.2(12)</td>
<td>701±100</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>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.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References for reaction O + CS₂ → COS + S


D. L. SINGLETON AND R. J. CVETANOVIĆ

References for reaction \( O + CS_2 \rightarrow CO + S_2 \) -- Continued


\[ O + CS_2 \rightarrow CO + S_2 \]

**O + Carbon disulfide**

A minor channel in the \( O+CS_2 \)-products.

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data type</th>
<th>T/K</th>
<th>k_0/k(ref), A_0/A(ref)</th>
<th>n</th>
<th>( B ), k_0 k err.</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>79 HSU/SHA</td>
<td>RL 298</td>
<td>0.014±0.002</td>
<td></td>
<td></td>
<td>2/2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RN 298</td>
<td>(3.51±0.45)(10)</td>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Flash photolysis-CO laser absorption technique.

The listed RL \( k_0 \) is the branching ratio for the channel \( O+CS_2 \rightarrow CO+S_2 \). The normalized (RN) \( k_0 \) is based on the ratio of 0.373 measured for the CO formed in the \( O+CS_2 \) and \( O+CS_2 \) reactions. The RN value was obtained using \( k(O+CS_2 \rightarrow COCH_2)=9.4(10) \) (73 HER/HUI) and the branching ratio (the RL value) and \( k(O+CS_2 \rightarrow products)=2.33(12) \) (77 GRA/GUT).

Recommended branching ratio \( k_0/k(O+CS_2 \rightarrow products) \)

**References for reaction \( O + CS_2 \rightarrow CO + S_2 \)**


79 HSU/SHA Bau, D.S.Y., Shab, W.M., Burks, T.L., and Lin, M.C., "Dynamics of reactions of \( O(3P) \) atoms with \( CS, CS_2, \) and \( OCC \)," Chem. Phys. 44, 143 (1979).
**CHEMICAL KINETIC DATA FOR REACTIONS OF OXYGEN WITH SULFUR COMPOUNDS**

0 + COS → products

0 + Carbon oxide sulfide

At lower T the only observed product is SO+CO. See rm. 0+COS=CO₂+S for a higher T rm. channel.

