

# Rate Constants for the Reactions of Atomic Oxygen ( $O^3P$ ) with Organic Compounds in the Gas Phase

Cite as: Journal of Physical and Chemical Reference Data **2**, 467 (1973); <https://doi.org/10.1063/1.3253125>  
Published Online: 29 October 2009

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# Rate Constants for the Reactions of Atomic Oxygen ( $O^3P$ ) With Organic Compounds in the Gas Phase

John T. Herron and Robert E. Huie

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Rate constants for the reactions of atomic oxygen ( $O^3P$ ) with organic compounds in the gas phase are compiled and critically evaluated. Data are given here as originally reported in the literature for a total of 107 organic reactants. From a critical evaluation of the data, recommended values for rate constants are given over specified temperature intervals, and where possible at 298 K and 1000 K. Estimated error limits are assigned to all recommended values.

**Key words:** Atomic oxygen; chemical kinetics; compilation; critical evaluation; gases; organic compounds; rate constants.

## Contents

	Page		Page
1. Introduction.....	468	3.3. Haloalkanes.....	485
1.1. General.....	468	Table 24. Chloromethane.....	485
1.2. Literature Coverage.....	468	Table 25. Bromomethane.....	486
1.3. Arrangement of Tables.....	468	Table 26. Tetrachloromethane.....	486
1.4. Experimental Techniques.....	468	Table 27. Chloroethane.....	487
1.5. Criteria for Evaluation.....	469	Table 28. Bromoethane.....	487
1.6. Units.....	470	Table 29. 2-Chloropropane.....	488
1.7. Concluding Remarks.....	470	Table 30. 2-Bromopropane.....	488
2. Recommended Values.....	470	Table 31. 2-Chlorobutane.....	489
Table 1. Alkanes.....	470	Table 32. 1-Chloro-2-methylpropane.....	489
Table 2. Cycloalkanes.....	471	Table 33. 2-Chloro-2-methylpropane.....	490
Table 3. Haloalkanes.....	472	Table 34. 1-Bromobutane.....	490
Table 4. Alkenes, Alkadienes, and Cycloalkenes.....	473	Table 35. 1-Bromo-2-methylpropane.....	491
Table 5. Haloalkenes and Haloalkadienes.....	473	Table 36. 1-Chloro-2,2-dimethylpropane.....	491
Table 6. Alkynes and Alkadiynes.....	474	Table 37. Miscellaneous Haloalkanes.....	492
Table 7. Benzene, Substituted Benzenes, and Pyridine.....	474	3.4. Alkenes, Alkadienes, and Cycloalkenes .....	492
Table 8. Alcohols, Aldehydes, and Miscellaneous Oxygen-Containing Compounds.....	475	Table 38. Ethylene.....	493
3. Absolute Rate Constants.....	475	Table 39. Propene.....	494
3.1. Alkanes.....	476	Table 40. 1-Butene.....	495
Table 9. Methane.....	476	Table 41. <i>cis</i> -2-Butene.....	495
Table 10. Ethane.....	476	Table 42. <i>trans</i> -2-Butene.....	496
Table 11. <i>n</i> -Butane.....	477	Table 43. 2-Methylpropene.....	496
Table 12. <i>n</i> -Pentane.....	478	Table 44. 2,3-Dimethyl-2-butene.....	497
Table 13. 2,2-Dimethylpropane.....	479	Table 45. Miscellaneous Alkenes and Alkadienes.....	497
Table 14. <i>n</i> -Hexane.....	479	Table 46. Cyclopentene and Cyclohexene .....	498
Table 15. 2,3-Dimethylbutane.....	480	3.5. Haloalkenes and Haloalkadienes.....	498
Table 16. <i>n</i> -Heptane.....	481	Table 47. Haloalkenes and Haloalkadienes .....	498
Table 17. <i>n</i> -Octane.....	481	3.6. Alkynes and Alkadiynes.....	499
Table 18. Miscellaneous alkanes.....	482	Table 48. Acetylene.....	500
3.2. Cycloalkanes.....	482	Table 49. Propyne, Butadiyne, and Dicyanoacetylene.....	501
Table 19. Cyclopropane and Cyclobutane .....	483	3.7. Benzene, Some Substituted Benzenes, and Pyridine.....	501
Table 20. Cyclopentane.....	483	Table 50. Benzene, Some Substituted Benzenes, and Pyridine.....	501
Table 21. Spiropentane.....	483	3.8. Alcohols, Aldehydes, and Miscellaneous Oxygen-Containing Compounds.....	502
Table 22. Cyclohexane.....	484	Table 51. Methanol.....	502
Table 23. Cycloheptane.....	484	Table 52. Ethanol and Isopropanol.....	503
		Table 53. Aldehydes.....	503

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	Page		Page
Table 54. Ketene and Ethylene Oxide.....	504	Table 61. Data of Smith.....	508
Table 55. Dimethyl Ether.....	504	Table 62. Data of Moss and Jennings.....	508
4. Relative Rate Constants.....	505	Table 63. Data of Neuman and Jonathan.....	509
Table 56. Data of Wilson and O'Donovan.....	505	Table 64. Data of Grovenstein and Mosher .....	509
Table 57. Data of Takezaki, Mori, and Kawa- saki.....	505	Table 65. Data of Tyerman, Ford and Endow, Scalla and Wu, Elias, Christie and Collins, and Sato and Cvetanovic.....	509
Table 58. Data of Cvetanovic and Co-workers...	505	5. Formula Index.....	510
Table 59. Data of Heicklen and Co-workers....	506	6. Author Index to Bibliography.....	511
Table 60. Data of Moss.....	507	7. Bibliography.....	514

## 1. Introduction

### 1.1. General

This compilation presents, in tabular and graphical form, experimentally derived rate data on the gas phase reactions of atomic oxygen in its ground electronic state ( $O^3P$ ) with organic compounds. Where the data are considered to be of sufficient reliability, recommended values of rate constants have been chosen at particular temperatures or over specified temperature intervals. Included are estimated upper and lower error limits on the recommended rate constants.

### 1.2. Literature Coverage

The period covered is from about 1957 through mid 1972. Papers published through late 1972 are included where possible. The earlier literature is covered in the reviews by Steacie [153],<sup>1</sup> Kaufman [117], and Cvetanovic [63].

### 1.3. Arrangement of Tables

Three kinds of tables are given. The first is a table of the recommended rate constants derived from a consideration of the reported experimental data. The upper and lower error limits are based upon estimates of the reliability of the experimental methods used in obtaining the data, and upon the number of independent experiments performed on the system. Error limits are given in terms of multiplying factors rather than the more usual plus or minus notation. If, for example, the upper and lower error limits on a rate constant  $k$  are given as 1.5 and 0.6, then the rate constant is estimated to be between 1.5  $k$  and 0.6  $k$ , or the rate constant is  $k^{(+0.5k)}_{(-0.4k)}$ . The recommended values are valid only at the specified temperatures, or over the specified temperature intervals. Extrapolation beyond these ranges should be undertaken with caution, particularly at higher temperatures where other reaction mechanisms may contribute to the overall rate constant. For convenience we have in many cases given the rate constant at 298 K and 1000 K based on extrapolations. In these cases (all noted in the tables) larger error limits normally have been assigned.

<sup>1</sup> Figures in brackets indicate literature references.

The second set of tables consists of compilations of the reported rate measurements on the reactions of atomic oxygen with organic compounds. Included in these tables are the results of absolute rate measurements taken, with a few exceptions which are noted, from tables and graphs reported in the literature. In addition, absolute rate constants derived from relative rate measurements are included in these tables. In the "No." column we give the number of individual rate measurements if this information can be ascertained from the paper. In the "Comments" column we briefly indicate the experimental technique used to obtain the data. These are discussed more fully in the next section. Error limits, where given, are those reported in the original source. In some cases, as indicated by footnotes, the data have been adjusted to account for the reaction stoichiometry or chain length. Where there are extensive data from different sources, we give the recommended values as a final entry. Otherwise the recommended values are not given in this section. Arrhenius plots are given whenever there are data covering a reasonable temperature interval. Solid lines are used to indicate the approximate temperature range over which the recommended values are valid. Dashed lines are extrapolations. In these tables and the tables of recommended values, an asterisk (\*) on a reference number means that data from that source were used in deriving the recommended value.

The last set of tables gives relative rate measurements and the absolute values derived from them. These relative rate constants have been put on an absolute basis by choosing certain reactants as standards, using the recommended values of this compilation. These standard reactions are indicated in the tables.

### 1.4. Experimental Techniques

Here we briefly describe the experimental techniques indicated in the comments column. Further details may be found in the referenced papers.

*Discharge flow*—Oxygen atoms are produced in a gas stream either by the dissociation of molecular oxygen in an electrical discharge (microwave, radio frequency, condensed, etc.), or by the dissociation of molecular nitrogen and the subsequent reaction  $N + NO \rightarrow N_2 + O$ . The stable reactant is added downstream and the reac-

tion monitored using one of several analytical techniques [109, 117].

*Discharge flow-e.s.r.*—A discharge flow system in which oxygen atoms are monitored using electron spin resonance spectroscopy. Kinetic measurements are performed usually with the stable reactant in excess [9].

*Discharge flow-mass spectrometry*—A discharge flow system in which reactants are monitored using mass spectrometry. Kinetic measurements are performed usually with atomic oxygen in excess [76].

*Discharge flow-air afterglow*—A discharge flow system in which oxygen atoms are monitored using the emission from the chemiluminescent reaction  $O + NO \rightarrow NO_2 + h\nu$  [10].

*Discharge flow-final products*—A discharge flow system in which the final reaction products are trapped in a cold trap and then analyzed. Rate constants are determined from the rate of accumulation of one or more of these products [131].

*Discharge flow-CH\* chemiluminescence*—A discharge flow system in which the reaction is monitored using the CH ( $A^2\Delta - X^2\Pi$ ) emission. Applicable to the acetylecne reaction only [36].

*Hg photosensitized decomposition of N<sub>2</sub>O*—Oxygen atoms are produced by the mercury photosensitized decomposition of nitrous oxide in a static system. Relative rate constants are determined by the competition of stable reactants for the oxygen atoms [63].

*Flow photolysis of NO<sub>2</sub>*—A flow system in which the oxygen atoms are produced by the photolysis of NO<sub>2</sub> [17].

*Flash photolysis-resonance fluorescence*—A static system in which oxygen atoms are produced by the flash photolysis of molecular oxygen or other source compounds. The decay of atomic oxygen in an excess of another reactant is monitored using the fluorescence of atomic oxygen resonance radiation [104].

*Flash photolysis-kinetic absorption*—Oxygen atoms produced as in flash photolysis-resonance fluorescence, and the atom decay monitored using the absorption of the resonance radiation [104].

*Pulsed photolysis-air afterglow*—The production of oxygen atoms by the mercury photosensitized decomposition of nitrous oxide is modulated by modulating the mercury resonance radiation and the atom concentration monitored using the reaction  $O + NO \rightarrow NO_2 + h\nu$ . Rate constants are determined from the phase shift between the air afterglow signal and the photolysis radiation [128].

*Flash photolysis-air afterglow*—Atomic oxygen is produced both by the direct flash photolysis of NO and the subsequent reaction  $N + NO \rightarrow N_2 + O$ . The atom concentration is monitored using the reaction  $O + NO \rightarrow NO_2 + h\nu$  [124].

*Flash photolysis-kinetic spectroscopy*—Atomic oxygen is produced by the flash photolysis of a source com-

ound and the reaction monitored by observing the formation of a reaction product, for example CS from  $O + CS_2 \rightarrow CS + SO$ . Relative rate constants are measured by adding a second reactant to compete for the oxygen atoms [55].

*Pulse radiolysis*—A reaction cell is filled to a high pressure, typically 5 MNm<sup>-2</sup>, with a dilute mixture of CO<sub>2</sub> and an organic reactant. An electron pulse impinging on the reaction cell through an aluminum window produces oxygen atoms. Rate constants are determined by measuring the rate of formation of a transient species using absorption spectroscopy [67].

*Flame structure*—Rate constants are determined by measuring the rate of disappearance of hydrocarbon in a premixed hydrocarbon-oxygen-hydrogen flame. The rate constant is determined by relating this rate to the calculated concentration of atomic oxygen [70].

*Ignition limits*—A mixture of CO, O<sub>2</sub>, and an organic reactant is heated and the ignition limit determined. If the mechanism of the primary oxygen atom-hydrocarbon reaction is known, the rate constant may be determined [62].

*Shock tube*—A mixture of CO, O<sub>2</sub>, and Ar containing a small amount of hydrocarbon is shock heated and the CO<sub>2</sub> concentration profile measured using infrared emission. Rate constants are calculated from the effect of the hydrocarbon on the CO<sub>2</sub> buildup [105].

*Theoretical*—Rate constants for atomic oxygen destruction reactions determined using the bond energy-bond order (BEBO) method [69].

### 1.5. Criteria for Evaluation

The tables of rate data contain material from many sources, both absolute and relative in nature. In choosing a recommended rate constant, we have in general given greater weight to absolute rate measurements. In turn, we have given greatest weight to absolute measurements based on a measurement of the rate of reactant loss rather than on the rate of formation of products. It is not always clear that a measured or reported rate constant refers to an elementary reaction. In some cases, it is necessary either to know, or to make assumptions about the nature of subsequent reactions before the primary reaction rate constant can be determined. Thus if a rate constant is based on the rate of decay of a reactant which is consumed in a secondary reaction, then the measured rate constant must be corrected by means of a stoichiometry factor or chain length in order to arrive at the correct rate constant for the primary reaction. Unrecognized secondary reactions which contribute to the decay of a reactant being measured would lead to erroneous results. In this evaluation, a primary criterion for the use of a set of rate data in choosing recommended values is the degree to which the experimental conditions are clearly defined. All rate data based on the collection and analysis of the final products of reactions from discharge-flow systems have been re-

jected. In such experiments the nature of the final products usually depends upon a complex multistep mechanism. The present knowledge of such systems is, in most cases, inadequate to relate directly the final products observed in a discharge-flow system to the primary atom-molecule reactions. A more detailed discussion of the choice of recommended values will be found in part 3. More general discussions of experimental methods which have been used in these studies and the mechanisms of the reactions of atomic oxygen with organic compounds can be found elsewhere [63, 117, and 202].

### 1.6. Units

SI (Système International) units are used throughout. Rate constants are reported in units of cubic centimeters per mole per second. The temperature dependence of the rate constant is given only in the form of the Arrhenius equation  $k = A \exp(-E/RT)$ , in which the activation energy  $E$  is replaced by the quantity  $E/R$  in units of absolute temperature.

Conversion factors used are as follows:

$$R = 8.314 \text{ J deg}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$1 \text{ cal mol}^{-1} = 4.184 \text{ J mol}^{-1}$$

### 1.7. Concluding Remarks

Measurement techniques in the field of gas kinetics have reached the point at which accuracy statements

approaching  $\pm 10$  percent are becoming credible. There are, however, several cases in which reported rate constants from different laboratories, each with an expected experimental uncertainty of about 10 percent, differ by as much as an order of magnitude. Unfortunately, we have not always been able to determine the causes of these discrepancies and unambiguously choose the better data. The areas of disagreement are discussed more fully elsewhere [202]. In some cases, therefore, our choice of a recommended rate constant was based on the total volume of data or the general consistency of an experimental technique when applied to a whole class of reactions. Newer and better measurements may prove us wrong. We recognize that our own involvement in the measurement of many rate constants reported here could lead to bias in the choice of recommended values. We know of no solution to this problem other than the criticism of the producers of the data and the users of these tables.

We thank Kay V. Fadely, Larry Ketron, and Margaret J. Moore for their assistance in the preparation of this compilation. The advice and encouragement of David Garvin, Lewis H. Gevantman and Henry M. Rosenstock are gratefully acknowledged. We also thank R. J. Cvitanovic for permission to use data prior to publication.

## 2. Recommended Values

In this section we give recommended rate constants for the reactions of atomic oxygen with organic compounds. These values are based upon an evaluation of the data given in detail in parts 3 and 4 of this work.

The basis for the selection of data used in arriving at a recommended value is found in part 3. Arrhenius plots, where given, are also given in part 3.

TABLE I. Recommended rate constants for the reactions of atomic oxygen with alkanes

Reactant	$T, \text{ K}$	Rate constant, $\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Error limits		Bibliography
			Upper	Lower	
Methane	350–1000	$2.1 \times 10^{13} \exp(-4550/T)$	1.3	0.7	1, 3, 4*, 5*, 6,
	1000	$2.2 \times 10^{11}$	1.3	0.7	9, 29*, 69,
	298	$\sim 1 \times 10^7$ <sup>a</sup>	2	0.3	70, 75*, 84,
Ethane	298–650	$2.5 \times 10^{13} \exp(-3200/T)$	1.3	0.7	6, 9*, 13, 60*,
	1000	$1.0 \times 10^{12}$ <sup>a</sup>	1.5	0.6	61, 69, 75*,
	298	$5.5 \times 10^8$	1.3	0.7	99*, 133
Propane	298	$9 \times 10^9$	2	0.7	13*, 62, 119, 129*
<i>n</i> -Butane	298–650	$3.0 \times 10^{13} \exp(-2920/T)$ $+ 4.6 \times 10^{13} \exp(-2410/T)$ <sup>b</sup>	1.3	0.7	7, 8, 10*, 58, 60*, 62, 98,
	1000	$5.8 \times 10^{12}$ <sup>a</sup>	1.5	0.6	119, 129,
	298	$1.6 \times 10^{10}$	1.3	0.7	133

TABLE 1. Recommended rate constants for the reactions of atomic oxygen with alkanes—Continued

Reactant	T, K	Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Error limits		Bibliography
			Upper	Lower	
<i>n</i> -Pentane	298–650	$2.9 \times 10^{13} \exp(-2920/T) + 8.0 \times 10^{13} \exp(-2320/T)$ <sup>b</sup>	1.3	0.7	60*
	1000	$9.6 \times 10^{12}$ <sup>a</sup>	1.5	0.6	
	298	$3.5 \times 10^{10}$	1.3	0.7	
2,2-Dimethylpropane	298–650	$5.9 \times 10^{13} \exp(-2920/T)$	1.4	0.7	7, 60*
	1000	$3.2 \times 10^{12}$ <sup>a</sup>	1.5	0.6	
	298	$3.3 \times 10^9$	1.4	0.7	
2-Methylbutane	307	$8.0 \times 10^{10}$	1.4	0.7	60*
<i>n</i> -Hexane	298–650	$2.9 \times 10^{13} \exp(-2920/T) + 1.1 \times 10^{14} \exp(-2250/T)$ <sup>b</sup>	1.3	0.7	60*
	1000	$1.3 \times 10^{13}$ <sup>a</sup>	1.5	0.6	
	298	$5.6 \times 10^{10}$	1.3	0.7	
2,3-Dimethylbutane	298–650	$5.9 \times 10^{13} \exp(-2920/T) + 3.1 \times 10^{13} \exp(-1650/T)$ <sup>c</sup>	1.3	0.7	60*
	1000	$9.1 \times 10^{12}$ <sup>a</sup>	1.6	0.5	
	298	$1.2 \times 10^{11}$	1.3	0.7	
<i>n</i> -Heptane	298–650	$2.9 \times 10^{13} \exp(-2920/T) + 1.2 \times 10^{14} \exp(-2190/T)$ <sup>b</sup>	1.3	0.7	58, 60*
	1000	$1.5 \times 10^{13}$ <sup>a</sup>	1.5	0.6	
	298	$7.7 \times 10^{10}$	1.3	0.7	
2,2-Dimethylpentane	307	$6.5 \times 10^{10}$	1.4	0.7	60*
2,4-Dimethylpentane	307	$1.0 \times 10^{11}$	1.4	0.7	60*
<i>n</i> -Octane	298–650	$2.9 \times 10^{13} \exp(-2920/T) + 9.3 \times 10^{13} \exp(-2030/T)$ <sup>b</sup>	1.3	0.7	2, 60*
	1000	$1.3 \times 10^{13}$ <sup>a</sup>	1.5	0.6	
	298	$1.0 \times 10^{11}$	1.3	0.7	
2,2,4-Trimethylpentane	307	$5.5 \times 10^{10}$	1.5	0.6	58, 60*
2,3,4-Trimethylpentane	307	$3 \times 10^{10}$	1.5	0.6	60*
2,2,3,3-Tetramethylbutane	307	$8 \times 10^9$	1.5	0.6	60*

<sup>a</sup> Note that this value is based on an extrapolation.<sup>b</sup> The rate constant is given as the sum of the rate constants for abstraction of primary and secondary hydrogen atoms. See section 3.1.<sup>c</sup> The rate constant is given as the sum of the rate constants for abstraction of primary and tertiary hydrogen atoms. See section 3.1.

TABLE 2. Recommended rate constants for the reactions of atomic oxygen with cycloalkanes

Reactant	T, K	Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Error limits		Bibliography
			Upper	Lower	
Cyclopropane	298	$5 \times 10^8$	2.0	0.5	12*, 13*, 88
Cyclobutane	298	$7 \times 10^9$	2.0	0.5	12*
Cyclopentane	298–650	$1.3 \times 10^{14} \exp(-2210/T)$	1.3	0.7	12, 102*
	1000	$1.4 \times 10^{13}$ <sup>a</sup>	1.5	0.6	
	298	$7.5 \times 10^{10}$	1.3	0.7	
Spiropentane	298–650	$4.0 \times 10^{13} \exp(-2890/T)$	1.3	0.7	102*
	1000	$2.2 \times 10^{12}$ <sup>a</sup>	1.5	0.6	
	298	$2.5 \times 10^9$	1.4	0.7	
Cyclohexane	298–650	$2.2 \times 10^{14} \exp(-2350/T)$	1.3	0.7	12, 47, 102*
	1000	$2.1 \times 10^{13}$ <sup>a</sup>	1.5	0.6	
	298	$8.3 \times 10^{10}$	1.3	0.7	

TABLE 2. Recommended rate constants for the reactions of atomic oxygen with cycloalkanes—Continued

Reactant	<i>T</i> , K	Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Error limits		Bibliography
			Upper	Lower	
Cycloheptane	298–650	$2.9 \times 10^{14} \exp(-2230/T)$	1.3	0.7	102*
	1000	$3.1 \times 10^{10}^a$	1.5	0.6	
	298	$1.6 \times 10^{11}$	1.5	0.7	

<sup>a</sup> Note that this value is based on an extrapolation.

TABLE 3. Recommended rate constants for the reactions of atomic oxygen with haloalkanes

Reactant	<i>T</i> , K	Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Error limits		Bibliography
			Upper	Lower	
Chloromethane	350–1000	$1.7 \times 10^{13} \exp(-3690/T)$	1.3	0.7	53*, 76*
	1000	$4.3 \times 10^{11}$	1.3	0.7	
	298	$7.2 \times 10^7^a$	1.5	0.6	
Bromomethane	350–1000	$3.0 \times 10^{13} \exp(-3800/T)$	2.0	0.5	53*, 76*
	1000	$7 \times 10^{11}$	2.0	0.5	
Tetrachloromethane	270–380	$2.0 \times 10^{10} \exp(-2260/T)$	1.5	0.6	42*, 84
	298	$1.2 \times 10^7$	1.5	0.6	
Chloroethane	340–650	$4.8 \times 10^{13} \exp(-3330/T)$	1.3	0.7	76*
	1000	$1.7 \times 10^{12}^a$	1.5	0.6	
	298	$6.7 \times 10^8^a$	1.5	0.6	
Bromoethane	340–650	$3.1 \times 10^{13} \exp(-3260/T)$	1.3	0.7	76*
	1000	$1.2 \times 10^{12}^a$	1.5	0.6	
	298	$5.6 \times 10^8^a$	1.5	0.6	
2-Chloropropane	340–650	$2.6 \times 10^{13} \exp(-2620/T)$	1.3	0.7	76*
	1000	$1.9 \times 10^{12}^a$	1.5	0.6	
	298	$4.0 \times 10^9^a$	1.5	0.6	
2-Bromopropane	340–650	$2.3 \times 10^{13} \exp(-2700/T)$	1.3	0.7	76*
	1000	$1.6 \times 10^{12}^a$	1.5	0.6	
	298	$2.8 \times 10^9^a$	1.5	0.6	
2-Chlorobutane	340–650	$3.6 \times 10^{13} \exp(-2530/T)$	1.3	0.7	76*
	1000	$2.8 \times 10^{12}^a$	1.5	0.6	
	298	$7.2 \times 10^9^a$	1.5	0.6	
1-Chloro-2-methylpropane	340–650	$3.6 \times 10^{13} \exp(-2520/T)$	1.3	0.7	76*
	298	$7.7 \times 10^9^a$	1.5	0.6	
2-Chloro-2-methylpropane	340–650	$2.6 \times 10^{13} \exp(-3010/T)$	1.3	0.7	76*
	1000	$1.3 \times 10^{12}^a$	1.5	0.6	
	298	$1.1 \times 10^9^a$	1.5	0.6	
1-Bromobutane	340–650	$4.4 \times 10^{13} \exp(-2680/T)$	1.3	0.7	76*
	1000	$3.0 \times 10^{12}^a$	1.5	0.6	
	298	$5.5 \times 10^9^a$	1.5	0.6	
1-Bromo-2-methylpropane	340–600	$3.4 \times 10^{13} \exp(-2510/T)$	1.3	0.7	76*
	298	$7.4 \times 10^9^a$	1.5	0.6	
1-Chloro-2,2-dimethylpropane	340–650	$3.2 \times 10^{13} \exp(-2670/T)$	1.3	0.7	76*
	1000	$2.2 \times 10^{12}^a$	1.5	0.6	
	298	$4.0 \times 10^9^a$	1.5	0.6	
1-Chloroheptane	298	$8 \times 10^{10}$	1.5	0.6	76*

<sup>a</sup> Note that this value is based on an extrapolation.

TABLE 4. Recommended rate constants for the reactions of atomic oxygen with alkenes, alkadienes, and cycloalkenes

Reactant	T, K	Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Error limits		Bibliography
			Upper	Lower	
Ethylene	200-500	$3.3 \times 10^{12} \exp(-565/T)$	1.2	0.8	10, 19, 25, 29, 57, 68, 71, 72, 87, 104,* 126, 128, 150, 199
	298	$4.9 \times 10^{11}$	1.2	0.8	
Propene	200-500	$2.5 \times 10^{12} \exp(-38/T)$	1.2	0.8	13, 14, 44, 57, 79, 126, 128, 149*, 150, 166, 199
	298	$2.2 \times 10^{12}$	1.2	0.8	
1-Butene	180-500	$2.3 \times 10^{12} \exp(-25/T) + 9.6 \times 10^{12} \exp(-990/T)^a$	1.2	0.8	11, 13, 14, 16, 19, 26, 128, 150, 166*, 199
	298	$2.3 \times 10^{12}$	1.2	0.8	
<i>cis</i> -2-Butene	250-500	$5.9 \times 10^{12} \exp(+165/T)$	1.2	0.8	2, 14, 19, 127, 128, 130*
	298	$1.0 \times 10^{13}$			
<i>trans</i> -2-Butene	298	$1.4 \times 10^{13}$	1.3	0.7	2, 14,* 92, 127*
2-Methylpropene	298	$1.2 \times 10^{13}$	1.3	0.7	11*, 14*, 19, 26*, 55*, 57, 128, 150, 199
1,3-Butadiene	298-400	$3.4 \times 10^{12} \exp(+380/T)$	1.3	0.7	121*
	298	$1.2 \times 10^{13}$	1.3	0.7	
1-Pentene	298	$2.8 \times 10^{12}$	1.3	0.7	17*
<i>cis</i> -2-Pentene	298	$1.1 \times 10^{13}$	1.3	0.7	14*, 17*
2-Methyl-2-butene	298-400	$3.9 \times 10^{12} \exp(+680/T)$	1.3	0.7	11*, 199
	298	$3.8 \times 10^{13}$	1.3	0.7	
1-Hexene	298	$3.1 \times 10^{12}$	1.3	0.7	127*
2,3-Dimethyl-2-butene	298-400	$3.4 \times 10^{12} \exp(+790/T)$	1.2	0.8	11, 14, 130* 199
	298	$4.8 \times 10^{13}$	1.2	0.8	
Cyclopentene	298-400	$3.3 \times 10^{12} \exp(+430/T)$	1.3	0.7	11*
	298	$1.4 \times 10^{13}$	1.3	0.7	
Cyclohexene	298-400	$2.8 \times 10^{12} \exp(+460/T)$	1.3	0.7	11*
	298	$1.3 \times 10^{13}$	1.3	0.7	

<sup>a</sup>The rate constant is given as the sum of two rate constants. See section 3.4.

TABLE 5. Recommended rate constants for the reactions of atomic oxygen with haloalkenes and haloalkadienes

Reactant	T, K	Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Error limits		Bibliography
			Upper	Lower	
Fluoroethylene	307	$2.6 \times 10^{11}$	1.3	0.7	77*
Chloroethylene	307	$5.2 \times 10^{11}$	1.3	0.7	77*
Bromoethylene	307	$4.9 \times 10^{11}$	1.3	0.7	77*
1,1-Difluoroethylene	307	$2.2 \times 10^{11}$	1.3	0.7	77*
1,2-Difluoroethylene	307	$2.7 \times 10^{11}$	1.3	0.7	77*
Tetrafluoroethylene	298-500	$7.7 \times 10^{11} \exp(-100/T)$	1.4	0.7	13*, 16*, 32
	298	$5 \times 10^{11}$	1.4	0.7	

TABLE 5. Recommended rate constants for the reactions of atomic oxygen with haloalkenes and haloalkadienes—Con.

Reactant	T, K	Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Error limits		Bibliography
			Upper	Lower	
2-Fluoropropene	296	$1.2 \times 10^{12}$	1.4	0.7	79*, 83*
3-Fluoropropene	296	$5.1 \times 10^{11}$	1.4	0.7	79*, 83*
1,1-Difluoropropene	296	$1.1 \times 10^{12}$	1.4	0.7	79*, 83*
3,3,3-Trifluoropropene	296	$2.6 \times 10^{10}$	1.4	0.7	44*, 79*, 83*
Hexafluoropropene	298–500 298	$3.6 \times 10^{11} \exp(-900/T)$ $1.7 \times 10^{10}$	1.4 1.4	0.7 0.7	13*, 15*
4-Fluoro-1-butene	296	$1.5 \times 10^{12}$	1.4	0.7	79*, 83
1,1,2-Trifluoro-1-butene	296	$2.0 \times 10^{12}$	1.4	0.7	79*, 83
2-Trifluoromethylpropene	296	$2.0 \times 10^{11}$	1.4	0.7	44*, 79*, 83*
1,3-Hexafluorobutadiene	305	$2.5 \times 10^{11}$	1.4	0.7	129*

TABLE 6. Recommended rate constants for the reactions of atomic oxygen with alkynes and alkadiynes

Reactant	T, K	Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Error limits		Bibliography
			Upper	Lower	
Acetylene	200–700	$1.4 \times 10^{13} \exp(-1500/T)$	1.2	0.8	13, 29*, 30*,
	1000	$3.3 \times 10^{12}$ <sup>a</sup>	1.4	0.7	31, 33*, 35*,
	298	$9.5 \times 10^{10}$	1.1	0.9	36, 37*, 51*, 56, 80*, 86*, 89, 91, 126*
Propyne	298	$4 \times 10^{11}$	2.0	0.5	29*
Butadiyne	300	$9 \times 10^{11}$	1.4	0.7	34*, 35*

<sup>a</sup> Note that this value is based on an extrapolation.

TABLE 7. Recommended rate constants for the reactions of atomic oxygen with benzene, substituted benzenes and pyridine

Reactant	T, K	Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Error limits		Bibliography
			Upper	Lower	
Benzene	250–500	$2.0 \times 10^{13} \exp(-2000/T)$	2.0	0.3	45, 47, 67*,
	298	$2.4 \times 10^{10}$	2.0	0.3	187*
Fluorobenzene	298	$2.7 \times 10^{10}$	2.0	0.5	67*, 90
Chlorobenzene	298	$3.1 \times 10^{11}$	2.0	0.5	67*
Toluene	298	$1.4 \times 10^{11}$	2.0	0.5	52*, 67*, 90
Ethylbenzene	298	$3.2 \times 10^{11}$	2.0	0.5	67*, 90
1,2-Dimethylbenzene	298	$6.7 \times 10^{11}$	2.0	0.5	67*, 90
1,3-Dimethylbenzene	298	$7.7 \times 10^{11}$	2.0	0.5	67*, 90
1,4-Dimethylbenzene	298	$4.5 \times 10^{11}$	2.0	0.5	67*, 90
Pyridine	298	$1.0 \times 10^{11}$	2.0	0.5	67*

TABLE 8. Recommended rate constants for the reactions of atomic oxygen with alcohols, aldehydes, and miscellaneous oxygen-containing compounds

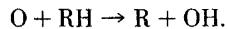
Reactant	T, K	Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Error limits		Bibliography
			Upper	Lower	
Ethanol	298	$8.7 \times 10^{10}$	1.5	0.6	40, 59*, 65
Isopropanol	298	$1.3 \times 10^{11}$	1.5	0.6	39*
Ketene	298	$5.3 \times 10^{11}$	1.3	0.7	82*
Ethylene oxide	298	$7 \times 10^8$	1.5	0.6	58*
Formaldehyde	300	$9.0 \times 10^{10}$	1.3	0.7	78*, 105
Monodeuteroformaldehyde	300	$4.9 \times 10^{10}$	1.3	0.7	35*, 51*
Dichloroformaldehyde	292	$6 \times 10^9$	2.0	0.5	42*, 77
Acetaldehyde	298–500	$1.4 \times 10^{13} \exp(-1140/T)$	2.0	0.5	41, 46*, 50*
	298	$3.1 \times 10^{11}$	2.0	0.5	66
Dimethyl ether	200–500	$5.9 \times 10^{12} \exp(-1520/T)$	1.3	0.7	48, 49, 58, 92,
	298	$3.4 \times 10^{10}$	1.3	0.7	141*

### 3. Absolute Rate Constants

#### 3.1. Alkanes

The only directly measured rate constants for these reactions have been obtained using discharge flow systems employing electron spin resonance, mass spectrometry or NO chemiluminescence detection techniques. In addition there are data derived from relative rate measurements obtained using both flow and static techniques. Where the data overlap, the rate constants are, in general, in agreement within the experimental error limits of the techniques. In some of the flow system measurements, higher rate constants were measured at the lower temperatures than would be predicted by an extrapolation from the higher temperature points. This effect was possibly due to reactions at the surface of the flow tube. For this reason, the low temperature data have been treated with caution.

The reactions of atomic oxygen with alkanes are interpreted in terms of a hydrogen atom abstraction mechanism, i.e.,



In general, the rate constant for an abstraction reaction depends on the strength of the C–H bond broken. Thus the rate constants for abstraction of primary, secondary, and tertiary H-atoms are expected to be in the order tertiary > secondary > primary. For an alkane having more than one kind of C–H bond the Arrhenius plot (i.e. a plot of the logarithm of the total rate constant vs  $1/T$ ) will therefore normally be curved, the degree of curvature depending both on the kinds and number of C–H bonds. There are no product analysis data available with which to determine directly the relative contribu-

tions due to abstraction at different C–H bond sites. A non-linear Arrhenius plot, however, can be represented as a sum of linear Arrhenius plots corresponding to abstraction of primary, secondary, or tertiary hydrogen atoms. Thus, 2,2-dimethylpropane, which has 12 primary hydrogens only, was chosen as the prototype primary hydrogen abstraction reaction. The rate constant for this reaction, corrected for the relative number of primary hydrogen atoms, was subtracted from the overall rate constants for the other alkanes and thereby the rate constants corresponding to abstraction from the other C–H sites were obtained. The magnitude of the contributions from different bond types is indicated in the Arrhenius plots. For the *n*-alkanes, the upper curve represents the total rate constant and the lower the total rate constant for reaction at secondary C–H bond sites. For 2,3-dimethylbutane the upper curve again represents the total rate constant while the lower represents the total rate constant for reaction at tertiary C–H bond sites.

It should be emphasized that non-linear Arrhenius plots can arise for reasons other than reaction at different C–H bond sites, and that there is no theoretical reason to expect that Arrhenius plots should be linear.

The data on methane and ethane have been evaluated recently [99], and that evaluation is accepted here. For the larger alkanes, the most extensive set of data is that of Herron and Huie [60] which is the basis for the recommended rate constants for most of these compounds. In those cases where more than one kind of C–H bond is involved, the rate constant is expressed as a sum of the rate constants for reaction at the different C–H bond sites.

TABLE 9. Rate constants for the reaction of atomic oxygen with methane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$2.0 \times 10^{13}$ $\exp(-4630/T)$		297-904	75 <sup>a,b,*</sup>	Discharge flow - e.s.r.
$1.33 \pm 0.02 \times 10^7$	4	297		
$9.7 \pm 0.3$	4	363		
$3.6 \pm 0.1 \times 10^8$	4	419		
$2.6 \pm 0.1 \times 10^9$	4	516		
$1.15 \pm 0.03 \times 10^{10}$	3	605		
$1.37 \pm 0.05 \times 10^{11}$	4	904		
$1 \times 10^{14}$ $\exp(-5000/T)$		388-555	4 <sup>a,c,d,*</sup>	Discharge flow - mass spectrometry
$2.0 \times 10^8$	9	388		
$8.9$	6	477		
$2.3 \times 10^9$	6	494		
$1.1 \times 10^{10}$	7	555		
$(7.1 \pm 3.5) \times 10^{12}$ $\exp(-3670 \pm 750/T)$		295-533	5 <sup>a,d,e,*</sup>	Discharge flow - air afterflow
$2.2 \times 10^7$		295		
$6.8$		368		
$1.1 \times 10^9$		485		
$4.2$		533		
$(7 \pm 2) \times 10^{12}$ $\exp(-3870 \pm 150/T)$		439-592	29 <sup>a,c,*</sup>	Discharge flow - e.s.r.
$1.2 \times 10^9$	3	459		
$2.2$	3	498		
$4.5$	3	546		
$8.4$	3	592		
$4 \pm 1.2 \times 10^8$		300	84	Discharge flow - e.s.r.
$2.0 \times 10^{13}$ $\exp(-3920/T)$		375-583	6	Discharge flow - final products
$5.8 \times 10^8$		375		
$3.6 \times 10^9$		438		
$9.9$		525		
$2.8 \times 10^{10}$		583		
$(5.6 \pm 2.4) \times 10^{13}$ $\exp(-4380 \pm 400/T)$		843-933	1	Ignition limits
$1.6 \times 10^{14}$ $\exp(-4000/T)$		1750-2575	105	Shock tube
$2.0 \times 10^7$		300	69	Theoretical
$1.0 \times 10^{12}$		1000		
$2.1 \times 10^{13}$ $\exp(-4550/T)$		350-1000	table 1	Recommended value
$2.2 \times 10^{11}$		1000		
$\sim 1 \times 10^7$		298		

<sup>a</sup> Individual rate constants are the reported overall rate constants divided by 3.8.

<sup>b</sup> Supersedes data given in reference [9].

<sup>c</sup> Data reported in graphical form only.

<sup>d</sup> Supersedes data given in reference [3].

<sup>e</sup> Data obtained in presence of molecular oxygen are not given.

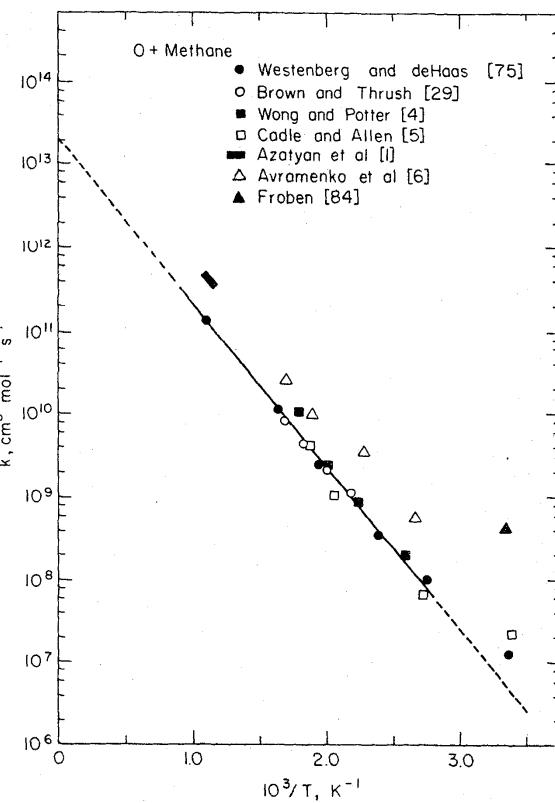


FIGURE 1. Arrhenius plot for the reaction of atomic oxygen with methane.

TABLE 10. Rate constants for the reaction of atomic oxygen with ethane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$1.8 \times 10^{13}$ $\exp(-3070/T)$		320-589	9 <sup>a,*</sup>	Discharge flow - e.s.r.
$1.2 \times 10^9$	2	320		
$1.5$	4	328		
$5.1 \pm 0.5$	5	378		
$1.1 \times 10^{10}$	3	424		
$4.0$		502		
$1.2 \times 10^{11}$	3	573		
$1.4 \pm 0.1$	5	589		
$3.5 \times 10^8$		272	75 <sup>a,b,*</sup>	Discharge flow - e.s.r.
$7.7$		300		
$2.0 \times 10^9$		338		
$1.0 \times 10^{11}$		615		
$5.4 \times 10^{12}$ $\exp(-2620/T)$	313	503	6	Discharge flow - final products
$1.3 \times 10^9$		313		
$2.0 \times 10^{10}$		468		
$2.9$		503		
$1.9 \times 10^9$	2	336	60 <sup>c,*</sup>	Discharge flow - mass spectrometry
$1.4 \times 10^{10}$	1	429		
$5.1$	1	508		
$2.0 \times 10^{11}$	1	595		

TABLE 10. Rate constants for the reaction of atomic oxygen with ethane—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
(8.4 ± 3.6) × 10 <sup>13</sup> exp (-3770 ± 300/T)		853–933	61	Ignition limits
6.3 × 10 <sup>8</sup>		300	69	Theoretical
5.0 × 10 <sup>12</sup>		1000		
2.1 × 10 <sup>9</sup>	2	297	13 <sup>d</sup>	Hg photosens.
5.3	4	343		decomp. of
1.1 × 10 <sup>10</sup>	4	398		N <sub>2</sub> O
2.8 <sup>+1.3</sup> × 10 <sup>13</sup> exp (-3270 ± 130/T)		303–364	133 <sup>b</sup>	
5.6 × 10 <sup>8</sup>		303		Discharge flow—
9.5		315		air afterglow
1.5 × 10 <sup>9</sup>		330		
2.1		341		
3.2		355		
3.4		364		
2.5 × 10 <sup>13</sup> exp (-3200/T)		298–650	table 1	Recommended value
1.0 × 10 <sup>12</sup>		1000		
5.5 × 10 <sup>8</sup>		298		

<sup>a</sup> Individual rate constants are the reported overall rate constants divided by 6.5.

<sup>b</sup> Data reported in graphical form only.

<sup>c</sup> Reactant C<sub>2</sub>H<sub>5</sub>D.

<sup>d</sup> Relative rate measurements, see table 59.

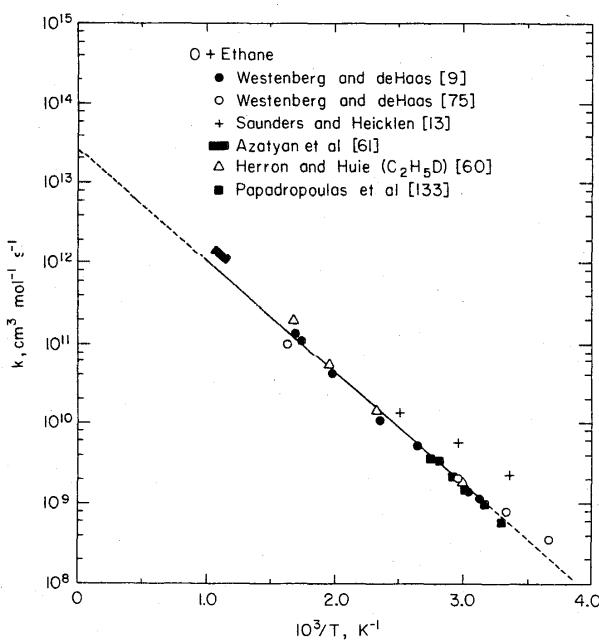


FIGURE 2. Arrhenius plot for the reaction of atomic oxygen with ethane.