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B</th>
<th>k.A</th>
<th>k err.</th>
<th>units</th>
<th>factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>65 ROL/REE</td>
<td>EX 298</td>
<td>6(9)</td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O produced by discharge in O₂. Measured O+SO chemiluminescence. k is approximate, with no details given. No CO₂ observed by mass spec. A reference is made to the channel forming CO₂ and S, as being less than 0.001 of the channel forming CO and SO.</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>65 SUL/NAR</td>
<td>EX *)</td>
<td>(5.5±0.8)(9)</td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T not specified: presumably room temperature. Discharge flow. O formed by microwave discharge of O₂. Consumption of COS determined by mass spec. Consumption of O matched the formation of CO. P=0.3-1.3 Torr.</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>67 HOY/WAG</td>
<td>EX 290-465</td>
<td>1.2(14)</td>
<td></td>
<td></td>
<td>2919±50</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge flow. O formed by microwave discharge of N₂ (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, SO₂, S₂O, and S were detected by mass spec. P=0.5-5 Torr.</td>
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</tr>
<tr>
<td>68 BON/KRO</td>
<td>EX 300-1150</td>
<td>6.5(13)</td>
<td></td>
<td></td>
<td>2768</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge flow. O formed by microwave discharge of O₂ or N₂ (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 CO₂, but not of SO₂, were observed as products.</td>
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</tr>
<tr>
<td>69 WES/DEH</td>
<td>EX 273-808</td>
<td>(1.9±0.7)(13)</td>
<td></td>
<td></td>
<td>2280±126</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge flow. O formed by microwave discharge of O₂ in He or Ar, or of N₂ (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], equaled consumption of O at 297 K. CO₂ (but not CO₂) was detected as a product by mass spectrometry.</td>
<td></td>
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</tr>
<tr>
<td>Reference Code, Notes</td>
<td>Data Type</td>
<td>T/K</td>
<td>k,k/ k(ref), A,A/A(ref)</td>
<td>n</td>
<td>B</td>
<td>k,A</td>
<td>k err.</td>
<td>Units Factor</td>
</tr>
<tr>
<td>----------------------</td>
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</tr>
<tr>
<td>71 KRE/SIM</td>
<td>RH</td>
<td>298-523</td>
<td>9.76(12)</td>
<td>2284</td>
<td>2</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ref. m. O + 2-trifluoromethylpropene (TFP). O formed by Hg-photosensitized decomposition of N_2O. Monitored CO yield as a function of the ratio of TFP to COS. The normalized (RH) values were obtained using A_{ref}=9.09(12), B_{ref}=1117. P(N_2O)=480-857 Torr at 298 K.</td>
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<tr>
<td>72 BRE/MIL</td>
<td>EX</td>
<td>287</td>
<td>(7.2±0.4)(9)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Discharge flow. O formed by microwave discharge of O_2 in He and monitored in excess COS by ESR. Details are not given. SO detected as product.</td>
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<tr>
<td>73 SCH</td>
<td>SE</td>
<td>270-1500</td>
<td>4.1(13)</td>
<td>2558±70</td>
<td>2</td>
<td></td>
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<tr>
<td>Suggested error limits of ± 35%.</td>
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<tr>
<td>74 KLE/STI</td>
<td>EX</td>
<td>253-503</td>
<td>(9.94±0.78)(12)</td>
<td>2156±28</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flash photolysis - resonance fluorescence. O formed by flash photolysis of O_2; its decay was measured by resonance fluorescence in excess COS and 50 Torr He or 40-200 Torr Ar.</td>
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<tr>
<td>75 WFI/TIM</td>
<td>EX</td>
<td>238-404</td>
<td>(1.2±0.2)(13)</td>
<td>2148±35</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge flow. O formed by microwave discharge in O_2 or N_2 (followed by N_2O rm.) diluted with He, was monitored in excess COS by ESR. P=0.69-1.49 at 295 K.</td>
<td></td>
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</tr>
<tr>
<td>76 BAV/DRY</td>
<td>SE</td>
<td>190-1200</td>
<td>1.8(13)</td>
<td>2250</td>
<td>2</td>
<td></td>
<td></td>
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<tr>
<td>Estimated uncertainty is 50% below 600 K and a factor of 3 above 600 K.</td>
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</tr>
<tr>
<td>76 MAN/ERA</td>
<td>EX</td>
<td>286</td>
<td>(8.37±0.84)(9)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flash photolysis - resonance fluorescence. Photolyzed mixtures of COS, O_2, Ar, and either CH_3F or CH_2F_2. Resonance fluorescence detection of O decay in excess COS. Rate was not significantly increased by vibrational excitation of COS.</td>
<td></td>
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</tr>
</tbody>
</table>

O + COS → products -- Continued

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k(k(ref), units factor</th>
<th>n</th>
<th>B, units factor</th>
<th>k,A k err.</th>
<th>B-B(ref)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78 YOS/SAI</td>
<td>EX</td>
<td>297</td>
<td>(7.1±0.7)(9)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Discharge flow. O formed by microwave discharge in O₂. 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.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>79 HSU/SHA</td>
<td>EX</td>
<td></td>
<td>*) 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).</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>80 ROB/SMI</td>
<td>EX</td>
<td>296</td>
<td>(1.0±0.1)(10)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Laser photolysis-chemiluminescence. O formed by laser photolysis of O₃ at 275nm. k was obtained by least squares fit of a reaction mechanism to the measured time dependence of the SOO₃ chemiluminescence. P(N₂)=100 Torr.</td>
<td></td>
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</tr>
<tr>
<td>81 KRI/WAG</td>
<td>EX 1900</td>
<td></td>
<td>1.8(13)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DE 298-1900</td>
<td></td>
<td>7.5(13)</td>
<td>0</td>
<td>2754</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DE 298-1900</td>
<td></td>
<td>7.4(12)</td>
<td>1.0</td>
<td>2057</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Shock tube. O generated by decomposition of N₂O 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 BOY/WAG and 68 BOM/KK).</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>84 BAU/COX</td>
<td>SE 298</td>
<td></td>
<td>8.4(9)</td>
<td>2</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SE 220-600</td>
<td></td>
<td>1.6(13)</td>
<td>2</td>
<td>2250±150</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>For discussion see 80 BAU/COX. Note that only data for T&lt;800 K are considered and that the data above 600 K are significantly higher than the fitted line.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85 DEM/HAR</td>
<td>SE 298</td>
<td></td>
<td>7.8(9)</td>
<td>2</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SE 1.3(13)</td>
<td></td>
<td>2200±150</td>
<td>2</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Averaged the room temp. data of 69 WES/DEH, 74 KLE/STI, 75 WEI/TIM, 76 MAN/BRA, 72 BEE/MIL; averaged the S values of 69 WES/DEH, 74 KLE/STI, 75 WEI/TIM.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Reference Code, Notes