TABLE 11. Rate constants for the reaction of atomic oxygen with n-butane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
(3.0 ± 1.0) × 10 <sup>13</sup> exp (-2110/T)		231–433	10*	Discharge flow—air afterglow
3.4 × 10 <sup>9</sup>	1	231		
6.3	1	246		
9.5	1	259		
1.4 × 10 <sup>10</sup>	1	280		
3.0	1	309		
4.8	1	330		
8.3	1	353		
1.06 × 10 <sup>11</sup>	2	373		
1.67	1	433		
2.9 <sup>+1.4</sup> × 10 <sup>13</sup> exp (-2920 ± 140/T) + 6.3 <sup>+1.4</sup> × 10 <sup>13</sup> exp (-2570 ± 80/T)		307–607	60*	Discharge flow—mass spectrometry
4.14 × 10 <sup>9</sup>				255
6.35				276
1.18 × 10 <sup>10</sup>				276
1.25				276
2.21				307
1.44				307
1.59				307
4.44				357
6.31				357
4.83				357
1.01 × 10 <sup>11</sup>				386
2.42				441
4.82				513
6.36				532
1.24 × 10 <sup>12</sup>				595
1.12				603
1.00				607
6.6 × 10 <sup>13</sup> exp (-2320 ± 500/T)		850–930	62	Ignition limits
7.8 × 10 <sup>13</sup> exp (-2100 ± 250/T)		870–920	119	Ignition limits
6.6 × 10 <sup>9</sup>		293	7	Discharge flow—final products
7.8 × 10 <sup>12</sup> exp (-2060/T)		313–468	8	Discharge flow—final products
1.1 × 10 <sup>10</sup>				313
3.3				378
6.0				423
1.0 × 10 <sup>11</sup>				468
1.3 × 10 <sup>10</sup>	5	307	58 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O
2.6	4	343		
5.0	5	398		
2.2 × 10 <sup>10</sup>		297	98 <sup>b</sup>	Hg photosens. decomp. of N <sub>2</sub> O
2.4 × 10 <sup>10</sup>		305	129 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O

TABLE 11. Rate constants for the reaction of atomic oxygen with *n*-butane—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$1.7_{-0.6}^{+1.3} \times 10^{13}$ $\exp(-2280 \pm 120/T)$		301–368	133 <sup>c</sup>	Discharge flow—air afterglow
$8.2 \times 10^9$		301		
$1.3 \times 10^{10}$		323		
1.9		330		
2.2		342		
2.3		353		
3.2		368		
$3.0 \times 10^{13}$ $\exp(-2920/T)$		298–650	table 1	Recommended value
$+4.6 \times 10^{13}$ $\exp(-2410/T)$				
$5.8 \times 10^{12}$		1000		
$1.6 \times 10^{10}$		298		

<sup>a</sup> Relative rate measurements, see table 59.<sup>b</sup> Relative rate measurements, see table 58.<sup>c</sup> Data reported in graphical form only.TABLE 12. Rate constants for the reaction of atomic oxygen with *n*-pentane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$2.9_{-1.6}^{+1.4} \times 10^{13}$ $\exp(-2920 \pm 140/T) +$ $8.0_{-1.5}^{+1.8} \times 10^{13}$ $\exp(-2320 \pm 80/T)$		307–597	60*	Discharge flow—mass spectrometry
$1.53 \times 10^{10}$			255	
1.22			255	
1.32			258	
2.38			276	
2.43			276	
2.06			276	
2.86			276	
4.72			307	
4.02			307	
4.57			307	
6.90			321	
$1.13 \times 10^{11}$			336	
$9.46 \times 10^{10}$			338	
$1.11 \times 10^{11}$			357	

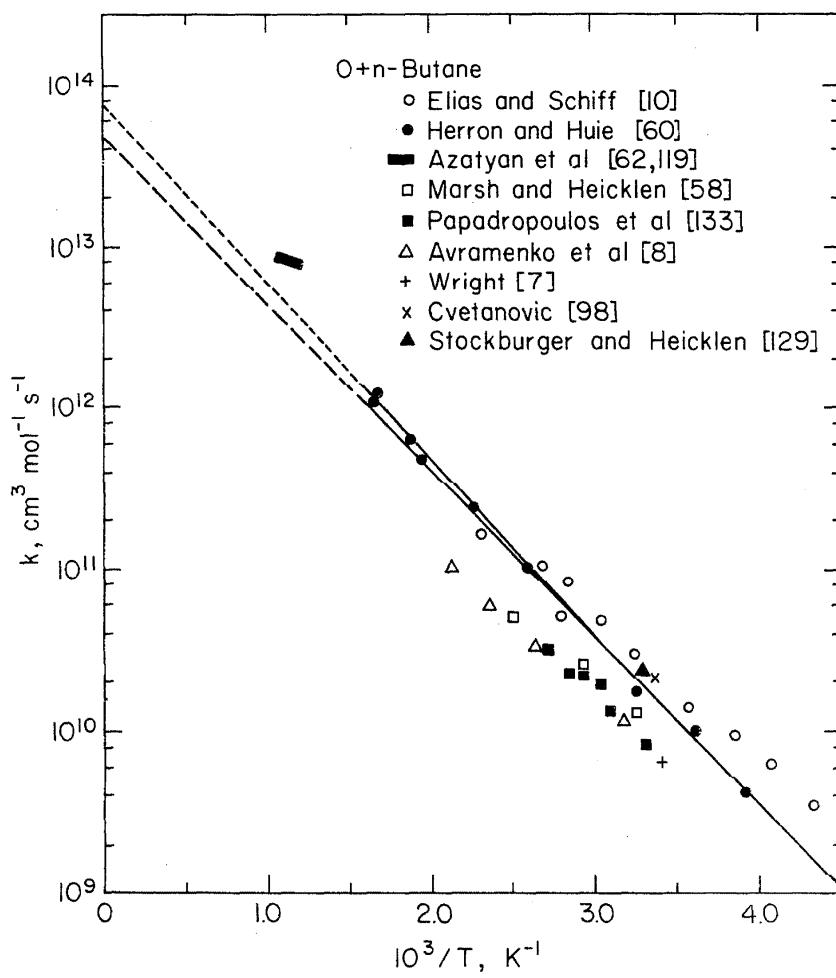
FIGURE 3. Arrhenius plot for the reaction of atomic oxygen with *n*-butane.

TABLE 12. Rate constants for the reaction of atomic oxygen with *n*-pentane—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
2.11		386		
4.30		437		
3.78		437		
4.32		441		
7.23		508		
$1.16 \times 10^{12}$		508		
2.17		593		
1.97		597		

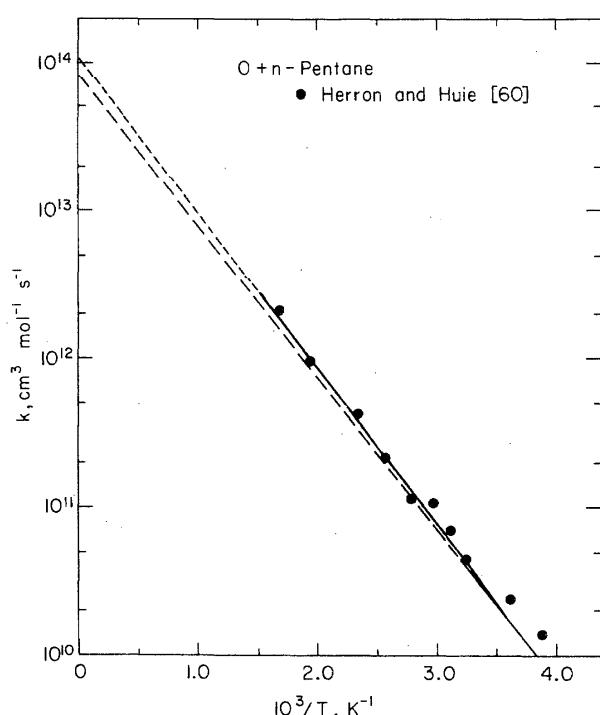
FIGURE 4. Arrhenius plot for the reaction of atomic oxygen with *n*-pentane.

TABLE 13. Rate constants for the reaction of atomic oxygen with 2,2-dimethylpropane—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
5.30		386		
8.29		437		
7.73		437		
9.03		441		
$1.55 \times 10^{11}$		508		
1.95		508		
5.97		593		
5.26		597		
$1.8 \times 10^9$		293	7	Discharge flow—final products

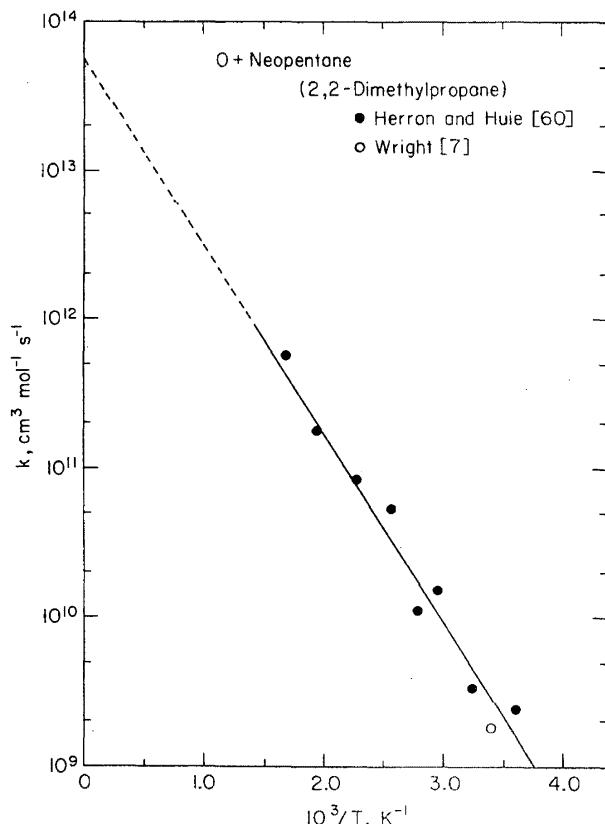


FIGURE 5. Arrhenius plot for the reaction of atomic oxygen with 2,2-dimethylpropane.

TABLE 13. Rate constants for the reaction of atomic oxygen with 2,2-dimethylpropane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$5.9_{-1.9}^{+2.8} \times 10^{13} \exp(-2920 \pm 140/T)$	307-597	60*		Discharge flow—mass spectrometry
$2.50 \times 10^9$		276		
2.55		276		
2.18		276		
3.78		307		
2.94		307		
3.42		307		
3.22		307		
$1.48 \times 10^{10}$		338		
1.09		357		
$8.05 \times 10^9$		357		
$1.14 \times 10^{10}$		357		
1.95		357		

TABLE 14. Rate constants for the reaction of atomic oxygen with *n*-hexane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$2.9_{-1.0}^{+1.4} \times 10^{13} \exp(-2920 \pm 140/T) + 10.7_{-1.9}^{+2.3} \times 10^{13} \exp(-2250 \pm 70/T)$	307-597	60*		Discharge flow—mass spectrometry
$1.95 \times 10^{10}$		247		
2.36		255		
2.37		255		
2.47		258		

TABLE 14. Rate constants for the reaction of atomic oxygen with *n*-hexane—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
3.86		276		
3.53		276		
3.16		276		
3.17		276		
4.15		276		
6.87		307		
6.19		307		
6.55		307		
7.50		307		
9.17		321		
1.46 × 10 <sup>11</sup>		335		
1.75		336		
1.40		338		
2.80		357		
3.18		386		
6.57		437		
6.45		437		
6.07		441		
1.07 × 10 <sup>12</sup>		508		
1.18		508		
3.17		593		
2.99		597		

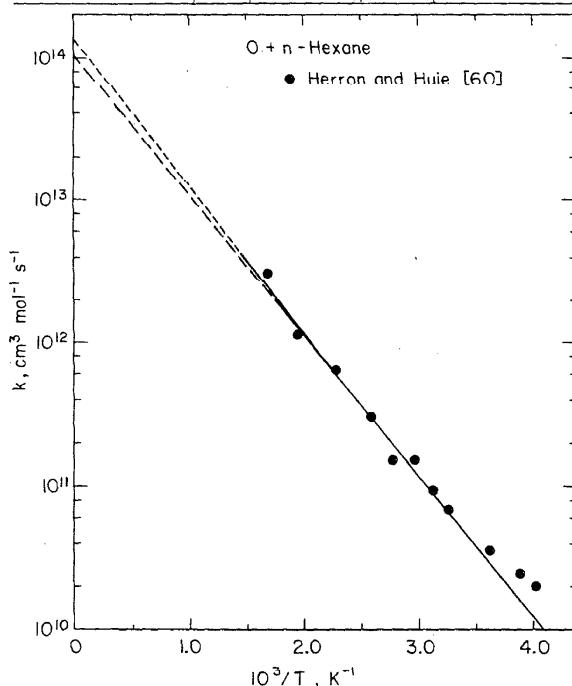
FIGURE 6. Arrhenius plot for the reaction of atomic oxygen with *n*-hexane.

TABLE 15. Rate constants for the reaction of atomic oxygen with 2,3-dimethylbutane—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
6.80 × 10 <sup>10</sup>			247	
7.14			249	
5.48			249	
9.00			254	
8.40			255	
7.23			255	
1.12 × 10 <sup>11</sup>			276	
9.49 × 10 <sup>10</sup>			276	
1.02 × 10 <sup>11</sup>			276	
8.47 × 10 <sup>10</sup>			276	
1.00 × 10 <sup>11</sup>			276	
1.81			307	
1.50			307	
1.61			307	
1.20			307	
1.60			321	
2.47			335	
3.21			336	
2.51			338	
2.80			357	
4.70			386	
3.58			386	
7.19			437	
8.84			437	
7.35			441	
1.09 × 10 <sup>12</sup>			508	
1.65			508	
2.95			593	
2.30			597	

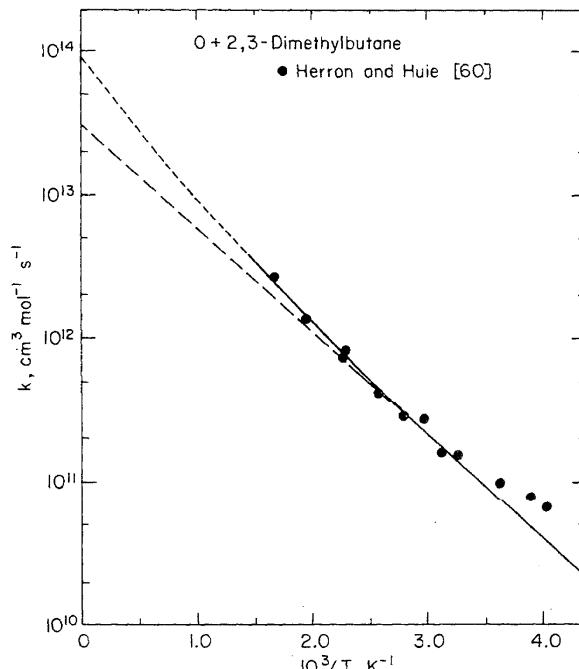


FIGURE 7. Arrhenius plot for the reaction of atomic oxygen with 2,3-dimethylbutane.

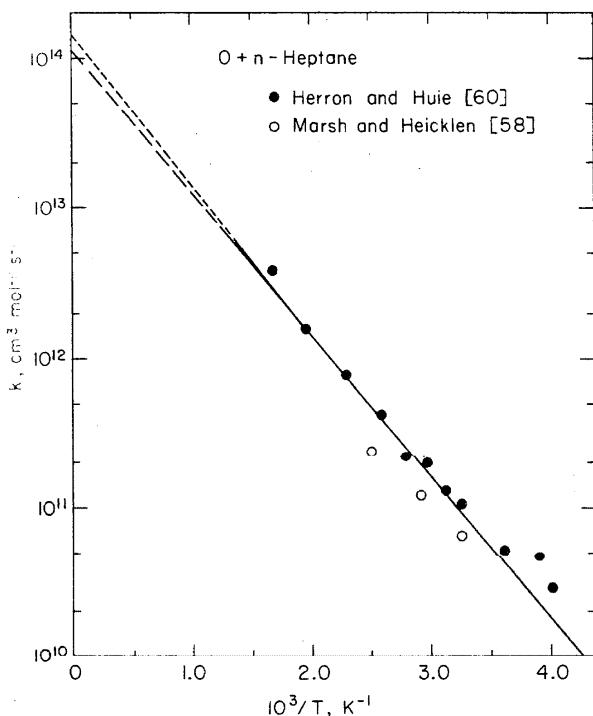


FIGURE 8. Arrhenius plot for the reaction of atomic oxygen with *n*-heptane.

TABLE 16. Rate constants for the reaction of atomic oxygen with *n*-heptane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$2.9^{+1.4}_{-1.0} \times 10^{13} \exp(-2920 \pm 140/T) + 11.9^{+2.4}_{-2.0} \times 10^{13} \exp(-2190 \pm 70/T)$	307-597	60*	Discharge flow—mass spectrometry	
$2.52 \times 10^{10}$	247			
3.23	249			
2.71	249			
5.25	255			
3.85	255			
5.01	255			
5.26	276			
5.80	276			
4.30	276			
4.75	276			
4.60	276			
6.47	276			
$1.12 \times 10^{11}$	307			
$8.97 \times 10^{10}$	307			
$1.04 \times 10^{11}$	307			
1.03	307			
1.27	321			
2.03	335			
2.25	336			
1.66	338			
2.16	357			
4.48	386			
7.96	437			
8.33	437			
6.96	441			
$1.36 \times 10^{12}$	508			

TABLE 16. Rate constants for the reaction of atomic oxygen with *n*-heptane—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
1.81		508		
4.00		593		
3.63		597		
$6.6 \times 10^{10}$	5	307	58 <sup>a</sup>	Hg photosens.
$1.1 \times 10^{11}$	6	343		decomp. of
2.1	5	398		N <sub>2</sub> O

<sup>a</sup> Relative rate measurements, see table 59.

TABLE 17. Rate constants for the reaction of atomic oxygen with *n*-octane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$2.9^{+1.4}_{-1.0} \times 10^{13} \exp(-2920 \pm 140/T) + 9.3^{+1.2}_{-1.1} \times 10^{13} \exp(-2030 \pm 50/T)$		307-597	60*	Discharge flow—mass spectrometry
$4.80 \times 10^{10}$		247		
$1.02 \times 10^{11}$		254		
$9.37 \times 10^{10}$		255		
6.29		255		
6.70		255		
$1.26 \times 10^{11}$		276		
$6.52 \times 10^{10}$		276		
8.52		276		
8.96		276		
2.13		276		
5.74		276		
5.05		276		
5.77		276		
8.12		276		
$1.36 \times 10^{11}$		307		
1.39		307		
1.29		307		
1.09		307		
1.07		307		
1.71		321		
2.73		336		
2.30		338		
3.11		357		
5.02		386		
8.80		437		
8.82		437		
9.22		441		
$1.59 \times 10^{12}$		508		
2.16		508		
3.28		593		
3.26		597		
$1.8 \times 10^{13} \exp(-2110/T)$		353-473	2	Discharge flow—final products
$4.6 \times 10^{10}$		353		
8.4		393		
$1.26 \times 10^{11}$		423		
1.99		473		

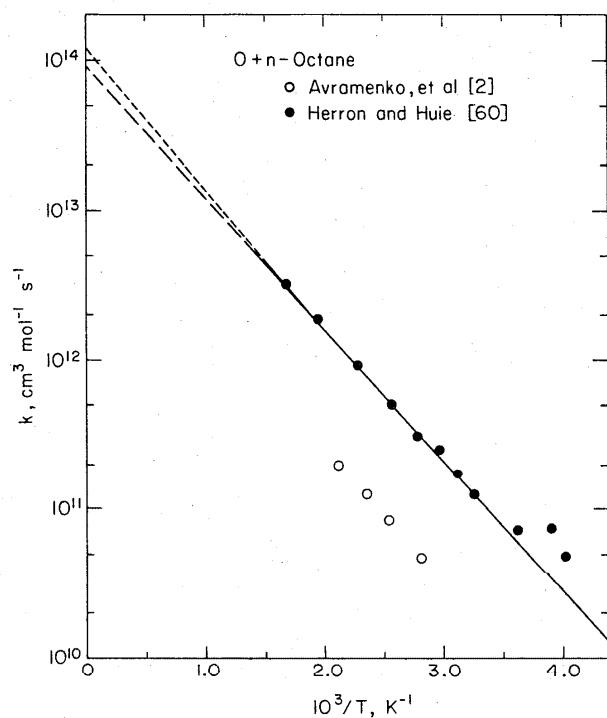


FIGURE 9. Arrhenius plot for the reaction of atomic oxygen with *n*-octane.

TABLE 18. Rate constants for the reaction of atomic oxygen with some miscellaneous alkanes

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
Propane $1.0 \times 10^{14}$ $\exp(-3120 \pm 500/T)$		850-930	62,119	Ignition limits
$8.1 \times 10^9$	3	297	13 <sup>a,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
$1.6 \times 10^{10}$	6	343		
3.7	3	398		
$9.9 \times 10^9$		305	129 <sup>a,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
2-Methylpropane $3.6 \times 10^9$		293	7	Discharge flow— final products
$3.5 \times 10^{10}$		298	164 <sup>b</sup>	Hg photosens. decomp. of N <sub>2</sub> O
2-Methylbutane $8.0 \times 10^{10}$	3	307	60*	Discharge flow— mass spec- trometry
2,2-Dimethylpentane $6.5 \times 10^{10}$	3	307	60*	Discharge flow— mass spec- trometry

TABLE 18. Rate constants for the reaction of atomic oxygen with some miscellaneous alkanes—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
2,4-Dimethylpentane $1 \times 10^{11}$	2	307	60*	Discharge flow— mass spec- trometry
3-Methylheptane $6.5 \times 10^{10}$		300	17	Flow photolysis of NO <sub>2</sub>
$2.6 \times 10^{11}$		298	17 <sup>b</sup>	Hg photosens. decomp. of N <sub>2</sub> O
2,2,4-Trimethyl- pentane $7 \times 10^{10}$	2	307	60*	Discharge flow— mass spec- trometry
$4.0 \times 10^{10}$	6	307	58 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O
5.8	5	343		
$1.1 \times 10^{11}$	6	398		
2,3,4-Trimethyl- pentane $3 \times 10^{11}$	2	307	60*	Discharge flow— mass spec- trometry
2,2,3,3-Tetramethyl- butane $8 \times 10^9$	2	307	60*	Discharge flow— mass spec- trometry

<sup>a</sup>Relative rate measurements, see table 59.

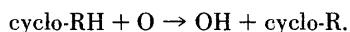
<sup>b</sup>Relative rate measurements, see table 65.

### 3.2. Cycloalkanes

There are essentially two sets of data available on the reactions of atomic oxygen with cycloalkanes, one covering the C<sub>5</sub>-C<sub>7</sub> compounds using discharge-flow techniques, the other covering the C<sub>3</sub>-C<sub>6</sub> compounds using Hg sensitized decomposition of N<sub>2</sub>O as the atom source. Although there is reasonable agreement between the two sets of data at room temperature, the derived Arrhenius parameters are not in such good agreement. Because of their greater temperature range, the discharge flow values are the basis for the recommended values.

The Arrhenius pre-exponential factors per C-H bond, and the activation energies for the reactions of atomic oxygen with cyclopentane, cyclohexane, and cycloheptane are almost identical to those found for abstraction of secondary H atoms from alkanes, which suggests

that the mechanisms in both cases are simple hydrogen atom abstractions



In the case of spiropentane the Arrhenius parameters are very close to those found for abstraction of primary H atoms, a result in accord with the higher C-H bond strength in spiropentane as compared with the larger and less-strained cycloalkanes.

The data on cyclopropane and cyclobutane are not extensive enough to lead to reliable Arrhenius parameters and recommended values are given only at 298 K. These two reactions clearly need further study.

TABLE 19. Rate constants for the reaction of atomic oxygen with cyclopropane and cyclobutane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
Cyclopropane				
5.2 × 10 <sup>8</sup>	3	298	13 a.*	Hg photosens. decomp. of N <sub>2</sub> O
1.2 × 10 <sup>9</sup>	2	343		
2.5	2	398		
4.7 × 10 <sup>8</sup>	7	298	12 a.*	Hg photosens. decomp. of N <sub>2</sub> O
8.9	8	343		
2.0 × 10 <sup>9</sup>	7	398		
5.4 × 10 <sup>8</sup>		298	88 b	Hg photosens. decomp. of N <sub>2</sub> O
Cyclobutane				
7.2 × 10 <sup>9</sup>	6	298	12 a.*	Hg photosens. decomp. of N <sub>2</sub> O
1.7 × 10 <sup>10</sup>	5	343		
3.1	7	398		

a Relative rate measurements, see table 59.

b Relative rate measurements, see table 65.