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data</th>
<th>T/K</th>
<th>( k,k(k_{\text{ref}}) )</th>
<th>( n )</th>
<th>( k ), A</th>
<th>k err.</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recommended value of ( k )</td>
<td>RE 298</td>
<td>8.0(9)</td>
<td></td>
<td></td>
<td>2</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Recommended values of Arrhenius A and B</td>
<td>RE 239-523</td>
<td>1.6(13)</td>
<td></td>
<td></td>
<td>2</td>
<td>2257±200</td>
<td></td>
</tr>
<tr>
<td>Recommended values of Arrhenius A and B</td>
<td>RE 239-1900</td>
<td>4.7(13)</td>
<td></td>
<td></td>
<td>2</td>
<td>2621±200</td>
<td></td>
</tr>
</tbody>
</table>

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 \( O + COS \rightarrow \) products


72 BRE/MIL Breckenridge, W.H., and Miller, T.A., "Kinetic study by EPR of the production and decay of \( SO(1D) \) in the reaction of \( O_2(1A_g) \) with \( SO(1D) \)," J. Chem. Phys. 56, 465 (1972).


Fig. 5. Arrhenius plot for the reaction $\text{O} + \text{CS} \rightarrow \text{products}$.

The line is calculated using the recommended $A$ and $B$ values at 239–1900K.
O + COS → CO₂ + S
O + Carbon oxide sulfide
A higher temperature path in the rm. O + COS → products

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data type</th>
<th>T/K</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, k,A k err.</th>
<th>B=B(ref) units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>82 TOP</td>
<td>EX 1200-1800</td>
<td>5.0(13)</td>
<td>5527±636</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Shock tube oxidation of COS. Monitored COS, O₂, CO, CO₂, SO₂ and total pressure. The relative rates of CO₂ and CO production at the beginning of the COS conversion phase were interpreted to estimate k for the rm. path O + COS → CO₂ + S.

Recommended value of k

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data type</th>
<th>T/K</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, k,A k err.</th>
<th>B=B(ref) units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE 1200</td>
<td>RE 1200-1900</td>
<td>5(11)</td>
<td>5(13) 5530±1000</td>
<td>2</td>
<td>3</td>
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</tr>
</tbody>
</table>

Recommended values of Arrhenius A and B

Based on the single determination (82 TOP). Additional data would be useful.

Reference for reaction O + COS → CO₂ + S


O + CH₃SH → products
O + Methanethiol

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

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data type</th>
<th>T/K</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, k,A k err.</th>
<th>B=B(ref) units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>76 SLA/GRA</td>
<td>EX 300</td>
<td>1.1(12)</td>
<td>2 1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Discharge flow. Rf mass spec. monitored decay of CH₃SH in excess O atoms. P=0.64-2.0 Torr.

78 KIR/VEY

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.
### Chemical Kinetic Data for Reactions of Oxygen with Sulfur Compounds

**O + CH₃SH → products -- Continued**

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k, k(k(ref)) A/A(A(ref))</th>
<th>n</th>
<th>B</th>
<th>k, A</th>
<th>k(err)</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>78 SLA/BAI</td>
<td>EX</td>
<td>252-496</td>
<td>(2.65±1.52)(10)</td>
<td>*</td>
<td>-135±189</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(*) n=4.53±0.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Discharge flow. Photoionisation mass spec. Monitored decay of CH₃SH 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].</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>81 NIP/SIN</td>
<td>EX</td>
<td>297-537</td>
<td>(6.58±5.05)(10)</td>
<td>*</td>
<td>-829±234</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(*) n=3.65±0.61</td>
<td></td>
<td></td>
<td>Phase shift technique with modulated [O] monitored by O₂/O₂ chemiluminescence. O atoms generated by Hg-photosensitized decomposition of N₂O. 81 NIP/SIN report the rate expression k = (9.16±1.02)(11) + (3.85±2.41)(13)x exp(-167±322)/T. [A, n, and B values listed here were calculated (87 SIN/CVE) from the data of 81 NIP/SIN].</td>
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</table>