TABLE 20. Rate constants for the reaction of atomic oxygen with cyclopentane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
1.3 <sup>+0.3</sup> <sub>-0.2</sub> × 10 <sup>14</sup> exp (-2210 ± 100/T)		307-652	102*	Discharge flow— mass spec- trometry
1.22 × 10 <sup>11</sup>		307		
0.99		307		
1.78		331		
1.49		339		
1.50		339		
5.70		415		
6.64		418		
5.01		419		
1.06 × 10 <sup>12</sup>		479		
1.59		493		
2.40		548		
3.36		557		

TABLE 20. Rate constants for the reaction of atomic oxygen with cyclopentane—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
2.13			564	
2.75			631	
5.41			647	
4.07			652	
5.2 × 10 <sup>10</sup>	6	298	12 <sup>a</sup>	Hg photosens.
8.2	8	343		decomp. of N <sub>2</sub> O
1.3 × 10 <sup>11</sup>	5	398		

<sup>a</sup> Relative rate measurements, see table 59.

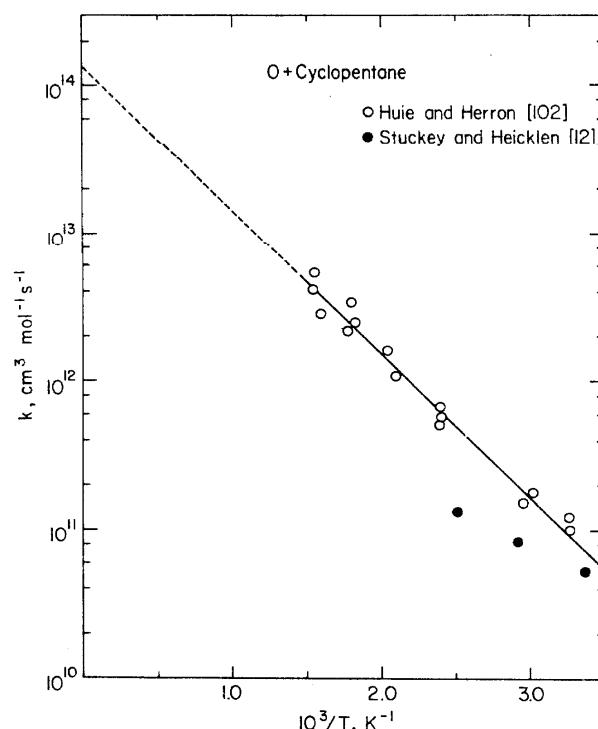


FIGURE 10. Arrhenius plot for the reaction of atomic oxygen with cyclopentane.

TABLE 21. Rate constants for the reaction of atomic oxygen with spiropentane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
4.0 <sup>+1.0</sup> <sub>-0.8</sub> × 10 <sup>13</sup> exp (-2890 ± 100/T)		337-652	102*	Discharge flow— mass spec- trometry
0.623 × 10 <sup>10</sup>		337		
1.01		339		
1.01		339		
0.792		339		
0.987		339		
0.614		339		
3.77		416		
4.47		417		
2.26		418		

TABLE 21. Rate constants for the reaction of atomic oxygen with spiropentane—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
1.18 × 10 <sup>11</sup>		473		
0.80		480		
2.03		548		
2.07		553		
1.61		564		
5.44		647		
5.48		651		
5.35		652		

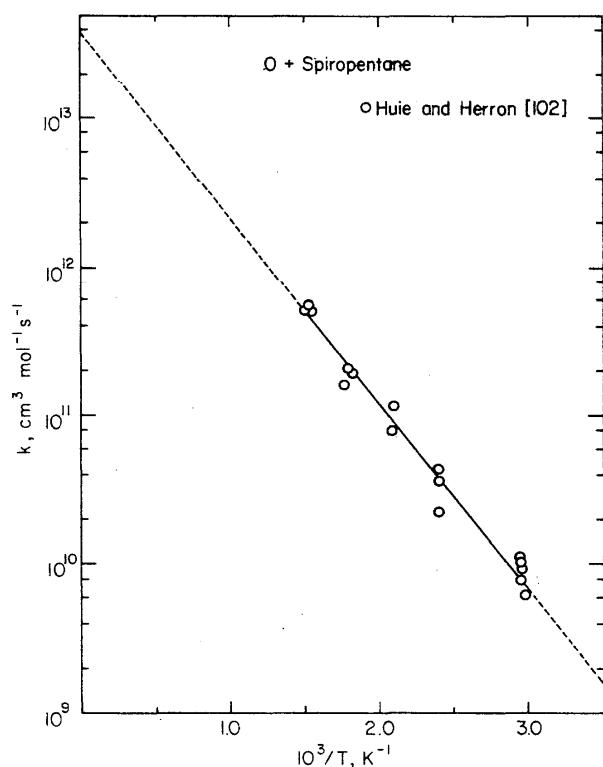


FIGURE 11. Arrhenius plot for the reaction of atomic oxygen with spiropentane.

TABLE 22. Rate constants for the reaction of atomic oxygen with cyclohexane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
2.2 <sub>-0.4</sub> × 10 <sup>14</sup> exp (-2350 ± 100/T)		307–692	102*	Discharge flow— mass spec- trometry
1.42 × 10 <sup>11</sup>		307		
1.37		307		
1.00		307		
2.12		331		
1.71		339		
1.87		339		
6.14		415		
7.53		418		
5.77		419		

TABLE 22. Rate constants for the reaction of atomic oxygen with cyclohexane—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
1.34 × 10 <sup>12</sup>		474		
1.74		493		
4.28		557		
3.52		564		
6.23		631		
7.74		647		
5.33		652		
5.4 × 10 <sup>10</sup>	6	298	12 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O
1.0 × 10 <sup>11</sup>	7	343		
1.6	6	392		
5.4 × 10 <sup>13</sup> exp (-2260/T)		353–493	47	Discharge flow— final products
8.7 × 10 <sup>10</sup>		353		
1.9 × 10 <sup>11</sup>		398		
4.7		458		
5.1		493		

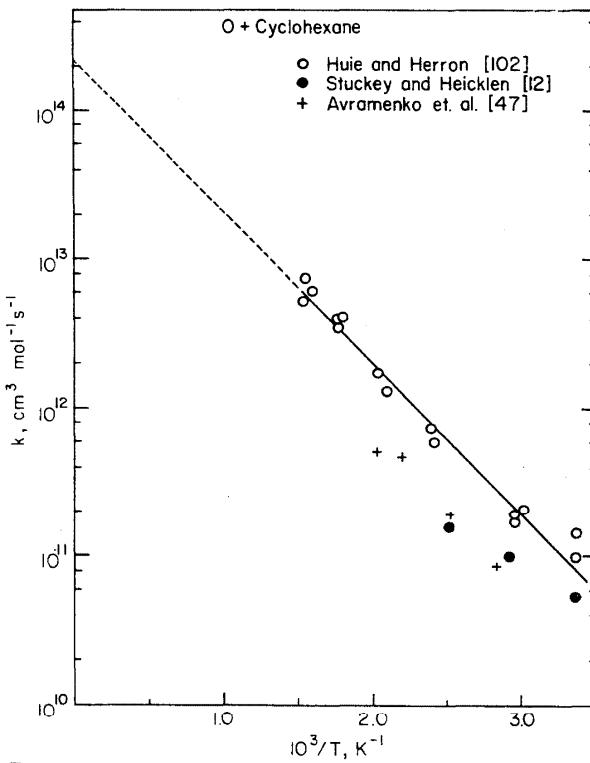
<sup>a</sup>Relative rate measurements, see table 59.

FIGURE 12. Arrhenius plot for the reaction of atomic oxygen with cyclohexane.

TABLE 23. Rate constants for the reaction of atomic oxygen with cycloheptane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
2.9 <sub>-0.7</sub> × 10 <sup>14</sup> exp (-2230 ± 140/T)		331–652	102*	Discharge flow— mass spec- trometry

TABLE 23. Rate constants for the reaction of atomic oxygen with cycloheptane—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
4.88 × 10 <sup>11</sup>		331		
3.68		339		
3.83		339		
1.37 × 10 <sup>12</sup>		418		
1.27		419		
1.80		474		
2.35		493		
4.86		548		
8.05		557		
4.11		564		
1.01 × 10 <sup>13</sup>		631		
1.24		647		
0.83		652		

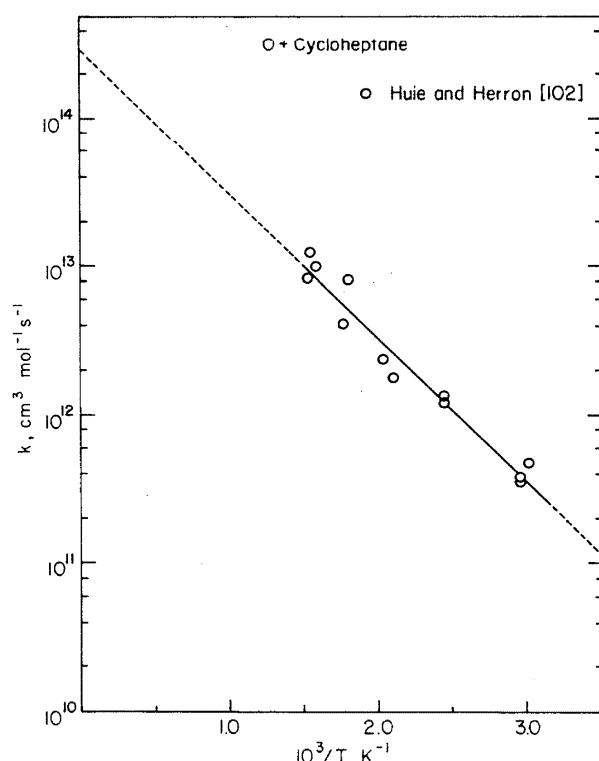
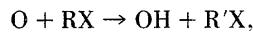


FIGURE 13. Arrhenius plot for the reaction of atomic oxygen with cycloheptane.

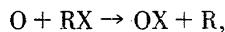
### 3.3. Haloalkanes

The reactions of atomic oxygen with the monohaloalkanes are probably simple hydrogen atom abstractions



where X represents a halogen atom.

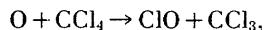
The corresponding halogen atom abstraction reaction



is too endothermic in the case of X = F, Cl, Br to be important at temperatures much below 1000 K. The case for X = I is not so clear, however, there being evidence that the iodine atom abstraction is rapid even at room temperature [60].

The only extensive set of data on these reactions is for the monochloro- and monobromoalkanes. As expected, the Arrhenius parameters are very similar to those for the unsubstituted alkanes. Although the Arrhenius plots are curved in some cases, corresponding to abstraction at different C-H bond sites, there are insufficient data to distinguish between contributions from different C-H bond types to the total rate constant. The recommended rate constants, which are based entirely on the results of discharge-flow experiments, are thus valid only over the range of the measurements. Extrapolation of the data to higher temperatures particularly in those cases where more than one type of C-H bond is involved, is not advised.

Data on the more heavily substituted haloalkanes are very limited. A study of the reaction of atomic oxygen with tetrachloromethane [42] indicated that the Arrhenius activation energy was  $18.8 \pm 1.3$  kJ mol<sup>-1</sup>, a value incompatible with the minimum activation energy required on the basis of the calculated heat of reaction for the abstraction reaction



of  $33.0 \pm 8.4$  kJ mol<sup>-1</sup>. To account for the observations the following primary reactions have been postulated [42]

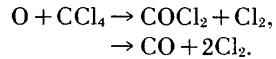


TABLE 24. Rate constants for the reaction of atomic oxygen with chloromethane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$2.5_{-0.5}^{+1.5} \times 10^{13}$ $\exp(-3880 \pm 220/T)$		381–607	76*	Discharge flow—mass spectrometry
$1.08 \times 10^9$		381		
$7.4 \times 10^8$		385		
9.8		385		
$3.48 \times 10^9$		434		
2.93		434		
5.22		437		
6.70		448		
$1.12 \times 10^{10}$		505		
1.38		506		
$6.88 \times 10^9$		508		
$1.48 \times 10^{10}$		513		
6.15		603		
3.88		603		
3.51		607		
3.48		607		
$\sim 2 \times 10^8$		353	53 a.*	Discharge flow—

TABLE 24. Rate constants for the reaction of atomic oxygen with chloromethane—Continued

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$4.8 \times 10^9$		468		mass spec-trometry
$4.3 \times 10^{10}$		638		
$3.4 \times 10^{11}$		949		
$1.7 \times 10^{13}$ $\exp(-3690/T)$		350–1000	table 3	Recommended value
$4.3 \times 10^{11}$		1000		
$7.2 \times 10^7$		298		

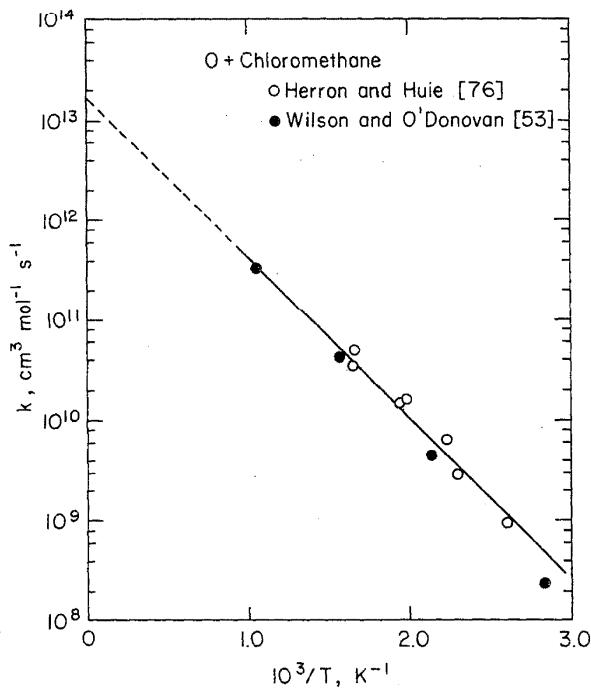
<sup>a</sup>Relative rate measurements, see table 56.

FIGURE 14. Arrhenius plot for the reaction of atomic oxygen with chloromethane.

TABLE 25. Rate constants for the reaction of atomic oxygen with bromomethane—Continued

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$2 \times 10^{11}$		613	53*	Discharge flow—mass spec-trometry
$1 \times 10^{12}$		966		
$3.0 \times 10^{13} \exp(-3800/T)$		350–1000	table 3	Recommended value
$7.0 \times 10^{11}$		1000		

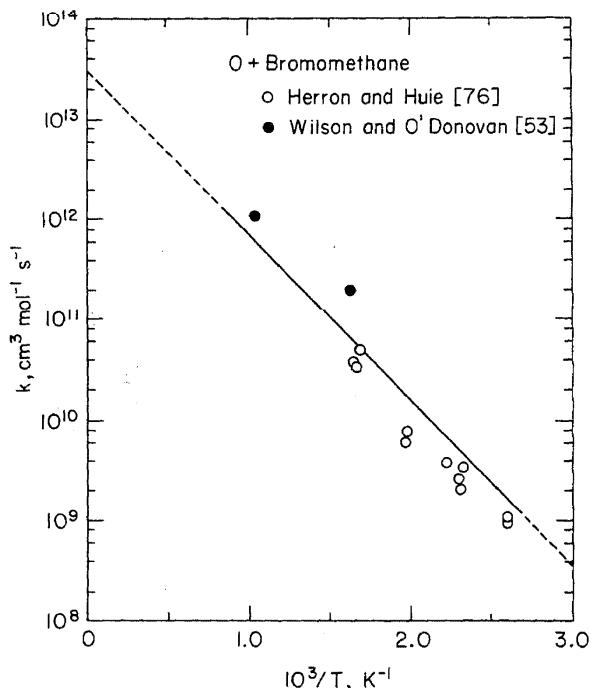
<sup>a</sup>Relative rate measurements, see table 56.

FIGURE 15. Arrhenius plot for the reaction of atomic oxygen with bromoethane.

TABLE 25. Rate constants for the reaction of atomic oxygen with bromomethane

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$\sim 1 \times 10^{13} \exp(-3500/T)$		385–595	76*	Discharge flow—mass spec-trometry
$9.6 \times 10^8$		385		
$1.13 \times 10^9$		385		
3.47		429		
2.01		433		
2.70		434		
3.82		448		
7.81		505		
6.03		508		
$5.10 \times 10^{10}$		595		

TABLE 26. Rate constants for the reaction of atomic oxygen with tetrachloromethane

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$2.0 \pm 0.9 \times 10^{10} \exp(-2260 \pm 150/T)$		277–373	42*	Discharge flow—air afterglow
$6.63 \times 10^6$	6	277		
9.88	4	283		
$1.13 \times 10^7$	11	292		
2.23	4	329		
5.68	4	373		
$1.5 \times 10^8$		300	84	Discharge flow—e.s.r.

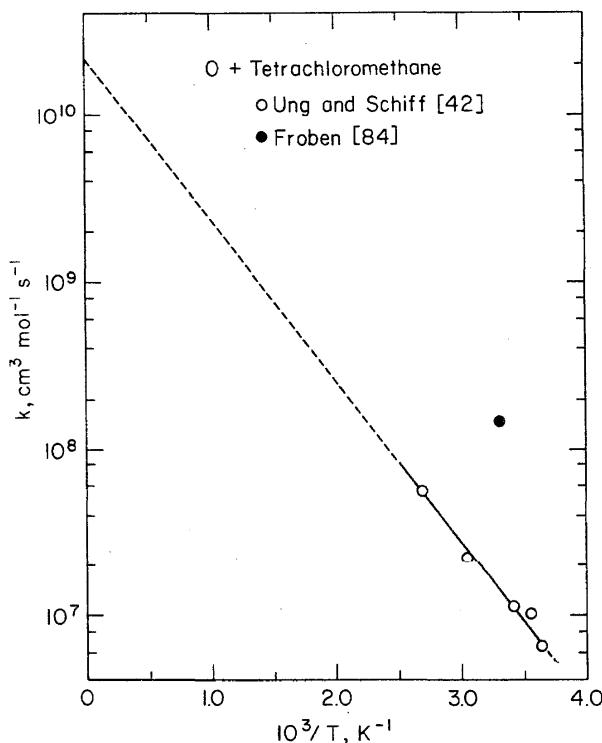


FIGURE 16. Arrhenius plot for the reaction of atomic oxygen with tetrachloromethane.

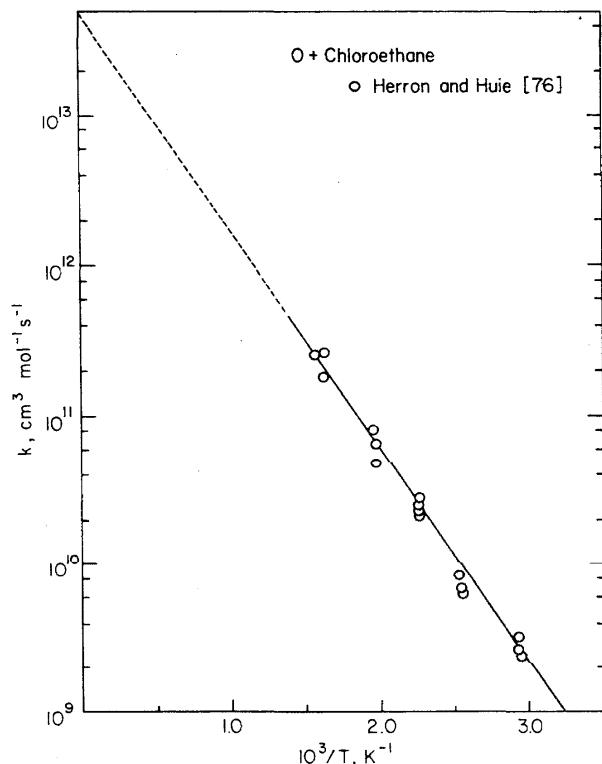


FIGURE 17. Arrhenius plot for the reaction of atomic oxygen with chloroethane.

TABLE 27. Rate constants for the reaction of atomic oxygen with chloroethane

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$4.8^{+1.1}_{-0.9} \times 10^{13}$ $\exp(-3330 \pm 90/T)$		336-662	76*	Discharge flow—mass spectrometry
$2.40 \times 10^9$		336		
3.23		336		
2.64		339		
6.32		381		
6.84		385		
8.15		390		
$2.43 \times 10^{10}$		434		
2.27		434		
2.09		437		
2.78		437		
4.70		505		
6.47		506		
7.04		513		
$1.81 \times 10^{11}$		603		
1.86		603		
2.58		607		
2.56		622		

TABLE 28. Rate constants for the reaction of atomic oxygen with bromoethane

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$3.1^{+0.9}_{-0.7} \times 10^{13}$ $\exp(-3260 \pm 110/T)$		336-607	76*	Discharge flow—mass spectrometry
$1.98 \times 10^9$		336		
2.39		336		
2.65		339		
4.92		385		
5.22		385		
5.81		390		
$2.01 \times 10^{10}$		433		
1.69		434		
2.13		448		
5.33		503		
4.99		505		
3.74		508		
$1.37 \times 10^{11}$		600		
1.69		603		
1.56		607		

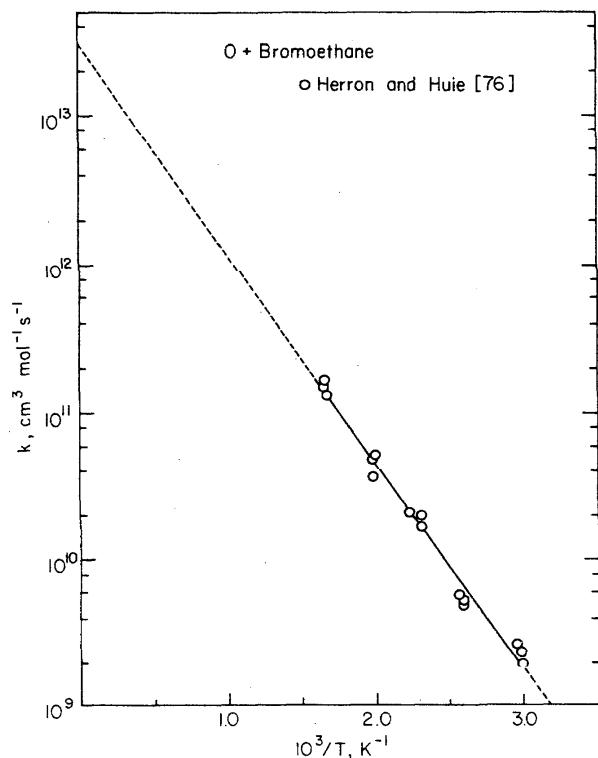


FIGURE 18. Arrhenius plot for the reaction of atomic oxygen with bromoethane.

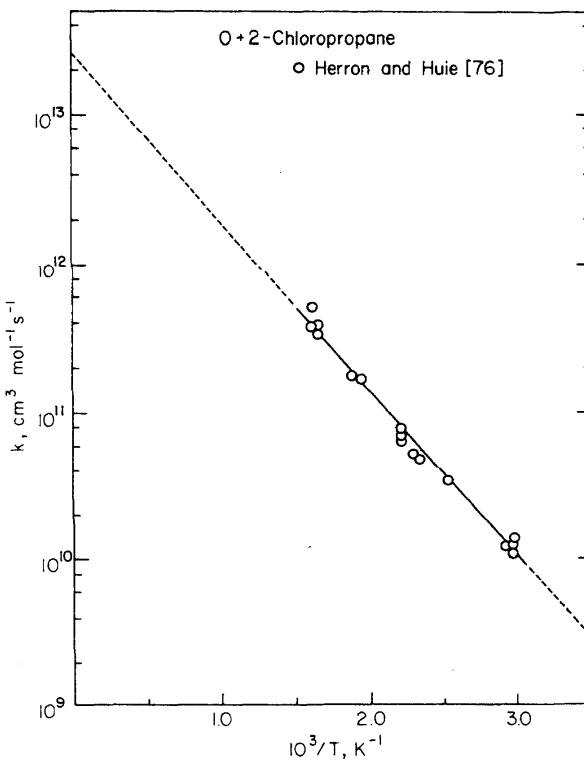


FIGURE 19. Arrhenius plot for the reaction of atomic oxygen with 2-chloropropane.