**Recommended values of k**

<table>
<thead>
<tr>
<th>Data Type</th>
<th>T/K</th>
<th>k, A</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE</td>
<td>298</td>
<td>1.2(12)</td>
<td>2 1.2</td>
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</table>

**Recommended values of Arrhenius parameters**

<table>
<thead>
<tr>
<th>Data Type</th>
<th>T/K</th>
<th>k, A</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE</td>
<td>252-661</td>
<td>*</td>
<td>*) *</td>
</tr>
</tbody>
</table>

*) 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 linear 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/VEF 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+CH₃SH-products is shown in Fig. 6.

---

**References for reaction O + CH₃SH → products**

70 SLA/URCA

78 KIR/VEF

78 SLA/BAI

---

References for reaction O + CH₃SH → products -- Continued


87 SIN/CVE Singleton, D.L., and Cvetanovic, R.J., The present evaluation.

---

Fig. 6. Arrhenius plot for the reaction O+CH₃SH→products.
The line is calculated using the modified Arrhenius Eqn. $k=A_1+A_2\text{exp}(-B/T)$ and the recommended values. $A_1=0.0(11)\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$, $A_2=1.0(10)\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$, $B=10611$.

---

O + CH₃SH → products
O + Ethanethiol
For potential run channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data T/K</th>
<th>k.k/k(ref), type A/A/A(ref)</th>
<th>n</th>
<th>R.</th>
<th>k.A</th>
<th>k.err. B-B(ref) units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>76 SLA/GRA</td>
<td>EX 300</td>
<td>1.7(12)</td>
<td>2</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Discharge flow. Photoionization mass spec. Monitored decay of CH₃SH in excess O atoms. P=0.64-2.6 Torr.

### Chemical Kineti Data for Reactions of Oxygen with Sulfur Compounds

**O + C₂H₅SH → Products -- Continued**

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data</th>
<th>T/K</th>
<th>k,k/k(ref)</th>
<th>n</th>
<th>B,</th>
<th>k,A</th>
<th>k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>78 KIR/VEY</strong></td>
<td>EX</td>
<td>304-421</td>
<td>(5.75±0.3)(12)</td>
<td>391±18</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>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.</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

| **78 SLA/BAI**        | EX   | 235-496 | (3.17±3.84)(9) | * | -1852±356 | 2 |
| *n=6.13±1.04          |
| Discharge flow. Photoionization mass spec. Monitored decay of C₂H₅SH in excess O atoms. P=0.719±2.18 Torr. [A, n, and B values were calculated (87 SIN/CVE) from the supplementary data of 78 SLA/BAI]. |

| **81 NIP/SIN**        | EX   | 300-574 | (1.78±0.71)(10) | * | -1313±122 | 2 |
| *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 N₂O. 81 NIP/SIN report the rate expression |
| \( k = (1.37±0.65)(12) + (8.73±4.6)(13) \times e^{-(2075±266)/T} \). |
| [A, n, and B values listed here were calculated (87 SIN/CVE) from the data of 81 NIP/SIN]. |

**Recommended Values 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 \( k=A_1+A_2e^{-(B/T)} \) with \( A_1=1.6(12), A_2=1.0(14), B=2196 \). As for OCH₃OH, 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/VEY.

The present recommended Arrhenius parameters, \( A_1, A_2 \) 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 \( O+C₂H₅SH \rightarrow \) products is shown in Fig. 7.
References for reaction $\text{O} + \text{C}_2\text{H}_5\text{SH} \rightarrow \text{products}


Fig. 7. Arrhenius plot for the reaction $\text{O} + \text{C}_2\text{H}_5\text{SH} \rightarrow \text{products}$. The line is calculated using the modified Arrhenius Eqn. $k = A_1 + A_2 \exp(-B/T)$ and the recommended values: $A_1 = 1.6(12)\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$, $A_2 = 1.0(14)\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$, $B = 2198$K.

### CHEMICAL KINETIC DATA FOR REACTIONS OF OXYGEN WITH SULFUR COMPOUNDS

**O + C₃H₇SH → products**

**O + 1-Propanethiol**

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

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B,E-B(ref)</th>
<th>k,A</th>
<th>k err.</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>78 KIR/VET</strong></td>
<td>EX</td>
<td>303-421</td>
<td>(8.33±0.54)(12)</td>
<td>494±22</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommended value of k</td>
<td>RE</td>
<td>298</td>
<td>1.6(12)</td>
<td>2</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommended values of Arrhenius A and B</td>
<td>RE</td>
<td>303-421</td>
<td>8.3(12)</td>
<td>494±50</td>
<td>2</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Based on the only data available (78 KIR/VET). Additional determinations would be useful.</td>
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</tbody>
</table>

#### References for reaction O + C₃H₇SH → products

**76 SLA/GRA**


**78 KIR/VET**


**81 CVE/SIN**


---

**O + C₄H₉SH → products**

**O + 1-Butanethiol**

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

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>T/K</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B,E-B(ref)</th>
<th>k,A</th>
<th>k err.</th>
<th>units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>78 KIR/VET</strong></td>
<td>EX</td>
<td>308-419</td>
<td>(5.78±0.33)(12)</td>
<td>321±19</td>
<td>2</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Recommended value of k</td>
<td>RE</td>
<td>298</td>
<td>2.0(12)</td>
<td>2</td>
<td>1.3</td>
<td></td>
<td></td>
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<tr>
<td>Recommended values of Arrhenius A and B</td>
<td>RE</td>
<td>308-419</td>
<td>5.8(12)</td>
<td>321±50</td>
<td>2</td>
<td>1.5</td>
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<tr>
<td>Based on the only data available (78 KIR/VET). Additional determinations would be useful.</td>
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</tbody>
</table>

---

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


---

$O + CH_{11}SH \rightarrow \text{products}$

$O + 1\text{-Pentanethiol}$

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

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data type</th>
<th>T/K</th>
<th>$k, k(k(\text{ref}) \cdot A, A/A(\text{ref}) \cdot n$</th>
<th>B-E(\text{ref})</th>
<th>k, A k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>78 KIR/VET</td>
<td>EX</td>
<td>302-409</td>
<td>$(0.18\pm0.35)(12)$</td>
<td>328e19</td>
<td>2</td>
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<tr>
<td>78 KIR/VET</td>
<td>RE</td>
<td>298</td>
<td>$2.1(12)$</td>
<td>2</td>
<td>1.3</td>
</tr>
<tr>
<td>Recommended value of k</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>78 KIR/VET</td>
<td>RE</td>
<td>302-409</td>
<td>$6.2(12)$</td>
<td>328e50</td>
<td>2</td>
</tr>
<tr>
<td>Recommended values of Arrhenius A and B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Based on the only data available (78 KIR/VET). Additional determinations would be useful.

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


0 + CH₃SCH₃ → products

0 + Methane. thiois-

Presumably 0 + CH₃SCH₃ → CH₃O + CH₄. For potential rm. channels see 76 SLA/GRA, 78 KIR/

VET, and 81 CVE/SIN.

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data</th>
<th>T/K</th>
<th>k,k(k(ref),</th>
<th>n</th>
<th>B,</th>
<th>k,A</th>
<th>k err.</th>
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<tr>
<td></td>
<td></td>
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<td>A,A(A(ref)</td>
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<td>B-B(ref)</td>
<td>units factor</td>
<td></td>
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<tr>
<td>74 CAD/MIC</td>
<td>EX</td>
<td>300</td>
<td>3.3(11)</td>
<td>2</td>
<td></td>
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</tr>
<tr>
<td>Discharge flow. Excess CH₃SCH₃, [O] monitored by OHO chemiluminescence.</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>76 LEE/TIM</td>
<td>EX</td>
<td>268-424</td>
<td>(8.56±0.42)(12)</td>
<td>-366±16</td>
<td>2</td>
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</tr>
<tr>
<td>Flash photolysis. [O] monitored by resonance fluorescence in excess CH₃SCH₃. O₂ used as source of O atoms. P=40-100 Torr (Ar).</td>
<td></td>
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</tr>
<tr>
<td>76 SLA/GRA</td>
<td>EX</td>
<td>300</td>
<td>3.8(13)</td>
<td>2</td>
<td>1.2</td>
<td></td>
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</tr>
<tr>
<td>Discharge flow. Photoionization mass spec. Monitored decay of CH₃SCH₃ in excess O atoms. P=0.8-1.9 Torr.</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>78 SLA/BAI</td>
<td>EX</td>
<td>252-493</td>
<td>(1.16±0.08)(13)</td>
<td>-306±22</td>
<td>2</td>
<td></td>
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</tr>
<tr>
<td>Discharge flow. Photoionization mass spec. Monitored decay of CH₃SCH₃ 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].</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>80 LEE/TAM1</td>
<td>EX</td>
<td>272-472</td>
<td>(7.71±0.72)(12)</td>
<td>-40±30</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>81 NIP/SIN</td>
<td>EX</td>
<td>298-557</td>
<td>(5.69±0.72)(12)</td>
<td>-450±41</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase shift technique with modulated [O] monitored by OHO chemiluminescence. O atoms generated by Hg-photosensitized decomposition of N₂O. P=22-56 Torr at 297 K.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