TABLE 29. Rate constants for the reaction of atomic oxygen with 2-chloropropane

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$2.6^{+0.5}_{-0.4} \times 10^{13} \exp(-2620 \pm 70/T)$	336-622	76*		Discharge flow—mass spectrometry
$1.13 \times 10^{10}$	336			
1.34	336			
1.39	339			
1.27	339			
1.22	343			
3.39	394			
4.75	429			
5.17	437			
6.86	451			
6.40	451			
7.79	451			
7.90	452			
$1.70 \times 10^{11}$	512			
1.77	532			
4.22	595			
3.38	603			
3.76	606			
3.29	607			
3.80	621			
5.12	622			

TABLE 30. Rate constants for the reaction of atomic oxygen with 2-bromopropane

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$2.3^{+0.5}_{-0.4} \times 10^{13} \exp(-2700 \pm 90/T)$	336-607	76*		Discharge flow—mass spectrometry
$7.53 \times 10^9$	336			
7.85	336			
9.92	339			
9.65	339			
$1.55 \times 10^{10}$	385			
1.61	385			
2.18	390			
6.76	433			
4.43	434			
5.17	437			
5.43	443			
$1.06 \times 10^{11}$	505			
1.05	506			
1.15	513			
2.91	603			
2.85	607			
2.91	607			

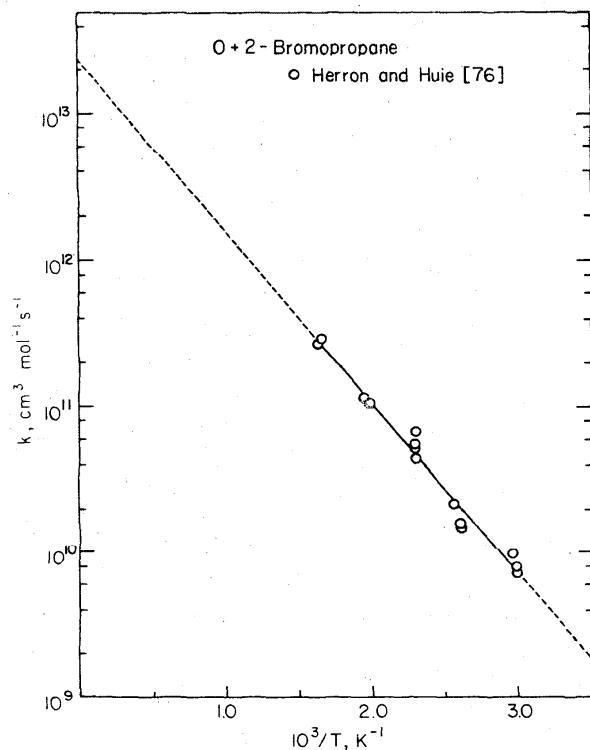


FIGURE 20. Arrhenius plot for the reaction of atomic oxygen with 2-bromopropane.

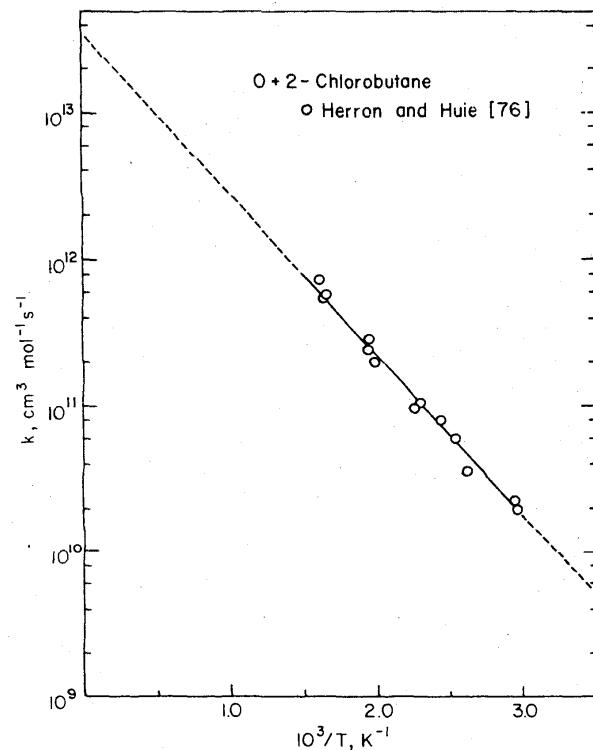


FIGURE 21. Arrhenius plot for the reaction of atomic oxygen with 2-chlorobutane.

TABLE 31. Rate constants for the reaction of atomic oxygen with 2-chlorobutane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$3.6_{-0.5}^{+0.6} \times 10^{13}$ $\exp(-2530 \pm 70/T)$		336-622	76*	Discharge flow—mass spectrometry
$2.02 \times 10^{10}$		336		
1.95		336		
2.25		339		
2.28		339		
3.63		381		
5.97		394		
8.03		410		
9.93		437		
9.66		443		
$1.03 \times 10^{11}$		443		
1.99		506		
2.90		512		
2.40		513		
5.78		604		
5.63		607		
7.29		622		

TABLE 32. Rate constants for the reaction of atomic oxygen with 1-chloro-2-methylpropane

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$3.6_{-0.8}^{+1.1} \times 10^{13}$ $\exp(-2520 \pm 110/T)$		336-607	76*	Discharge flow—mass spectrometry
$2.31 \times 10^{10}$		336		
1.99		339		
2.64		339		
6.40		381		
4.72		390		
5.91		394		
8.50		434		
$1.01 \times 10^{11}$		443		
1.13		443		
1.88		505		
2.13		506		
2.43		512		
2.55		513		
7.26		603		
7.16		607		
6.83		607		

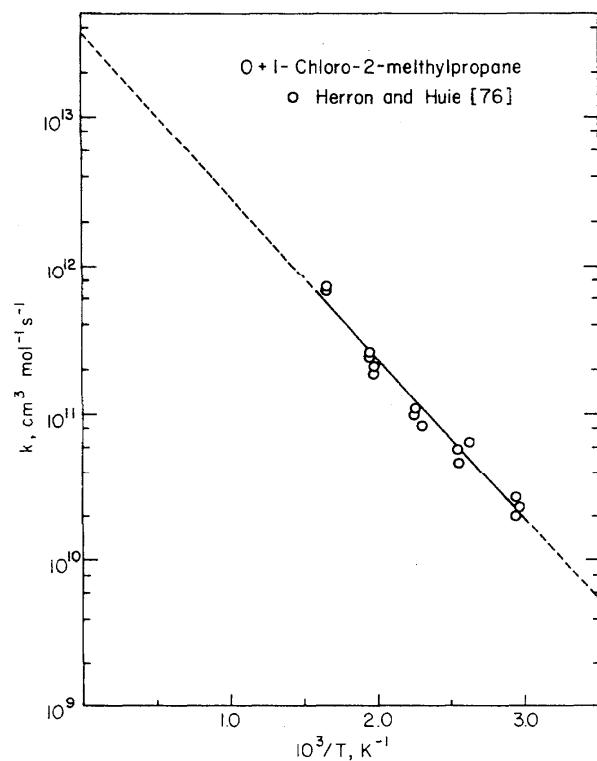


FIGURE 22. Arrhenius plot for the reaction of atomic oxygen with 1-chloro-2-methylpropane.

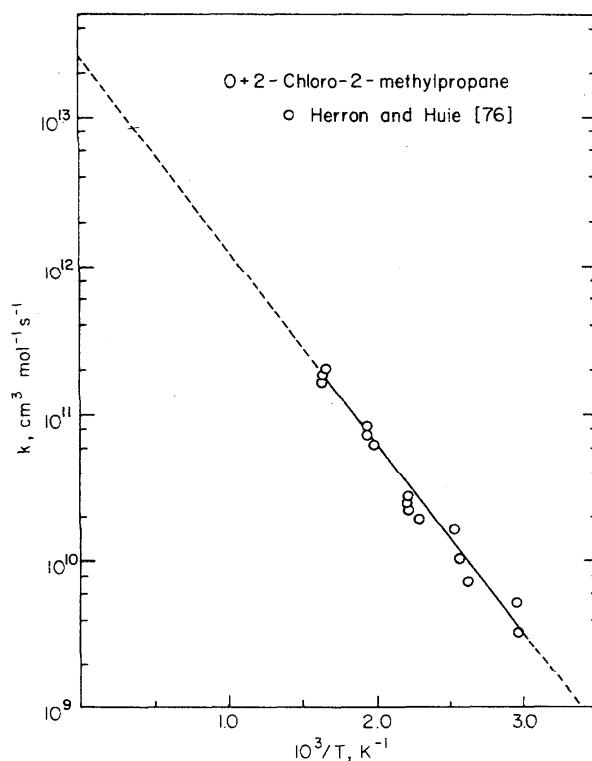


FIGURE 23. Arrhenius plot for the reaction of atomic oxygen with 2-chloro-2-methylpropane.

TABLE 33. Rate constants for the reaction of atomic oxygen with 2-chloro-2-methylpropane

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$2.6_{-0.6}^{+0.8} \times 10^{13}$ exp( $-3010 \pm 110/T$ )	336-607	76*		Discharge flow—mass spectrometry
$3.34 \times 10^8$		336		
5.22		339		
3.33		339		
7.28		381		
$1.05 \times 10^{10}$		390		
1.65		394		
1.96		410		
2.46		437		
2.32		437		
2.70		452		
6.40		506		
8.63		512		
7.65		513		
$2.06 \times 10^{11}$		603		
2.08		607		
1.69		607		

TABLE 34. Rate constants for the reaction of atomic oxygen with 1-bromobutane

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$4.4_{-0.7}^{+0.9} \times 10^{13}$ exp( $-2680 \pm 90/T$ )	336-607	76*		Discharge flow—mass spectrometry
$1.67 \times 10^{10}$		336		
1.62		336		
2.01		339		
3.41		385		
3.53		385		
4.86		390		
9.71		433		
9.34		434		
9.36		448		
$1.94 \times 10^{11}$		503		
2.38		505		
1.92		508		
4.93		600		
6.71		603		
3.90		607		

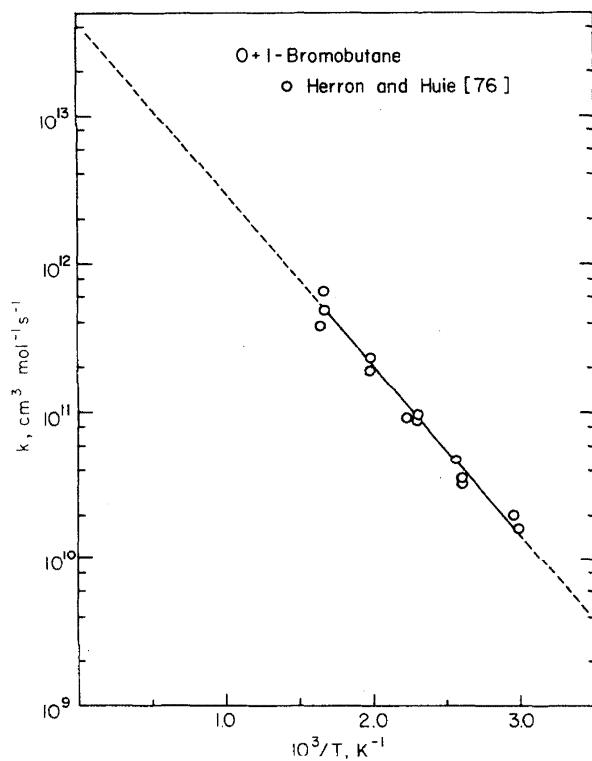


FIGURE 24. Arrhenius plot for the reaction of atomic oxygen with 1-bromobutane.

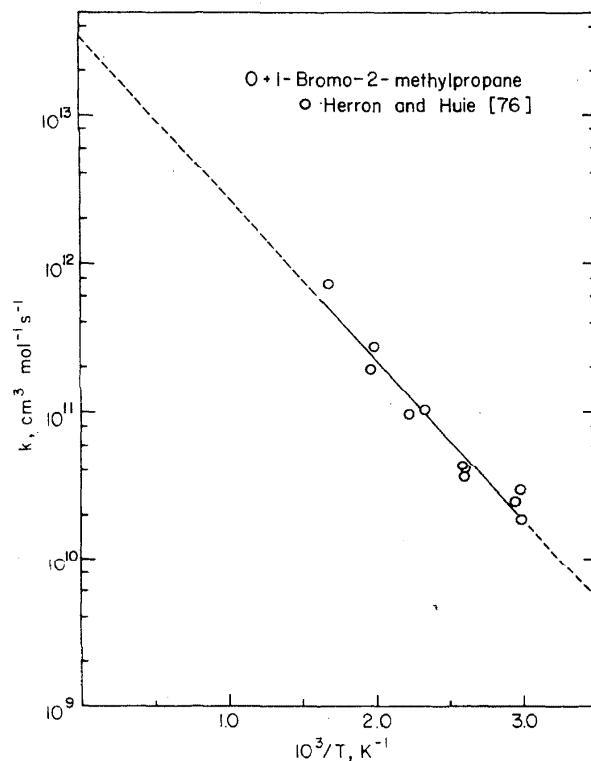


FIGURE 25. Arrhenius plot for the reaction of atomic oxygen with 1-bromo-2-methylpropane.

TABLE 35. Rate constants for the reaction of atomic oxygen with 1-bromo-2-methylpropane

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$3.4_{-1.2}^{+2.1} \times 10^{13}$ $\exp(-2510 \pm 190/T)$	336-595	76*		Discharge flow—mass spectrometry
$1.87 \times 10^{10}$	336			
2.95	336			
2.47	339			
3.57	385			
4.12	385			
4.35	387			
$1.01 \times 10^{11}$	429			
$9.79 \times 10^{10}$	448			
$2.70 \times 10^{11}$	503			
1.92	508			
7.29	595			

TABLE 36. Rate constants for the reaction of atomic oxygen with 1-chloro-2,2-dimethylpropane

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$3.2_{-0.4}^{+0.6} \times 10^{13}$ $\exp(-2670 \pm 80/T)$	336-607	76*		Discharge flow—mass spectrometry
$1.38 \times 10^{10}$	336			
1.13	339			
1.41	339			
2.07	381			
3.32	394			
4.91	410			
6.59	437			
7.39	437			
7.24	443			
$1.44 \times 10^{11}$	506			
1.83	512			
1.73	513			
4.56	603			
3.66	606			
4.11	607			

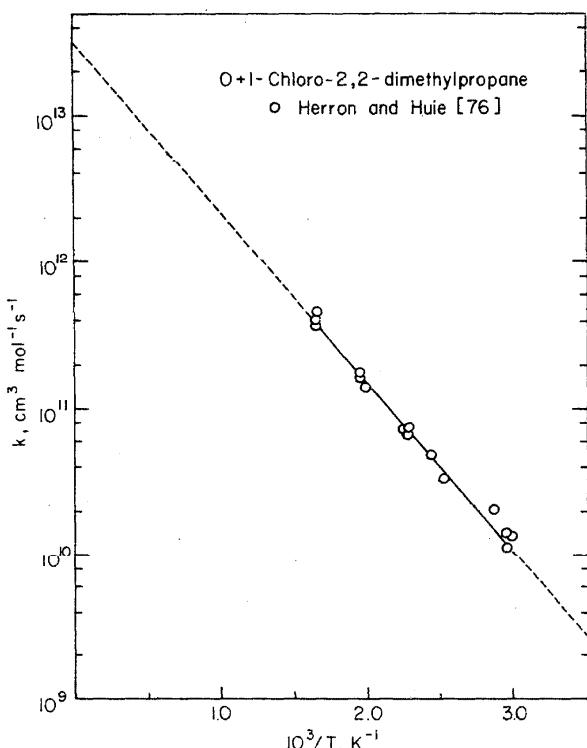


FIGURE 26. Arrhenius plot for the reaction of atomic oxygen with 1-chloro-2,2-dimethylpropane.

TABLE 37. Rate constants for the reaction of atomic oxygen with some miscellaneous haloalkanes

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
Fluoromethane $7.8 \times 10^{12} \exp(-4880 \pm 400/T)$		858-948	64	Ignition limits
Difluoromethane $2.65 \times 10^{12} \exp(-4430/T)$		873-953	81	Ignition limits
Trifluoromethane $\leq 2 \times 10^9$		$\leq 1000$	53 <sup>a</sup>	Discharge flow—mass spectrometry
Trichloromethane $1.5 \times 10^9$		300	84	Discharge flow—e.s.r.
1,2-Dichloroethane $1.2 \times 10^{13} \exp(-2770/T)$	1	353	54	Discharge flow—final products
$6.6 \times 10^9$	2	393		
8.9	1	433		
$1.61 \times 10^{10}$	1	473		
6.0				
1-Chloroheptane $\sim 8 \times 10^{10}$		298	76*	Discharge flow—mass spectrometry

<sup>a</sup> Relative rate measurements, see table 56.

### 3.4. Alkenes, Alkadienes, and Cycloalkenes

The mechanisms of the reactions of atomic oxygen with olefins have been studied in great detail by Cvetanovic and co-workers [63]. The general mechanism consists of the electrophilic addition of the oxygen atom to the double bond of the olefin followed by rearrangement and decomposition or stabilization of the adduct.

There is an extensive body of both absolute and relative rate measurements for these reactions. Two sets of absolute measurements have been made as a function of temperature for a series of alkenes. Although these data lead to different values of the Arrhenius parameters, the disagreement in rate constants is at worst a factor of two. In our opinion the flow data are subject to greater uncertainty because of the possibility of complications due to secondary reactions, and therefore the flash photolysis—resonance fluorescence data have been chosen as the basis for the recommended values. However a measurement of the rate constant at room temperature for the ethylene reaction using the flash photolysis—NO chemiluminescence technique [126] gives a value about 30 percent lower than that obtained using the flash photolysis—resonance fluorescence technique [104]. Although this is a relatively small uncertainty for gas kinetic rate measurements, it is outside the combined experimental uncertainty. We do not know the reason for the different results, and can see nothing basically wrong in either technique. In the case of the propene reaction, again at room temperature, the two techniques give identical results. Unfortunately these are the only reactions for which data are available using both techniques.

In general the Arrhenius plots for these reactions are linear, the one exception being 1-butene. This has been interpreted as arising from a competing hydrogen atom abstraction reaction at the  $\alpha$  C-H bond site. The curved Arrhenius plot was resolved into two linear plots corresponding to addition and abstraction. This format is used here for convenience, but it must be emphasized that the argument is purely a kinetic one, and there is no supporting evidence.

Absolute rate measurements on the *cis*-2-butene and 2,3-dimethyl-2-butene reactions indicate that these reactions have negative Arrhenius activation energies. This also appears to be the case for 1,3-butadiene, 2-methyl-2-butene, cyclopentene, and cyclohexene based on relative rate measurements. Conner, et al. [106] first suggested that this might be the case for some reactions of group VI atoms, and it now has been observed also for reactions involving atomic tellurium [106] and sulfur [201]. The extrapolation of these rate constants outside of the limits of the measurements should be undertaken with caution.

TABLE 38. Rate constants for the reaction of atomic oxygen with ethylene

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$8.4 \times 10^{12} \exp(-800/T)$		223–613	19	Discharge flow—air afterglow
$2.5 \times 10^{11}$	2	223		
5.7	3	300		
9.8	2	413		
$1.3 \times 10^{12}$	2	463		
1.3	1	488		
2.1	3	613		
$3 \times 10^{13}$		1400–1860	71	Flame structure
$1.44 \pm 0.05 \times 10^{11}$	5	195	25 <sup>a</sup>	Discharge flow—e.s.r.
$2.05 \pm 0.1$	5	226		
$3.3 \pm 0.1$	5	273		
$4.5 \pm 0.3$	12	298		
$7.4 \pm 0.1$	4	381		
$1.78 \pm 0.05 \times 10^{12}$	6	548		
$1.96 \pm 0.05$	3	555		
$3.4 \pm 0.2$	4	715		
$3.26 \pm 0.18 \times 10^{12} \exp(-565 \pm 16/T)$		232–500	104 <sup>*</sup>	Flash photolysis-resonance fluorescence
$2.76 \times 10^{11}$	2	232		
3.42	3	256		
4.48	1	284		
5.03	31	298		
6.35	2	341		
6.91	3	379		
7.62	2	398		
8.04	2	406		
9.15	1	451		
$1.09 \times 10^{12}$	1	500		
$5.30 \times 10^{11}$	4	298	104 <sup>*</sup>	Flash photolysis-kinetic absorption
$5.22 \times 10^{11}$	2	298	104	Discharge flow—mass spectrometry
5.60	7	307		
$4.2 \times 10^{11}$		298	199 <sup>d</sup>	Pulsed photolysis-air afterglow
$1.4 \pm 0.5 \times 10^{14} \exp(-4080 \pm 250/T)$		840–930	68 <sup>b</sup>	Ignition limits

TABLE 38. Rate constants for the reaction of atomic oxygen with ethylene—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$2.18 \pm 1.11 \times 10^{11}$		298	72	Discharge flow—mass spectrometry
$6 \times 10^{10} \exp(-680/T)$		313–503	57	Discharge flow—final products
$7.3 \times 10^9$		313		
9.3		353		
9.0		393		
$1.3 \times 10^{10}$		403		
1.3		416		
1.7		503		
$3.2 \pm 0.4 \times 10^{11}$		298	29 <sup>c</sup>	Discharge flow—e.s.r.
$3.8 \pm 0.4 \times 10^{11}$		298	126	Flash photolysis-air afterglow
$3.1 \pm 0.3 \times 10^{11}$		298	87	Discharge flow—mass spectrometry
$1.1 \pm 0.4 \times 10^{13} \exp(-800/T)$		223–465	10	Discharge flow—air afterglow
$3.2 \times 10^{11}$	2	223		
3.5	1	243		
4.1	2	258		
5.7	1	273		
6.9	23	293		
$1.05 \times 10^{12}$	1	350		
1.06	2	373		
1.35	1	407		
1.90	2	465		
$3.3 \times 10^{12} \exp(-565/T)$		200–500	table 4	Recommended value
$4.9 \times 10^{11}$		298		

<sup>a</sup> Individual rate constants are reported overall rate constants divided by 2.0.

<sup>b</sup> Pre-exponential factor incorrectly given as  $1.4 \times 10^{12}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. Correct value inferred from data given in reference [74].

<sup>c</sup> Rate constant is reported overall rate constant divided by 3.5.

<sup>d</sup> Supercedes data given in references [128] and [150].