81 NIP/SIN

RL 300  | 13.8±0.9  | 2/2 |
RN 300  | (3.32±0.25)(13) | 2 |

Reference AN. O + 1-butene - products

O formed by Hg-photosensitized decomposition of N₂O. Monitored the rate of formation of butane oxide and n-butanal as a function of the ratio of reactants. The above RN k value was calculated (81 NIP/SIN) using kₐ₈=2.42(12) cm³/mole⁻¹s⁻¹.
O + CH$_3$SCH$_3$ → products -- Continued

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data</th>
<th>T/K type</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, B-B(ref)</th>
<th>units factor</th>
<th>k,A k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>84 BAU/COX</td>
<td>SE</td>
<td>298</td>
<td>3.0(13)</td>
<td>2</td>
<td>1.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SE</td>
<td>270-560</td>
<td>7.8(12)</td>
<td></td>
<td>-409±100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Data</th>
<th>T/K type</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, B-B(ref)</th>
<th>units factor</th>
<th>k,A k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE</td>
<td>298</td>
<td>3.1(13)</td>
<td>2</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Recommended values of Arrhenius A and B

<table>
<thead>
<tr>
<th>Data</th>
<th>T/K type</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B, B-B(ref)</th>
<th>units factor</th>
<th>k,A k err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE</td>
<td>252-557</td>
<td>8.2(12)</td>
<td></td>
<td>-397±100</td>
<td></td>
<td>2 1.3</td>
</tr>
</tbody>
</table>

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=288-557 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$_3$SCH$_3$ → products are shown in Fig. 8.

References for reaction O + CH$_3$SCH$_3$ → products


87 SIN/CVE Singleton, D.L., and Cvetanovic, R.J., The present evaluation.
Fig. 8. Arrhenius plots for the reaction O + CH₃CH₂SCH₂ → products.
The line is calculated using the recommended A and B values.

O + cy-CH₂SCH₂ → products
O + Ethylene episulfide
The exclusive primary products appear to be CH₂=CH₂ + SO (76 LEE/TIM, 87 SIN).

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data</th>
<th>T/K</th>
<th>k,k/k(ref).</th>
<th>n</th>
<th>B</th>
<th>k A k err.</th>
<th>units factor</th>
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<tbody>
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<td></td>
<td></td>
<td>type</td>
<td></td>
<td></td>
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<tr>
<td>76 LEE/TIM</td>
<td>EX</td>
<td>288-424</td>
<td>(8.07±0.54)(12)</td>
<td>18±20</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flash photolysis. [O] monitored by resonance fluorescence in excess cy-CH₂SCH₂. O₂ used as source of O atoms. P=40-100 Torr (Ar).</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommended value of k</td>
<td>RE</td>
<td>298</td>
<td>7.6(12)</td>
<td>2</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommended values of Arrhenius A and B</td>
<td>RE</td>
<td>288-424</td>
<td>8.1(12)</td>
<td>18±50</td>
<td>2</td>
<td>1.5</td>
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<tr>
<td>Based on the only data available (76 LEE/TIM). Additional determinations would be useful.</td>
<td></td>
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</tbody>
</table>

References for reaction O + cy-CH₂SCH₂ → products


87 SIN  Singleton, D.L., Unpublished data.
0 + cy-CHBNCCH → products

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data type</th>
<th>T/K</th>
<th>k,k/k(ref), A,A/A(ref)</th>
<th>n</th>
<th>B</th>
<th>k,A k err. B-B(ref) units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>81 LEE/TAN</td>
<td>EX</td>
<td>262-448</td>
<td>(2.01±0.20)(13)</td>
<td>569±30</td>
<td>2</td>
<td></td>
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</tbody>
</table>

Discharge flow. O formed by microwave discharge of O_{2} 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).

| 65 TAB/URE             | EX        | 394-525 | (1.52±0.2)(12)       | 121 | 2 |

Discharge flow. O formed by microwave discharge in H_{2}O and Ar. The intensity of emission from excited O_{2} was determined at fixed reaction time for various initial excess thiophene concentrations. P < 2 Torr.

Recomendation 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. (370-525K), 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-CHBNCCH-products is shown in Fig. 9.

References for reaction 0 + cy-CHBNCCH → products


Fig. 9. Arrhenius plots for the reaction O\textsuperscript{cy}-CH\textsubscript{3}SCH\textsubscript{3}CH\textsubscript{3}-products.

\[ O + \text{CH}_{3}\text{SSCH}_{3} \rightarrow \text{products} \]
\[ O + \text{Disulfide, dimethyl} \]

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

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data</th>
<th>T/K</th>
<th>k,k/k(ref), n</th>
<th>B, k, A, k err.</th>
<th>E-B(ref) units factor</th>
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</thead>
<tbody>
<tr>
<td>80 LEE/TAN2</td>
<td>EX</td>
<td>270-320</td>
<td>(1.28±0.13)(14)</td>
<td>0</td>
<td>2</td>
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<tr>
<td>Discharge flow. [O] monitored by resonance fluorescence in excess sulfide. P=0.52-2.60 Torr.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>81 NIP/SIN</td>
<td>EX</td>
<td>206-571</td>
<td>(2.62±0.42)(13)</td>
<td>-25±61</td>
<td>2</td>
</tr>
<tr>
<td>Phase shift technique with modulated [O] monitored by O\textsuperscript{+}NO chemiluminescence. O atoms formed by Hg-photosensitized decomposition of N\textsubscript{2}O.</td>
<td></td>
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</table>
O + CH$_3$SSCH$_3$ → products — Continued

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data Type</th>
<th>$k/k^{(ref)}$, A/A$^{(ref)}$, B/B$^{(ref)}$</th>
<th>n</th>
<th>a, k, A k err. units factor</th>
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<tbody>
<tr>
<td>81 NIP/SIN</td>
<td>PL 300</td>
<td>24.5 ± 1.5</td>
<td>2/2</td>
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<tr>
<td></td>
<td>RN 300</td>
<td>(5.9 ± 0.37)(13)</td>
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</tbody>
</table>

Reference note: O + 1-Butene → products

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) cm$^3$ mole$^{-1}$ s$^{-1}$.

84 BAU/COX

<table>
<thead>
<tr>
<th>Data Type</th>
<th>$k/k^{(ref)}$, A/A$^{(ref)}$, B/B$^{(ref)}$</th>
<th>n</th>
<th>a, k, A k err. units factor</th>
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</thead>
<tbody>
<tr>
<td>SE 298</td>
<td>7.8(13)</td>
<td>2 2</td>
<td></td>
</tr>
<tr>
<td>SE 290-570</td>
<td>3.3(13)</td>
<td>-250 ± 100 2 2</td>
<td></td>
</tr>
</tbody>
</table>

Averaged the room temp. data of 80 LEX/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 $k^{ref}$ value.

Recommended values of $k$

<table>
<thead>
<tr>
<th>Data Type</th>
<th>$k/k^{(ref)}$, A/A$^{(ref)}$, B/B$^{(ref)}$</th>
<th>n</th>
<th>a, k, A k err. units factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE 298</td>
<td>6.0(13)</td>
<td>2 1.2</td>
<td></td>
</tr>
<tr>
<td>RE 290-570</td>
<td>2.6(13)</td>
<td>-250 ± 100 2 1.5</td>
<td></td>
</tr>
</tbody>
</table>

Recommended values of Arrhenius A and B

Based on the data of 81 NIP/SIN and assuming linear Arrhenius plot.