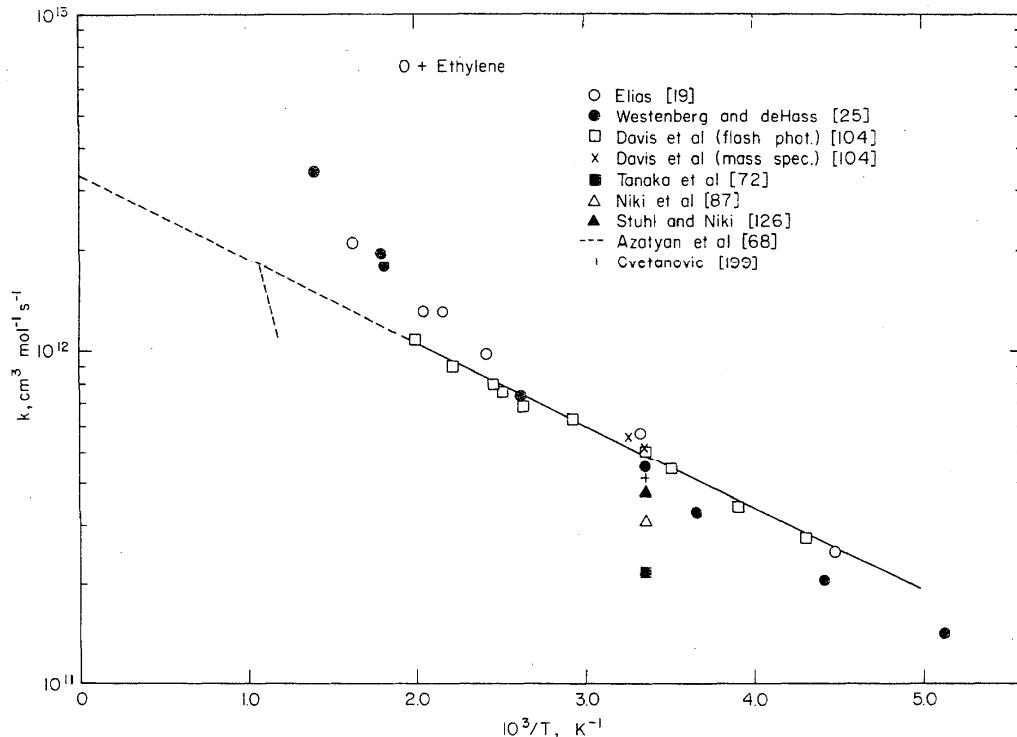


FIGURE 27. Arrhenius plot for the reaction of atomic oxygen with ethylene. For clarity the data of references [10], [29], [57], and [71] have been omitted.

TABLE 39. Rate constants for the reaction of atomic oxygen with propene

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
2.2 ± 0.2 × 10 <sup>12</sup>		300	126	Flash photolysis-air afterglow
1.72 × 10 <sup>12</sup> exp (-1500/T)		361–482	57	Discharge flow—final product
2.6 × 10 <sup>10</sup>		361		
3.9		401		
6.0		453		
8.8		482		
2.6 × 10 <sup>12</sup>		298	14 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O
2.3 × 10 <sup>12</sup>		297	13 <sup>b</sup>	Hg photosens. decomp. of N <sub>2</sub> O
1.9		343		
2.4		398		
2.1 × 10 <sup>12</sup>		296	79 <sup>c</sup> , 44 <sup>c</sup>	Hg photosens. decomp. of N <sub>2</sub> O
2.0 × 10 <sup>12</sup>		298	199 <sup>d</sup>	Pulsed photolysis-air afterglow
2.9 × 10 <sup>11</sup>		910	74	Ignition limits

TABLE 39. Rate constants for the reaction of atomic oxygen with propene—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
2.5 ± 0.20 × 10 <sup>12</sup> exp (-38 ± 22/T)			201–424	149*
2.08 × 10 <sup>12</sup>	1	201		Flash photolysis-resonance fluorescence
2.17	1	212		
2.04	2	230		
2.14	1	247		
2.22	14	298		
2.32	2	333		
2.31	2	368		
2.00	1	380		
2.13	1	385		
2.45	1	424		
2.07 × 10 <sup>12</sup>	1	215	166	Flash photolysis-resonance fluorescence
2.27	1	257		
2.40	1	298		
2.5 × 10 <sup>12</sup> exp (-38/T)		200–500	table 4	Recommended value
2.2 × 10 <sup>12</sup>		298		

<sup>a</sup> Relative rate measurements, see table 58.

<sup>b</sup> Relative rate measurements, see table 59.

<sup>c</sup> Relative rate measurements, see table 62.

<sup>d</sup> Supersedes data given in references [128] and [150].

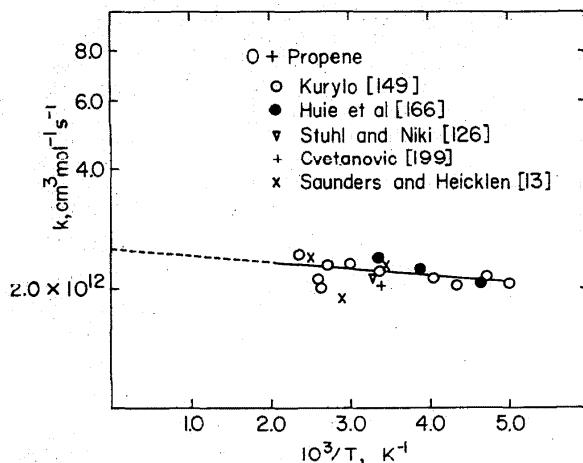


FIGURE 28. Arrhenius plot for the reaction of atomic oxygen with propene.

TABLE 40. Rate constants for the reaction of atomic oxygen with 1-butene

Rate constant, cm³ mol⁻¹ s⁻¹	No.	Temp. K	Ref.	Comments
$2.8 \times 10^{12}$		298	26 <sup>a</sup>	Hg photosens. decomp. of N₂O
$2.4 \times 10^{12}$		298	199 <sup>d</sup>	Pulsed photolysis-air afterglow
$2.3 \pm 1.1 \times 10^{12} \exp (-25 \pm 105/T)$ $+ 9.6 \pm 5.4 \times 10^{12} \exp (-990 \pm 220/T)$	190-491	166 <sup>e,*</sup>	Flash photolysis-resonance fluorescence	
$1.95 \times 10^{12}$	1	190		
2.00	5	200		
2.11	2	215		
1.96	5	226		
2.18	1	248		
2.24	5	272		
2.18	1	274		
2.46	10	298		
2.82	1	343		
2.69	3	370		
3.17	1	403		
3.22	3	472		
3.39	4	484		
3.57	1	491		
$1.3 \times 10^{13} \exp (-430/T)$	223-663	19	Discharge flow— air afterglow	
$1.92 \times 10^{12}$		223		
3.12		300		
5.10		488		
6.60		663		
$2.6 \times 10^{12}$		300	19 <sup>a</sup>	Discharge flow— air afterglow
3.1		423		
$2.9 \times 10^{12}$		298	14 <sup>b</sup>	Hg photosens. decomp. of N₂O
$2.7 \times 10^{12}$		299	11 <sup>b</sup>	Hg photosens. decomp. of N₂O
2.6		399		

TABLE 40. Rate constants for the reaction of atomic oxygen with 1-butene—Continued

Rate constant, cm³ mol⁻¹ s⁻¹	No.	Temp. K	Ref.	Comments
$2.3 \times 10^{12}$		397	16 <sup>c</sup>	Hg photosens. decomp. of N₂O
$1.8 \times 10^{12}$		297	13 <sup>c</sup>	Hg photosens. decomp. of N₂O
2.2		343		
2.5		398		
$2.3 \times 10^{12} \exp (-25/T) + 9.6 \times 10^{12} \exp (-990/T)$		180-500	table 4	Recommended value
$2.3 \times 10^{12}$		298		

<sup>a</sup> Relative rate measurements, see table 65.

<sup>b</sup> Relative rate measurements, see table 58.

<sup>c</sup> Relative rate measurements, see table 59.

<sup>d</sup> Supercedes data given in references [128] and [150].

<sup>e</sup> Supercedes data given in reference [118].

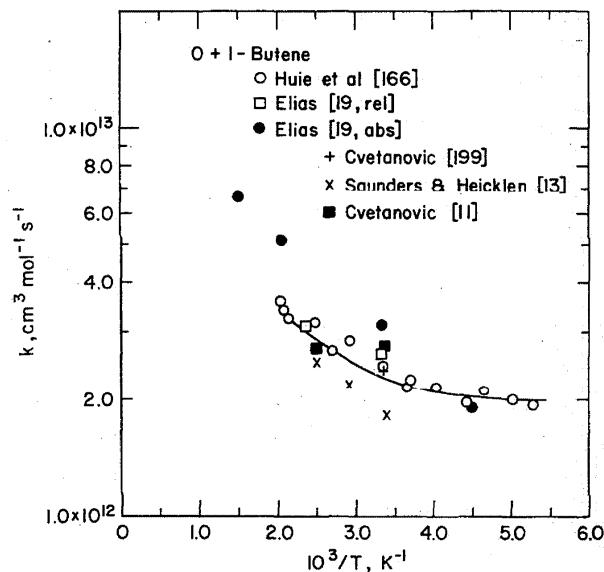


FIGURE 29. Arrhenius plot for the reaction of atomic oxygen with 1-butene.

TABLE 41. Rate constants for the reaction of atomic oxygen with cis-2-butene

Rate constant, cm³ mol⁻¹ s⁻¹	No.	Temp. K	Ref.	Comments
$2.3 \times 10^{13} \exp (-180/T)$		300-523	19	Discharge flow— air afterglow
$1.26 \times 10^{13}$		300		
1.62		523		

TABLE 41. Rate constants for the reaction of atomic oxygen with *cis*-2-butene—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$2.55 \times 10^{12} \exp(-1900/T)$		356–503	2	Discharge flow—final products
$1.2 \times 10^{10}$		356		
2.7		413		
3.8		458		
6.3		503		
$1.1 \times 10^{13}$		300	127 <sup>b</sup>	Hg photosens. decomp. of N <sub>2</sub> O
$1.1 \times 10^{13}$		298	14 <sup>b</sup>	
$5.89 \pm 0.27 \times 10^{12}$ $\exp(+165 \pm 15/T)$		268–443	130*	Flash photolysis—resonance fluorescence
$1.13 \times 10^{13}$	1	268		
1.07	1	270		
1.03	1	273		
1.03	10	298		
$9.09 \times 10^{12}$	2	361		
8.82	2	402		
8.85	1	421		
8.61	2	443		
$9.2 \times 10^{12}$		298	199	Pulsed photolysis—air afterglow
$5.9 \times 10^{12} \exp(+165/T)$		250–500	table 4	Recommended value
$1.0 \times 10^{13}$		298		

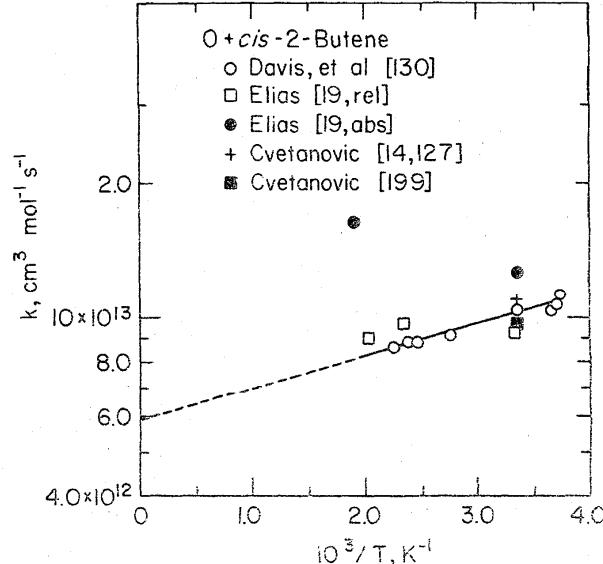
<sup>a</sup> Relative rate measurements, see table 65.<sup>b</sup> Relative rate measurements, see table 58.TABLE 42. Rate constants for the reaction of atomic oxygen with *trans*-2-butene

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$2.55 \times 10^{12} \exp(-1900/T)$		363–523	2	Discharge flow—final product
$1.4 \times 10^{10}$		363		
2.2		398		
4.7		473		
6.9		523		
$1.4 \times 10^{13}$		299	127 <sup>a, *</sup>	Hg photosens. decomp. of N <sub>2</sub> O
$1.4 \times 10^{13}$		298	14 <sup>a, *</sup>	Hg photosens. decomp. of N <sub>2</sub> O
$1.1 \times 10^{13}$		308	92 <sup>b</sup>	Hg photosens. decomp. of N <sub>2</sub> O
1.2		324		
1.7		343		
1.2		363		
1.1		375		

<sup>a</sup> Relative rate measurements, see table 58.<sup>b</sup> Relative rate measurements, see table 63.

TABLE 43. Rate constants for the reaction of atomic oxygen with 2-methylpropene

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$2.0 \times 10^{12} \exp(-200/T)$		300–523	19	Discharge flow—air afterglow
$9.9 \times 10^{12}$		300		
$1.3 \times 10^{13}$		523		
$2.4 \times 10^{12} \exp(-1280/T)$		318–538	57	Discharge flow—final products
$4.7 \times 10^{10}$		318		
9.0		398		
$2.0 \times 10^{11}$		498		
2.3		538		
$1.1 \times 10^{13}$		298	14 <sup>a, *</sup>	Hg photosens. decomp. of N <sub>2</sub> O
$1.2 \times 10^{13}$		299	11 <sup>a, *</sup>	Hg photosens. decomp. of N <sub>2</sub> O
$7.7 \times 10^{12}$		403		
$1.5 \times 10^{13}$		298	26 <sup>b, *</sup>	Hg photosens. decomp. of N <sub>2</sub> O
$9.1 \times 10^{12}$		298	55 <sup>c, *</sup>	Flash photolysis—kinetic spectroscopy
8.7		410		
$9.8 \times 10^{12}$		298	199 <sup>d</sup>	Pulsed photolysis—air afterglow

<sup>a</sup> Relative rate measurements, see table 58.<sup>b</sup> Relative rate measurements, see table 65.<sup>c</sup> Relative rate measurements, see table 61.<sup>d</sup> Supersedes data given in references [128] and [150].FIGURE 30. Arrhenius plot for the reaction of atomic oxygen with *cis*-2-butene.

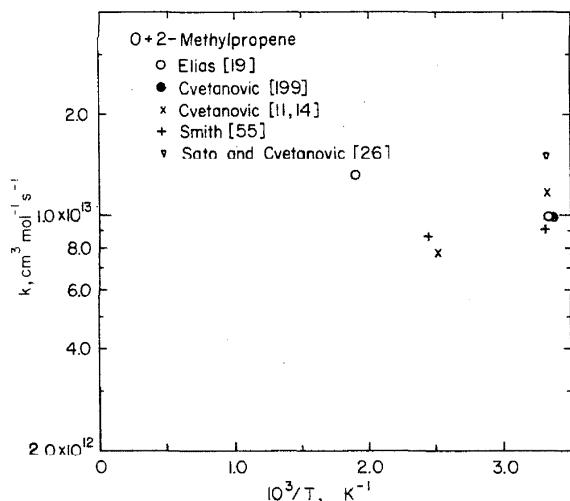


FIGURE 31. Arrhenius plot for the reaction of atomic oxygen with 2-methylpropene.

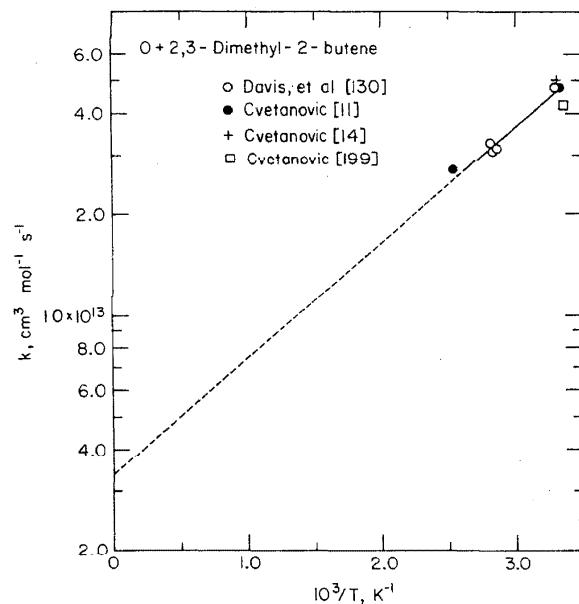


FIGURE 32. Arrhenius plot for the reaction of atomic oxygen with 2,3-dimethyl-2-butene.

TABLE 44. Rate constants for the reaction of atomic oxygen with 2,3-dimethyl-2-butene

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
$5.0 \times 10^{13}$		298	14*	Hg photosens. decomp. of $\text{N}_2\text{O}$
$4.8 \times 10^{13}$		300	11	Hg photosens. decomp. of $\text{N}_2\text{O}$
2.7		393		
$3.36 \pm 0.64 \times 10^{12}$ $\exp(+790 \pm 60/T)$		298-355	130*	Flash photolysis-resonance fluorescence
$4.76 \times 10^{13}$	4	298		
3.13	2	348		
3.05	1	352		
3.27	2	355		
$4.3 \times 10^{13}$		298	199	Pulsed photolysis-air afterglow
$3.4 \times 10^{12} \exp(+790/T)$		298-400	table 4	Recommended value
$4.8 \times 10^{13}$		298		

\* Relative rate measurements, see table 58.

TABLE 45. Rate constants for the reactions of atomic oxygen with some miscellaneous alkenes and alkadienes

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
1,3-Budadiene				
$1.2 \times 10^{13}$		299	121 a.*	Hg. photosens. decomp. of $\text{N}_2\text{O}$
$8.7 \times 10^{12}$		400		
1-Pentene				
$2.85 \times 10^{12}$		300	17*	Flow photolysis of $\text{NO}_2$
cis-2-Pentene				
$1.09 \times 10^{13}$		300	17*	Flow photolysis of $\text{NO}_2$
1.1 $\times 10^{13}$		298	14 a.*	Hg photosens. decomp. of $\text{N}_2\text{O}$
2-Methyl-2-butene				
$3.8 \times 10^{13}$		299	11 a.*	Hg photosens. decomp. of $\text{N}_2\text{O}$
2.2		393		
$3.1 \times 10^{13}$		298	199	Pulsed photolysis-air afterglow
1-Hexene				
$3.1 \times 10^{12}$		299	127 a.*	Hg photosens. decomp. of $\text{N}_2\text{O}$

\* Relative rate measurements, see table 58.

TABLE 46. Rate constants for the reactions of atomic oxygen with cyclopentene and cyclohexene

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
Cyclopentene $1.4 \times 10^{13}$ $9.8 \times 10^{12}$		299	11 <sup>a,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
		399		
Cyclohexene $1.3 \times 10^{13}$ $8.8 \times 10^{12}$		298	11 <sup>a,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
		400		

<sup>a</sup> Relative rate measurements, see table 58.

### 3.5. Haloalkenes and Haloalkadienes

The mechanisms of the reactions of atomic oxygen with the haloalkenes are probably similar to those of the alkene reactions, consisting of addition to the double bond followed by fragmentation or stabilization of the adduct. The fragmentation products of the haloalkene reactions can differ considerably from the comparable alkene reactions because of the differences in the carbon-hydrogen and carbon-halogen bond strengths.

Although the kinetics of many of these reactions have been studied, no single reaction has been sufficiently well investigated by different techniques to permit a high degree of confidence in the reported rate constants. Only a few of the reactions have been studied over a significant temperature range, none by absolute techniques. Most disturbing, where there is overlap in the data, the agreement is not particularly good even when using apparently identical experimental techniques. The kinetics of these reactions need more careful study, and at present, the existing data should be viewed with some caution.

One set of absolute rate measurements were made using the discharge flow-mass spectrometry technique. These data have been accepted. The other recommended rate constants are based primarily on relative rate measurements using the mercury photosensitized decomposition of nitrous oxide.

TABLE 47. Rate constants for the reactions of atomic oxygen with some haloalkenes—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
Chloroethylene $5.2 \times 10^{11}$	10	307	77*	Discharge flow—mass spec-trometry
Bromoethylene $4.9 \times 10^{11}$	9	307	77*	Discharge flow—mass spec-trometry
1,1-Difluoroethylene $2.2 \times 10^{11}$	8	307	77*	Discharge flow—mass spec-trometry
$1.1 \times 10^{11}$		296	146 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O
1,2-Difluoroethylene ( <i>cis</i> and <i>trans</i> ) $2.7 \times 10^{11}$	5	307	77*	Discharge flow—mass spec-trometry
<i>cis</i> -1,2-Difluoro- ethylene $1.5 \times 10^{11}$		296	146 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O
<i>trans</i> -1,2-Difluoro- ethylene $2.6 \times 10^{11}$		296	146 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O
Trifluoroethylene $2.7 \times 10^{11}$		296	146 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O
Tetrafluoroethylene $5.3 \times 10^{11}$	9	297	13 <sup>b,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
5.3	9	343		
5.7	3	398		
$5.0 \times 10^{11}$		297	16 <sup>b,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
$5.0 \times 10^{11}$		296	32 <sup>c</sup>	Flash photoly-sis—kinetic spectroscopy
$9.1 \times 10^{11}$		296	146 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O

TABLE 47. Rate constants for the reactions of atomic oxygen with some haloalkenes

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
Fluoroethylene $2.6 \times 10^{11}$	13	307	77*	Discharge flow—mass spec-trometry
$1.9 \times 10^{11}$		296	146 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O

TABLE 47. Rate constants for the reactions of atomic oxygen with some haloalkenes—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
Trifluorochloroethylene $2.7 \times 10^{11}$ 7.9		296 419	32 <sup>c</sup>	Flash photolysis—kinetic spectroscopy
1,1-Difluoro-2,2-dichloroethylene $3.5 \times 10^{11}$ 5.5		296 419	32 <sup>c</sup>	Flash photolysis—kinetic spectroscopy
2-Fluoropropene $1.0 \times 10^{12}$		296	79 <sup>d,*</sup> 83 <sup>d,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
3-Fluoropropene $4.4 \times 10^{11}$		296	79 <sup>d,*</sup> 83 <sup>d,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
1,1-Difluoropropene $9.5 \times 10^{11}$		296	79 <sup>d,*</sup> 83 <sup>d,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
3,3,3-Trifluoropropene $2.3 \times 10^{10}$		296	44 <sup>d,*</sup> 79 <sup>d,*</sup> 83 <sup>d,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
Hexafluoropropene $1.7 \times 10^{10}$ 2.4 3.8	5 3 3	297 343 399	13 <sup>b,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
$1.7 \times 10^{10}$		297	15 <sup>b,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
4-Fluoro-1-butene $1.3 \times 10^{12}$		296	79 <sup>d,*</sup> 83 <sup>d,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
1,1,2-Trifluoro-1-butene $2.1 \times 10^{12}$		296	79 <sup>d,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
$1.9 \times 10^{12}$		296	79 <sup>d,*</sup> 83 <sup>d</sup>	Hg. photosens. decomp. of N <sub>2</sub> O
2-Trifluoromethylpropene $1.7 \times 10^{11}$		296	44 <sup>d,*</sup> 79 <sup>d,*</sup> 83 <sup>d,*</sup>	Hg photosens. decomp. of N <sub>2</sub> O
$2.6 \times 10^{11}$		296	146 <sup>a</sup>	Hg photosens. decomp. of N <sub>2</sub> O

TABLE 47. Rate constants for the reactions of atomic oxygen with some haloalkenes—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
1,3-Hexafluorobutadiene $2.5 \times 10^{11}$			305	129 <sup>b,*</sup> Hg. photosens. decomp. of N <sub>2</sub> O

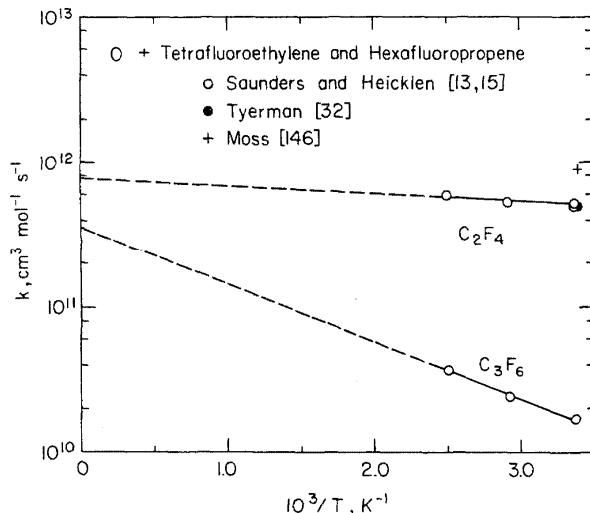
<sup>a</sup> Relative rate measurement, see table 60.<sup>b</sup> Relative rate measurement, see table 59.<sup>c</sup> Relative rate measurement, see table 65.<sup>d</sup> Relative rate measurement, see table 62.