Arrenius plot for O+CH$_3$SSCH$_3$→products is shown in Fig. 10.

References for reaction O + CH$_3$SSCH$_3$ → products

80 LEX/TAN

81 CVE/SIN

81 NIP/SIN

83 SIN/IRW

84 BAU/COX
Fig. 10. Arrhenius plot for the O\textbullet\textsubscript{2}+SCF\textsubscript{2}→products reaction.
The line is calculated using the recommended A and B values.

O + SCF\textsubscript{2} → products

O + Carbonothioic difluoride

<table>
<thead>
<tr>
<th>Reference Code</th>
<th>Notes</th>
<th>Data</th>
<th>T/K</th>
<th>k\textbullet\textsubscript{2}/k\textbullet\textsubscript{ref}</th>
<th>n</th>
<th>R</th>
<th>k A</th>
<th>k arr.</th>
<th>B-B(ν5 ref)</th>
<th>units factor</th>
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<tbody>
<tr>
<td>78 SLA/GUT</td>
<td></td>
<td>EX</td>
<td>250-493</td>
<td>(7.35±1.1)\textbullet(12)</td>
<td>376±48</td>
<td>2</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
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<td></td>
<td>Discharge flow. O formed by microwave discharge of O\textsubscript{2} in He. Decay of SCF\textsubscript{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\textsubscript{2}.</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>RE</td>
<td>208</td>
<td>2.1(12)</td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td>RE</td>
<td>259-493</td>
<td>7.4(12)</td>
<td>376±100</td>
<td>2</td>
<td>1.5</td>
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<td></td>
<td>recommended values of Arrhenius A and B</td>
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</table>

Based on the only data available (79 SLA/GUT). Additional determinations would be useful.
Reference for reaction $O + SC\ell_2 \rightarrow \text{products}$

$O + SC\ell_2 \rightarrow \text{products}$

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data</th>
<th>T/K</th>
<th>$k,k/(\text{ref.})$</th>
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<th>$B$</th>
<th>$k,A$</th>
<th>$k$ err.</th>
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<tbody>
<tr>
<td></td>
<td>EX</td>
<td>251-493</td>
<td>(1.86±0.33)(13)</td>
<td>-58±53</td>
<td>2</td>
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</table>

Discharge flow. $O$ formed by microwave discharge of $O_2$ in He. Decay of $SC\ell_2$ 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; $SO\ell_2$ and $SC\ell_2ClO$.

Recommended value of $k$

<table>
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<tr>
<th>Reference Code, Notes</th>
<th>T/K</th>
<th>$k$</th>
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Recommended values of Arrhenius $A$ and $B$

<table>
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<td>1.9(13)</td>
<td>-80±100 2 1.5</td>
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</table>

Based on the only data available (78 SLA/GUT). Additional determinations would be useful.

Reference for reaction $O + SC\ell_2 \rightarrow \text{products}$

$O + SC\ell_2 \rightarrow \text{products}$

$O + cy-CF_2SCF_2S \rightarrow \text{products}$

$O + 1,3\text{-dithiocarbamate, 2,2,4,4-tetrafluoro-}$

<table>
<thead>
<tr>
<th>Reference Code, Notes</th>
<th>Data</th>
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<th>$B$</th>
<th>$k,A$</th>
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<tr>
<td></td>
<td>EX</td>
<td>253-493</td>
<td>(1.42±0.31)(13)</td>
<td>855±84</td>
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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 forms $SC\ell_2 + SC\ell_2$.
CHEMICAL KINETIC DATA FOR REACTIONS OF OXYGEN WITH SULFUR COMPOUNDS

<table>
<thead>
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<th>Reference Code, Notes</th>
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<th>n</th>
<th>B, B(ref)</th>
<th>k, A</th>
<th>k err</th>
<th>units factor</th>
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<tr>
<td></td>
<td>RE 298</td>
<td>8.1(11)</td>
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<td>1.3</td>
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<td></td>
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<tr>
<td>Recommended value of k</td>
<td>RE 253-493</td>
<td>1.4(13)</td>
<td>855±100</td>
<td>2</td>
<td>1.5</td>
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</table>

Based on the only data available (79 SLA/GUT). Additional determinations would be useful.

Reference for reaction O + cy-CF$_2$SCF$_2$S → products