FIGURE 33. Arrhenius plot for the reaction of atomic oxygen with tetrafluoroethylene and hexafluoropropene.

### 3.6. Alkynes and Alkadiynes

The reaction of atomic oxygen with acetylene has been extensively studied over a wide range of temperatures. The reported rate data are in good agreement. The recommended values are based entirely on absolute measurements obtained under discharge-flow conditions using mass spectrometry or electron spin resonance detection. Absolute rate constants have also been obtained from measurements of the chemiluminescence intensity of CH\* produced in this reaction under flow conditions. These data are somewhat uncertain because of the difficulty in calibration of the chemiluminescent intensity, but are within 20 to 30 percent of the recommended value at all temperatures. More importantly they support the activation energy assignment.

In addition to the absolute measurements there are relative rate measurements which also support the choice of the recommended values.

For the other alkynes and alkadiynes there are few data. Propyne and butadiyne have been studied near 300 K using discharge flow techniques, and these results are accepted. In the case of dicyanoacetylene only a limiting value is reported, and no recommended value is given.

TABLE 48. Rate constants for the reaction of atomic oxygen with acetylene

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$1.2 \times 10^{13} \exp(-1510/T)$		243-673	33 <sup>a,b,*</sup>	Discharge flow—mass spectrometry, e.s.r.
$3.0 \times 10^{10}$		243		
4.8		264		
6.0		286		
$1.1 \times 10^{11}$		308		
2.0		356		
4.2		425		
9.3		555		
$1.4 \times 10^{12}$		673		
$9.6 \times 10^{10}$		295	37	Discharge flow—e.s.r.
$2.0 \times 10^{13} \exp(-1610/T)$		230-450	80 <sup>a,*</sup>	Discharge flow—e.s.r.
$6.6 \pm 0.2 \times 10^9$	6	195		
$1.82 \pm 0.11 \times 10^{10}$	6	228		
$8.9 \pm 0.3$	12	298		
$2.48 \pm 0.02 \times 10^{11}$	4	369		
$5.9 \pm 0.2$	7	450		
$1.90 \pm 0.10 \times 10^{12}$	4	597		
$2.00 \pm 0.07$	2	616		
$9.2 \pm 0.4 \times 10^{10}$		298	29 <sup>a,*</sup>	Discharge flow—e.s.r.
$1.1 \times 10^{11}$		298	86 <sup>*</sup>	Discharge flow—e.s.r.
$5.3 \pm 1.7 \times 10^{10}$		298	36	Discharge flow—mass spectrometry, CH* chemiluminescence
$1.43 \pm 0.50 \times 10^{13} \exp(-3150 \pm 200/T)$	27	273-729	89 <sup>b</sup>	Discharge flow—CH* chemiluminescence
$9.0 \pm 1.8 \times 10^{10}$		298	30 <sup>*</sup>	Discharge flow—mass spectrometry
$1-2 \times 10^{13}$		1000-1500	56	Flame structure
$1.7 \times 10^{11} \exp(-1560/T)$		393-563	31	Discharge flow—final products
$3.3 \times 10^9$		393		
5.5		453		
9.0		488		
$1.0 \times 10^{10}$		563		
$1.1 \times 10^{11}$		298	35 <sup>*</sup> , 51 <sup>*</sup>	Discharge flow—mass spectrometry
$1.0 \times 10^{11}$		297	13 <sup>c</sup>	Hg photosens. decomp. of N <sub>2</sub> O
1.6		343		
3.3		398		

TABLE 48. Rate constants for the reaction of atomic oxygen with acetylene—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$7.89 \times 10^{10}$		300	126 <sup>*</sup>	Flash photolysis—air afterglow
$1.4 \times 10^{13} \exp(-1500/T)$		200-700	table 6	Recommended value
$3.3 \times 10^{12}$		1000		
$9.5 \times 10^{10}$		298		

<sup>a</sup> Individual rate constants are reported overall constants divided by 2.0.

<sup>b</sup> Reported in graphical form only.

<sup>c</sup> Relative rate measurements, see table 59.

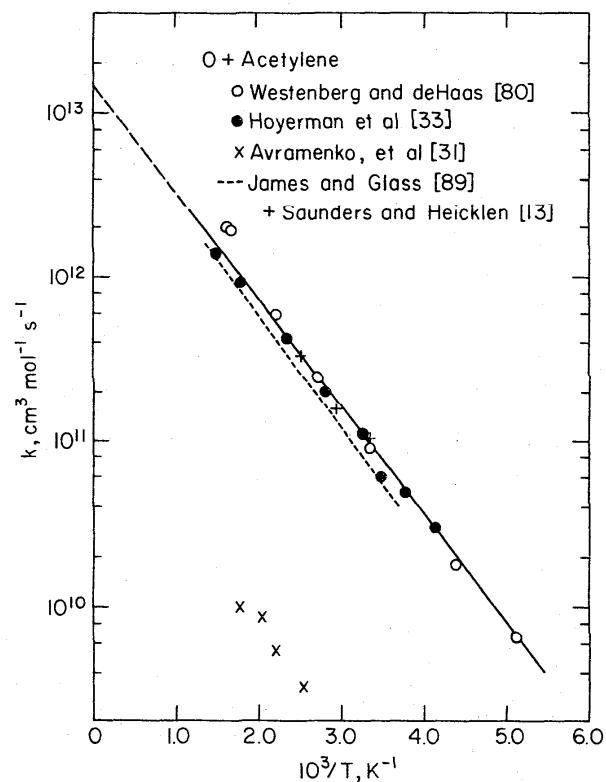


FIGURE 34. Arrhenius plot for the reaction of atomic oxygen with acetylene. For clarity most of the room temperature data have been omitted (references [29], [30], [35], [36], [37], [51], [86], and [126], as well as the data of reference [56]).

TABLE 49. Rate constants for the reactions of atomic oxygen with propyne, butadiyne, and dicyanoacetylene

Rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
Propyne $4 \pm 1 \times 10^{11}$		298	29*	Discharge flow—e.s.r.
Butadiyne $9.0 \pm 1.2 \times 10^{11}$		300	34*, 35*	Discharge flow—mass spectrometry
Dicyanoacetylene $< 2.2 \times 10^{10}$		300	94	Discharge flow—air afterglow

### 3.7. Benzene, Some Substituted Benzenes, and Pyridine

The only reactant in this category which has been studied in any detail is benzene. Absolute rate measurements at different temperatures have been made under discharge flow conditions using mass spectrometry and electron spin resonance detection. In addition, absolute rate measurements have been made at 298 K using the pulse radiolysis technique. There are also relative rate measurements made at two different temperatures. In both temperature dependence studies serious experimental problems were encountered. In the case of the photolysis experiments large amounts of polymers were formed which complicated the kinetic analysis. In the flow discharge work there was evidence for heterogeneous reactions, including the formation of polymeric material on the reactor walls.

The recommended values are based on the absolute measurements and in particular the discharge flow data. Of the latter data only the results obtained using mass spectrometric detection are free of the necessity of a stoichiometry or chain length correction. This is not the case with the e.s.r. data. To arrive at an empirical stoichiometry factor both mass spectrometric and e.s.r. data were plotted in Arrhenius form, and the ratio of slopes, about 4.0, taken as the stoichiometry factor.

The recommended value is tentative in nature and experimental confirmation is desirable.

In the case of the toluene reaction there is an absolute rate measurement at 298 K and relative rate measurements at 393 and 493 K. The data are not extensive enough to lead to recommended rate constants other than at 298 K.

For the other reactants in this category there is only one source of data, the absolute measurements at 298 K using the pulse radiolysis technique. These are accepted.

There is an extensive set of rate measurements on a large group of substituted benzenes which gives the relative rates of formation of the volatile phenolic prod-

ucts [90]. It is not clear, however, how these partial rate factors may be related to overall relative rates, so that these data are not used. (See table 64.)

TABLE 50. Rate constants for the reactions of atomic oxygen with benzene, some substituted benzenes, and pyridine

Rate constants, $\text{cm}^3 \text{mol}^{-2} \text{s}^{-1}$	No.	Temp. K	Ref.	Comments
Benzene				
$1.7 \times 10^{13}$ $\exp(-2370/T)$		338–493	47	Discharge flow—final products
$1.6 \times 10^{10}$		338		
4.2		373		
8.1		453		
$1.6 \times 10^{11}$		493		
$3.6 \times 10^{10}$		298	67*	Pulse radiolysis
$6.6 \times 10^{10}$		393	45*	Hg photosens. decomp. of $\text{N}_2\text{O}$
$1.5 \times 10^{11}$		494		
$3.8 \pm 1.5 \times 10^{13}$ $\exp(-2210 \pm 250/T)$		255–305	187*	Discharge flow—mass spectrometry
$7.43 \times 10^9$	6	255		
8.24	9	262		
$1.12 \times 10^{10}$	3	272		
2.72	11	302		
2.99	2	305		
$6.5 \times 10^{10}$	5	344	187 <sup>b, *</sup>	Discharge flow—e.s.r.
7.4	5	364		
$1.9 \times 10^{11}$	4	407		
2.4	5	459		
3.2	3	482		
$2.0 \times 10^{13} \exp(-2000/T)$		250–500	table 7	Recommended value
$2.4 \times 10^{10}$		298		
Fluorobenzene				
$2.7 \times 10^{10}$		298	67*	Pulse radiolysis
Chlorobenzene				
$3.1 \times 10^{11}$		298	67*	Pulse radiolysis
Toluene				
$1.4 \times 10^{11}$		298	67*	Pulse radiolysis
$1.7 \times 10^{11}$		393	52 <sup>a, *</sup>	Hg photosens. decomp. of $\text{N}_2\text{O}$
3.2		493		
Ethylbenzene				
$3.2 \times 10^{11}$		298	67*	Pulse radiolysis
1,2-Dimethylbenzene				
$6.7 \times 10^{11}$		298	67*	Pulse radiolysis
1,3-Dimethylbenzene				
$7.7 \times 10^{11}$		298	67*	Pulse radiolysis
1,4-Dimethylbenzene				
$4.5 \times 10^{11}$		298	67*	Pulse radiolysis

TABLE 50. Rate constants for the reactions of atomic oxygen with benzene, some substituted benzenes, and pyridine—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
Pyridine $1.0 \times 10^{11}$		298	67*	Pulse radiolysis

\* Relative rate measurements, see table 58.

<sup>b</sup> Individual rate constants are the reported overall rate constants divided by 4.0.

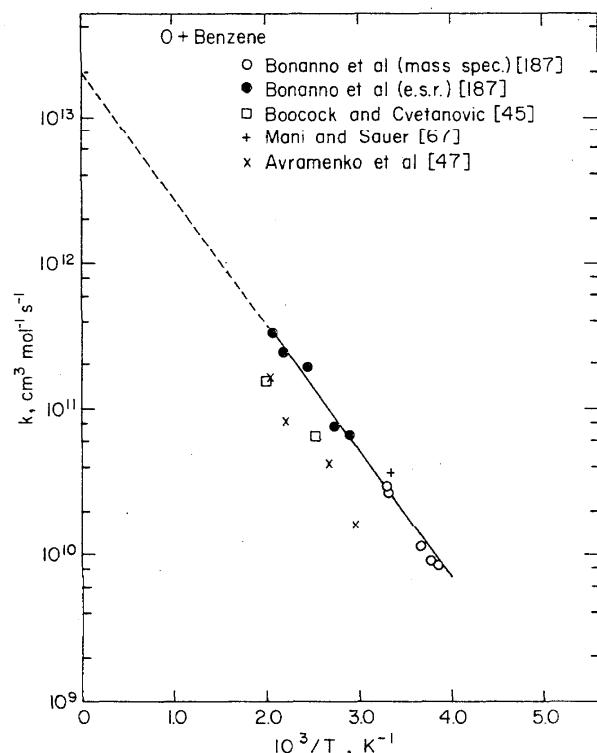


FIGURE 35. Arrhenius plot for the reaction of atomic oxygen with benzene.

### 3.8. Alcohols, Aldehydes, and Miscellaneous Oxygen Containing Compounds

Although there is a considerable body of rate data available on oxygen containing reactants, much of it is unreliable (all data based on final product analysis are rejected) and only in the cases of acetaldehyde and dimethyl ether are rate constants recommended at other than room temperature.

The methanol reaction has been studied under discharge flow conditions using electron spin resonance detection. However, it was established in that work that heterogeneous processes were important. In addition the derived Arrhenius pre-exponential factors per C-H bond ( $0.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) appear to be abnormally low when compared to those observed for the alkanes (5 to  $20 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). For these reasons these data are rejected and no recommended values are given.

Acetaldehyde has also been studied under discharge flow conditions using the air afterglow technique. In addition there are relative rate measurements near room temperature. The recommended values are based on both the absolute and relative measurements. The data, however, scatter considerably and a more definitive measurement over a wider temperature range would be desirable. The recommended rate constant refers to abstraction of the aldehydic H atom. At higher temperatures abstraction of  $\alpha$ -H atoms will also occur and the Arrhenius plot will curve upward.

In the case of dimethyl ether there are extensive sets of both absolute and relative rate data. The absolute measurements involved discharge flow systems using both mass spectrometry and electron spin resonance detection. The electron spin resonance data require correction for stoichiometry or chain length. In the original work a value of 2.0 was used. We have chosen to fit these data by picking a stoichiometry factor which brings the mass spectrometric and electron spin resonance data into agreement over their common temperature range. This factor, 2.6, was then used to correct the electron spin resonance data over the whole of the measurements. In addition, there is a series of relative rate measurements which in general lead to lower rate constants. The absolute measurements are the sole basis for the recommended values. We note, however, that the recommended value leads to an Arrhenius pre-exponential factor of  $1.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  which as in the case of the reported methanol data appears to be low when compared to the data for the alkanes.

For the other compounds considered here both absolute and relative rate data were used to arrive at recommended values at room temperature only.

TABLE 51. Rate constants for the reaction of atomic oxygen with methanol

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
$5.1 \times 10^{11} \exp(-1560/T)$		347–506	43	Discharge flow—final products
$5.4 \times 10^9$		347		
6.0		353		
7.1		363		
6.3		363		
4.2		363		
$1.05 \times 10^{10}$		389		
$8.4 \times 10^9$		393		
$1.11 \times 10^{10}$		395		
$7.2 \times 10^9$		399		
$1.60 \times 10^{10}$		423		
1.75		483		
2.74		506		
$1.70 \pm 0.66 \times 10^{12} \exp(-1150 \pm 100/T)$		273–438	141 <sup>a</sup>	Discharge flow—e.s.r.
$1.14 \pm 0.09 \times 10^{10}$	3	273		
$1.55 \pm 0.18$	5	298		
$2.38 \pm 0.06$	4	332		

TABLE 51. Rate constants for the reaction of atomic-oxygen with methanol—Continued

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
3.21 ± 0.06	3	363		
3.95 ± 0.66	4	391		
6.65 ± 0.15	5	426		
7.60 ± 0.13	5	438		

<sup>a</sup> Individual rate constants are the reported overall rate constants divided by 2.0.

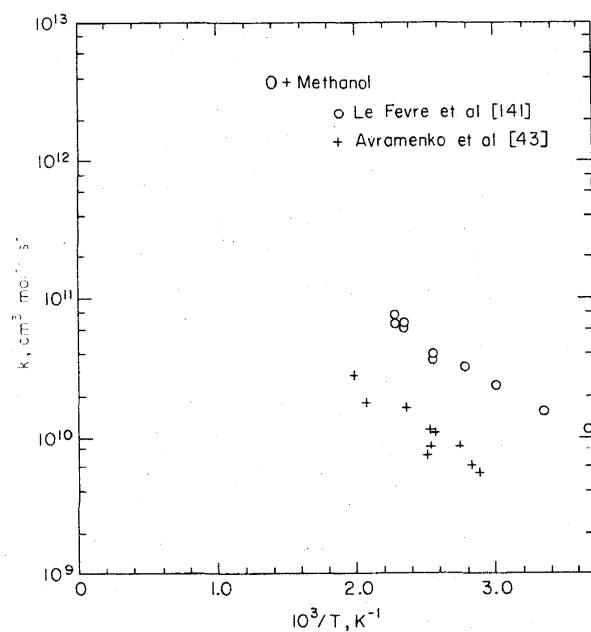


FIGURE 36. Arrhenius plot for the reaction of atomic oxygen with methanol.

TABLE 52. Rate constants for the reactions of atomic oxygen with ethanol and isopropanol

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
Ethanol				
6.3 × 10 <sup>12</sup> exp (-2010/T)		343–523	40	Discharge flow—final products
1.96 × 10 <sup>10</sup>		343		
4.27		403		
9.39		463		
1.38 × 10 <sup>11</sup>		523		
(1.6 ± 0.7) × 10 <sup>13</sup> exp (-2770 ± 500/T)		903–963	65	Ignition limits
8.7 × 10 <sup>10</sup>		298	59 <sup>a,*</sup>	Hg photosens. decomp of N <sub>2</sub> O
Isopropanol				
1.3 × 10 <sup>11</sup>		298	39 <sup>a,*</sup>	Hg photosens. decomp of N <sub>2</sub> O

<sup>a</sup> Relative rate measurements, see table 58.

TABLE 53. Rate constants for the reaction of atomic oxygen with some aldehydes

Rate constant, cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	No.	Temp. K	Ref.	Comments
Formaldehyde 9.0 × 10 <sup>10</sup>		300	78*	Discharge flow—mass spectrometry
6 × 10 <sup>13</sup>		1750–2575	105	Shock tube
Monodeuteroformaldehyde 4.9 × 10 <sup>10</sup>		300	35*, 51*	Discharge flow—mass spectrometry
Difluoroformaldehyde ≤ 2 × 10 <sup>10</sup>		307	77	Discharge flow—mass spectrometry
Dichloroformaldehyde 6 × 10 <sup>9</sup>		273	42*	Discharge flow—air afterglow
≤ 2 × 10 <sup>10</sup>		307	77	Discharge flow—mass spectrometry
Acetaldehyde (1.1 ± 0.3) × 10 <sup>13</sup> exp (-1160/T)		299–476	50*	Discharge flow—air afterglow
2.7 × 10 <sup>11</sup>		299		
6.4		299		
5.4		369		
7.4		412		
1.2 × 10 <sup>12</sup>		476		
3.6 × 10 <sup>11</sup> exp (-1380 ± 250/T)		343–428	41	Discharge flow—final products
6.6 × 10 <sup>9</sup>	1	343		
7.4	1	353		
1.11 × 10 <sup>10</sup>	2	373		
1.14	1	393		
1.42	1	428		
3.4 × 10 <sup>11</sup>		298	46 <sup>a,*</sup>	Hg photosens. decomp of N <sub>2</sub> O
2.0 × 10 <sup>11</sup>		293	66 <sup>b</sup>	Hg photosens. decomp of N <sub>2</sub> O
1.4 × 10 <sup>13</sup> exp (-1140/T)		298–500	table 8	Recommended value
3.1 × 10 <sup>11</sup>		298		
Propionaldehyde				
1.05 × 10 <sup>11</sup> exp (-1430/T)		398–523	40	Discharge flow—final products
2.69		398		
3.7		423		
4.6		463		
6.6		523		

<sup>a</sup> Relative rate measurements, see table 58.

<sup>b</sup> Relative rate measurements, see table 65.

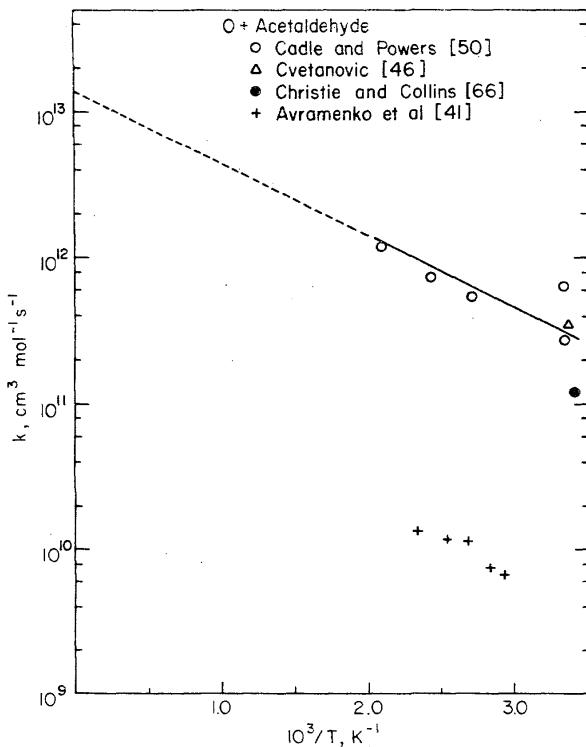


FIGURE 37. Arrhenius plot for the reaction of atomic oxygen with acetaldehyde.

TABLE 54. Rate constants for the reactions of atomic oxygen with ketene and ethylene oxide

Rate constant, cm³ mol⁻¹ s	No.	Temp. K	Ref.	Comments
Ketene $5.3 \times 10^{11}$		298	82*	Discharge flow—mass spectrometry
Ethylene Oxide $7.3 \times 10^8$	13	307	58 <sup>a,*</sup>	
0.7	7	343		Hg photosens. decomp. of N₂O
$1.3 \times 10^9$	8	398		

<sup>a</sup> Relative rate measurements, see table 59.

TABLE 55. Rate constants for the reaction of atomic oxygen with dimethyl ether

Rate constant, cm³ mol⁻¹ s⁻¹	No.	Temp. K	Ref.	Comments
$2.1 \times 10^{10}$	7	307	58 <sup>a</sup>	Hg photosens. decomp. of N₂O
2.7	5	343	58 <sup>a</sup>	
5.0	5	398		
$1.6 \times 10^{10}$	4	303	49 <sup>b</sup>	Hg photosens. decomp. of N₂O
3.7	1	335		
7.5	1	366		
$1.3 \times 10^{11}$	1	394		
2.1	1	426		

TABLE 55. Rate constants for the reaction of atomic oxygen with dimethyl ether—Continued

Rate constant, cm³ mol⁻¹ s⁻¹	No.	Temp. K	Ref.	Comments
$1.8 \times 10^{10}$	3	311	92 <sup>c</sup>	Hg photosens. decomp. of N₂O
1.5	3	323		
2.0	3	338		
2.5	3	353		
2.8	3	363		
3.7	3	373		
$5 \pm 1 \times 10^{12} \exp (-1430 \pm 100/T)$		217–366	141 <sup>d,*</sup>	Discharge flow—e.s.r.
$6.19 \pm 0.73 \times 10^9$	4	217		
$1.17 \pm 0.06 \times 10^{10}$	3	245		
$2.27 \pm 0.20$	5	273		
$3.09 \pm 0.52$	4	298		
$3.45 \pm 0.34$	4	298		
$6.31 \pm 0.96$	4	336		
$8.62 \pm 1.19$	4	366		
$1.59 \pm 0.10 \times 10^{10}$	4	254	141*	Discharge flow—mass spec-trometry
$1.57 \pm 0.25$	5	261		
$2.57 \pm 0.25$	4	273		
$2.27 \pm 0.40$	5	283		
$3.74 \pm 0.30$	6	300		

<sup>a</sup> Relative rate measurements, see table 59.

<sup>b</sup> Relative rate measurements, see table 57.

<sup>c</sup> Relative rate measurements, see table 63.

<sup>d</sup> Individual rate constants are the reported overall rate constants divided by 2.6.

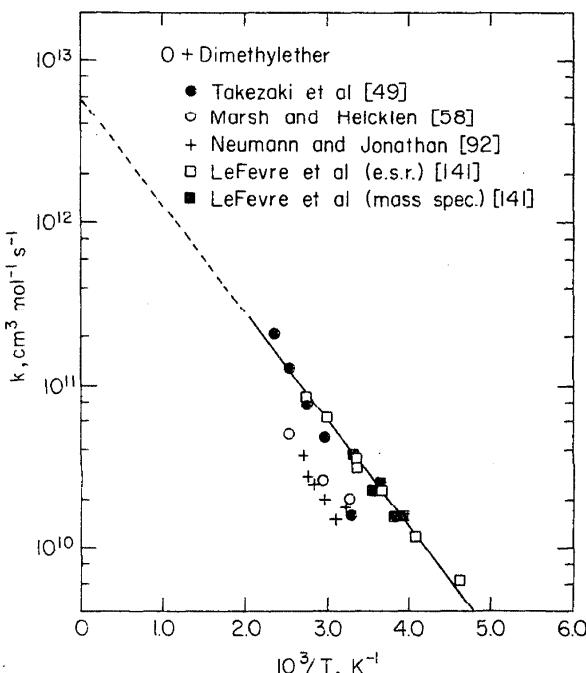


FIGURE 38. Arrhenius plot for the reaction of atomic oxygen with dimethylether.

## 4. Relative Rate Constants

TABLE 56. Relative rate measurements of Wilson and O'Donovan

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-10} k_A^a \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Ref.
$\text{CH}_3\text{Cl}$	$\text{CH}_4$	353	$\sim 3.4$		$\sim 0.022$	53
		468	$2.83 \pm 0.07$		0.48	
		638	$2.16 \pm 0.04$		4.3	
		949	$1.76 \pm 0.05$		34	
$\text{CH}_3\text{Br}$	$\text{CH}_4$	613	$13 \pm 2$		20	
		966	$5 \pm 1$		100	
$\text{CF}_3\text{H}$	$\text{CH}_4$	$\leq 1000$	$< 0.01$		$< 0.2$	

<sup>a</sup> All derived rate constants,  $k_A$ , are based on absolute rate constants for methane (table 1) and the rate ratios in this table.

TABLE 57. Relative rate measurements of Takezaki, Mori, and Kawasaki

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-11} k_A^a \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Ref.
$\text{CH}_3\text{OCH}_3$	$n\text{-C}_4\text{H}_{10}$	303	0.90	4	0.29	49
		335	0.96	1	0.37	
		366	1.05	1	0.75	
		394	1.06	1	1.3	
		426	1.14	1	2.1	

<sup>a</sup> All derived rate constants,  $k_A$ , are based on absolute rate constants for *n*-butane (table 1) and the rate ratios in this table.

TABLE 58. Relative rate measurements of Cvetanovic [11, 14, 46, 98, 127], Jones and Cvetanovic [52], Kato and Cvetanovic [39, 59], Cvetanovic and Doyle [121], and Boocock and Cvetanovic [45]

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-11} k_A^a \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Ref.
$n\text{-C}_4\text{H}_{10}$	$\text{C}_2\text{H}_4$	298	$0.045 \pm 0.014$		0.22	98
1-C <sub>4</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub>	298	6.3		30	14
cis-2-C <sub>4</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub>	298	22		110	14
cy-C <sub>6</sub> H <sub>10</sub>	C <sub>2</sub> H <sub>4</sub>	298	$26.78 \pm 0.38$	4	130	11
		400	$11.16 \pm 0.28$	4	88	
CH <sub>3</sub> CHO	C <sub>2</sub> H <sub>4</sub>	298	$0.7 \pm 0.1$		3.4	46
cy-C <sub>5</sub> H <sub>8</sub>	cy-C <sub>6</sub> H <sub>10</sub>	299	$1.103 \pm 0.056$	5	142	11
		399	$1.109 \pm 0.084$	4	98	
1-C <sub>4</sub> H <sub>8</sub>	cy-C <sub>5</sub> H <sub>8</sub>	298	0.194		28	14
		299	$0.191 \pm 0.006$	6	27	11
		399	$0.268 \pm 0.010$	6	26	
iso-C <sub>4</sub> H <sub>8</sub>	cy-C <sub>5</sub> H <sub>8</sub>	298	0.794		110	14
		299	$0.838 \pm 0.020$	6	120	11
		403	$0.792 \pm 0.011$	5	77	
C(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>3</sub>	cy-C <sub>5</sub> H <sub>8</sub>	299	$2.66 \pm 0.07$	4	380	11
		393	$2.19 \pm 0.09$	5	220	
C(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	cy-C <sub>5</sub> H <sub>8</sub>	298	3.48		500	14
		300	$3.41 \pm 0.02$	3	480	11
		393	$2.69 \pm 0.14$	4	270	
C <sub>6</sub> H <sub>6</sub>	cy-C <sub>5</sub> H <sub>8</sub>	393	$(6.55 \pm 0.66) \times 10^{-3}$		0.66	45
		494	$(18.4 \pm 1.6) \times 10^{-3}$		1.5	
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	cy-C <sub>5</sub> H <sub>8</sub>	393	$(17.45 \pm 1.2) \times 10^{-3}$	4	1.7	52
		495	$(40.2 \pm 1.1) \times 10^{-3}$	3	3.2	
1,3-C <sub>4</sub> H <sub>6</sub>	cy-C <sub>5</sub> H <sub>8</sub>	299	$0.810 \pm 0.018$		120	121
		400	$0.884 \pm 0.011$		87	
cis-2-C <sub>4</sub> H <sub>8</sub>	cy-C <sub>5</sub> H <sub>8</sub>	300	$0.801 \pm 0.014$	4	110	127
trans-2-C <sub>4</sub> H <sub>8</sub>	cy-C <sub>5</sub> H <sub>8</sub>	299	$0.951 \pm 0.042$	5	140	127

TABLE 58. Relative rate measurements of Cvetanovic [1], 14, 46, 98, 127], Jones and Cvetanovic [52], Kato and Cvetanovic [39, 59], Cvetanovic and Doyle [121], and Boocock and Cvetanovic [45]—Continued

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-11} k_A^a$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Ref.
1-C <sub>6</sub> H <sub>12</sub>	cy-C <sub>5</sub> H <sub>8</sub>	299	0.218 ± 0.004	5	31	127
C <sub>3</sub> H <sub>6</sub>	1-C <sub>4</sub> H <sub>8</sub>	298	0.943		26	14
cis-2-C <sub>4</sub> H <sub>8</sub>	1-C <sub>4</sub> H <sub>8</sub>	298	3.57		100	14
iso-C <sub>4</sub> H <sub>8</sub>	1-C <sub>4</sub> H <sub>8</sub>	298	4.22		120	14
cis-2-C <sub>5</sub> H <sub>10</sub>	1-C <sub>4</sub> H <sub>8</sub>	298	3.80		110	14
C <sub>2</sub> H <sub>5</sub> OH	1-C <sub>4</sub> H <sub>8</sub>	298	0.031 ± 0.004		0.87	59
2-C <sub>3</sub> H <sub>7</sub> OH	1-C <sub>4</sub> H <sub>8</sub>	298	0.0464		1.3	39
trans-2-C <sub>4</sub> H <sub>8</sub>	iso-C <sub>4</sub> H <sub>8</sub>	298	1.13		130	14

<sup>a</sup> All derived rate constants,  $k_A$ , are based on absolute rate constants for ethylene (table 4) and the rate ratios in this table.

TABLE 59. Relative rate measurements of Saunders and Heicklen [13, 15, 16], Stuckey and Heicklen [12], Marsh and Heicklen [58], and Stockburger and Heicklen [129]

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-11} k_A^a$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Ref.
C <sub>2</sub> F <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	297	1.031		5.0	16
C <sub>2</sub> F <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	297	1.10 ± 0.18	9	5.3	13
		343	0.855 ± 0.038	3	5.3	
		398	0.735 ± 0.065	3	5.7	
C <sub>3</sub> F <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	297	0.0357 ± 0.0060	5	0.17	13
		343	0.0385 ± 0.0041	3	0.24	
		398	0.0488 ± 0.0036	3	0.38	
C <sub>3</sub> F <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	297	0.0345		0.17	15
1,5-C <sub>4</sub> F <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	305	0.50		2.5	129
C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> F <sub>4</sub>	297	0.193 ± 0.020	3	1.0	13
		343	0.296 ± 0.03	4	1.6	
		398	0.566 ± 0.014	3	3.3	
C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> F <sub>4</sub>	297	4.27 ± 0.66	5	23	13
		343	3.47 ± 0.28	9	19	
		398	4.26 ± 0.41	3	24	
1-C <sub>4</sub> H <sub>8</sub>	C <sub>2</sub> F <sub>4</sub>	297	4.3		23	16
1-C <sub>4</sub> H <sub>8</sub>	C <sub>2</sub> F <sub>4</sub>	297	3.41 ± 0.30	4	18	13
		343	4.06 ± 0.34	4	22	
		398	4.42 ± 0.51	3	25	
C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> F <sub>6</sub>	297	0.122 ± 0.006	2	0.021	13
		343	0.22 ± 0.04	4	0.053	
		398	0.30 ± 0.11	4	0.11	
C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> F <sub>6</sub>	297	0.47 ± 0.03	3	0.081	13
		343	0.67 ± 0.09	6	0.16	
		398	0.96 ± 0.09	3	0.37	

## RATE CONSTANTS FOR REACTIONS OF ATOMIC OXYGEN

507

TABLE 59. Relative rate measurements of Saunders and Heicklen [13, 15, 16], Stuckey and Heicklen [12], Marsh and Heicklen [58], and Stockburger and Heicklen [129]—Continued

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-11} k_A^a$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Ref.
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	C <sub>3</sub> F <sub>6</sub>	307	0.69 ± 0.01	5	0.13	58
		343	1.06 ± 0.05	4	0.26	
		398	1.31 ± 0.08	5	0.50	
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	C <sub>3</sub> F <sub>6</sub>	307	3.6 ± 0.3	5	0.66	58
		343	4.7 ± 0.5	6	1.1	
		398	5.4 ± 0.4	5	2.1	
C <sub>8</sub> H <sub>18</sub> (2,2,4-Tri-methylpentane)	C <sub>3</sub> F <sub>6</sub>	307	2.2 ± 0.1	6	0.40	58
		343	2.4 ± 0.2	5	0.58	
		398	2.9 ± 0.7	6	1.1	
cy-C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> F <sub>6</sub>	297	0.030 ± 0.013	3	0.0052	13
		343	0.050 ± 0.013	2	0.012	
		398	0.066 ± 0.008	2	0.025	
cy-C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> F <sub>6</sub>	298	0.027 ± 0.004	7	0.0047	12
		343	0.037 ± 0.009	8	0.0089	
		398	0.052 ± 0.007	7	0.020	
cy-C <sub>4</sub> H <sub>8</sub>	C <sub>3</sub> F <sub>6</sub>	298	0.41 ± 0.04	6	0.072	12
		343	0.70 ± 0.08	5	0.17	
		398	0.80 ± 0.16	7	0.31	
cy-C <sub>5</sub> H <sub>10</sub>	C <sub>3</sub> F <sub>6</sub>	298	3.0 ± 0.6	6	0.52	12
		343	3.4 ± 0.6	8	0.82	
		398	3.4 ± 0.4	5	1.30	
cy-C <sub>6</sub> H <sub>12</sub>	C <sub>3</sub> F <sub>6</sub>	298	3.1 ± 0.6	6	0.54	12
		343	4.3 ± 1.0	7	1.0	
		398	4.2 ± 1.1	6	1.6	
C <sub>2</sub> H <sub>4</sub> O (Ethylene oxide)	C <sub>3</sub> F <sub>6</sub>	307	0.040 ± 0.004	13	0.0073	58
		343	0.036 ± 0.003	7	0.0087	
		398	0.034 ± 0.005	8	0.013	
C <sub>2</sub> H <sub>6</sub> O (Dimethyl ether)	C <sub>3</sub> F <sub>6</sub>	307	1.17 ± 0.09	7	0.21	58
		343	1.12 ± 0.05	5	0.27	
		398	1.30 ± 0.15	5	0.50	
C <sub>3</sub> H <sub>8</sub>	1,3-C <sub>4</sub> F <sub>6</sub>	305	0.039		0.099	129
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	1,3-C <sub>4</sub> F <sub>6</sub>	305	0.093		0.24	129

<sup>a</sup> All derived rate constants,  $k_A$ , are based on absolute rate constants for ethylene (table 4) and the rate ratios in this table.

TABLE 60. Relative rate measurements of Moss

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-11} k_A^a$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Ref.
C <sub>2</sub> H <sub>3</sub> F	C <sub>2</sub> H <sub>4</sub>	296	0.38		1.8	146
1,1-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>			0.22		1.1	
cis-1,2-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>			0.32		1.5	
trans-1,2-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>			0.54		2.6	

TABLE 60. Relative rate measurements of Moss—Continued

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-11} k_A^a$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Ref.
C <sub>2</sub> HF <sub>3</sub>			0.57		2.7	
C <sub>2</sub> F <sub>4</sub>			1.60		9.1	
CH <sub>3</sub> C(CF <sub>3</sub> )CH <sub>2</sub>			0.55		2.6	

<sup>a</sup> All derived rate constants,  $k_A$ , are based on absolute rate constants for ethylene (table 4) and the rate ratios in this table.

TABLE 61. Relatives rate measurements of Smith

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-12} k_A^a$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Ref.
1-C <sub>4</sub> H <sub>8</sub>	CS <sub>2</sub>	298	0.78 ± 0.08	4		55
		410	0.83 ± 0.08	4		
<i>iso</i> -C <sub>4</sub> H <sub>8</sub>	CS <sub>2</sub>	298	3.1 ± 0.3	4		
		410	2.5 ± 0.3	4		
<i>iso</i> -C <sub>4</sub> H <sub>8</sub>	1-C <sub>4</sub> H <sub>8</sub>	298	4.0		9.1	
		410	3.0		8.7	

<sup>a</sup> All derived rate constants,  $k_A$ , are based on absolute rate constants for 1-butene (table 4) and the rate ratios in this table.

TABLE 62. Relative rate measurements of Moss and Jennings

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-12} k_A^a$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Ref.
CH <sub>3</sub> CFCH <sub>2</sub>	1-C <sub>4</sub> H <sub>8</sub>	296	0.46		1.0	79, 83
CH <sub>2</sub> FCH <sub>2</sub> CHCH <sub>2</sub>	1-C <sub>4</sub> H <sub>8</sub>	296	0.575		1.3	79, 83
CH <sub>3</sub> C(CF <sub>3</sub> )CH <sub>2</sub>	1-C <sub>4</sub> H <sub>8</sub>	296	0.077		0.17	79, 83 44
C <sub>3</sub> H <sub>6</sub>	1-C <sub>4</sub> H <sub>8</sub>	296	0.93		2.1	79, 44
CH <sub>2</sub> FCHCH <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	296	0.21		0.44	79, 83
CH <sub>3</sub> CHCF <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	296	0.45		0.95	79, 83
CH <sub>3</sub> CH <sub>2</sub> CFCF <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	296	1.00		2.1	79
CF <sub>3</sub> CHCH <sub>2</sub>	CH <sub>3</sub> C(CF <sub>3</sub> )CH <sub>2</sub>	296	0.131		0.023	79, 83, 44
CH <sub>3</sub> CH <sub>2</sub> CFCF <sub>2</sub>	CH <sub>3</sub> C(CF <sub>3</sub> )CH <sub>2</sub>	296	11.0		1.9	79, 83

<sup>a</sup> All derived rate constants,  $k_A$ , are based on absolute rate constants for 1-butene (table 4) and the rate ratios in this table.

TABLE 63. Relative rate measurements of Neumann and Jonathan

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-10} k_A^a$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Ref.
$\text{CH}_3\text{OCH}_3$	<i>cis</i> -2-C <sub>4</sub> H <sub>8</sub>	311	$1.85 \times 10^{-3}$	3	1.8	92
		323	$1.61 \times 10^{-3}$	3	1.5	
		338	$2.08 \times 10^{-3}$	3	2.0	
		353	$2.70 \times 10^{-3}$	3	2.5	
		363	$3.13 \times 10^{-3}$	3	2.8	
		373	$4.17 \times 10^{-3}$	3	3.7	
<i>trans</i> -2-C <sub>4</sub> H <sub>8</sub>	$\text{CH}_3\text{OCH}_3$	308	1010	3	110	
		324	790	3	120	
		343	820	3	170	
		363	450	3	120	
		375	340	3	110	

<sup>a</sup> All derived rate constants,  $k_A$ , are based on absolute rate constants for the *cis*-2-butene reaction (table 4) and the rate ratios in this table.

TABLE 64. Relative rate measurements of Grovenstein and Mosher

Reactant A	Reactant B	T, K	$k_B/k_B^a$	No.	$k_A$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Ref.
$\text{C}_6\text{H}_5\text{CH}_3$	$\text{C}_6\text{H}_6$	303	4.37			90
$\text{C}_6\text{H}_5\text{C}_2\text{H}_5$			4.95			
<i>o</i> -C <sub>6</sub> H <sub>4</sub> -(CH <sub>3</sub> ) <sub>2</sub>			10.0			
<i>m</i> -C <sub>6</sub> H <sub>4</sub> -(CH <sub>3</sub> ) <sub>2</sub>			23.0			
<i>p</i> -C <sub>6</sub> H <sub>4</sub> -(CH <sub>3</sub> ) <sub>2</sub>			9.77			
$\text{C}_6\text{H}_5\text{C}-(\text{CH}_3)_3$			3.60			
1,2,3-C <sub>6</sub> H <sub>3</sub> -(CH <sub>3</sub> ) <sub>3</sub>			25.0			
1,3,5-C <sub>6</sub> H <sub>3</sub> -(CH <sub>3</sub> ) <sub>3</sub>			80.0			
$\text{C}_6\text{H}_5\text{OCH}_3$			$\geq 13.2$			
$\text{C}_6\text{H}_5\text{F}$			0.67			
$\text{C}_6\text{H}_5\text{CF}_3$			0.29			

<sup>a</sup> Ratio of total rates of production of phenols with respect to the rate of production of phenol from benzene. It is not certain that this is equivalent to the ratio of total rate constants, so that derived values of  $k_A$  are not given.

TABLE 65. Relative rate measurements of Tyerman [32], Ford and Endow [17], Scala and Wu [88], Elias [19], Christie and Collins [66], Sato and Cvitanovic [26], and Paraskevopoulos and Cvitanovic [164].

Reactant A	Reactant B	T, K	$k_A/k_B$	No.	$10^{-11} k_A^a$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Ref.
$\text{C}_2\text{F}_4$	$\text{C}_2\text{H}_4$	296	$1.05 \pm 0.05$	5.0	32	
$\text{C}_6\text{H}_{18}$ (3-Methyl-heptane)	$\text{C}_2\text{H}_4$	298	0.54	2.6	17	
<i>cis</i> -C <sub>3</sub> H <sub>6</sub>	$\text{C}_2\text{H}_4$	298	$1.12 \times 10^{-4}$	$5.4 \times 10^{-5}$	88	
1-C <sub>4</sub> H <sub>8</sub>	$\text{C}_2\text{H}_4$	300	5.4	4	26	
		423	3.7	4	31	
<i>cis</i> -2-C <sub>4</sub> H <sub>8</sub>	1-C <sub>4</sub> H <sub>8</sub>	300	4.0	2	92	
		423	3.2	3	96	
		488	2.7	2	90	
CF <sub>2</sub> CFCI	$\text{C}_2\text{F}_4$	296	$0.51 \pm 0.04$	2.7	32	
		419	$1.36 \pm 0.10$	7.9		
CF <sub>2</sub> CCl <sub>2</sub>	$\text{C}_2\text{F}_4$	296	$0.67 \pm 0.06$	3.5	32	
		419	$0.95 \pm 0.10$	5.5		
CH <sub>3</sub> CHO	NO <sub>2</sub>	293	$0.036 \pm 0.06$	2.0	66	
1-C <sub>4</sub> H <sub>8</sub>	NO <sub>2</sub>	298	0.48	28	26	
<i>iso</i> -C <sub>4</sub> H <sub>8</sub>	NO <sub>2</sub>	298	2.6	150	26	
(CH <sub>3</sub> ) <sub>3</sub> CH	1-C <sub>4</sub> H <sub>8</sub>	298	0.014	0.35	164	

<sup>a</sup> All derived rate constants,  $k_A$ , are based on absolute rate constants for ethylene (table 4), 1-butene (table 4), tetrafluoroethylene (table 5) and NO<sub>2</sub> (ref. [168]), and the rate ratios in this table.

## 5. Formula Index

	Page		Page
$\text{CH}_4$		$\text{C}_7\text{H}_{16}$	
Methane.....	470, 476	<i>n</i> -Heptane.....	471, 478, 507
$\text{C}_2\text{H}_2$		2,2-Dimethylpentane.....	471, 482
Acetylene.....	474, 500, 506	2,4-Dimethylpentane.....	471, 482
$\text{C}_2\text{H}_4$		$\text{C}_8\text{H}_{10}$	
Ethylene.....	473, 493, 505, 506, 507, 508, 509	Ethylbenzene.....	474, 501, 509
$\text{C}_2\text{H}_6$		1,2-Dimethylbenzene.....	474, 501, 509
Ethane.....	470, 476, 506	1,3-Dimethylbenzene.....	474, 501, 509
$\text{C}_3\text{H}_4$		1,4-Dimethylbenzene.....	474, 501, 509
Propyne.....	474, 501, 506	$\text{C}_8\text{H}_{18}$	
$\text{C}_3\text{H}_6$		<i>n</i> -Octane.....	471, 478
Cyclopropane.....	471, 483, 507, 509	3-Methylheptane.....	482, 509
Propene.....	473, 494, 506, 508	2,2,4-Trimethylpentane.....	471, 482, 507
$\text{C}_3\text{H}_8$		2,3,4-Trimethylpentane.....	471, 482
Propane.....	470, 482, 506, 507	2,2,3,3-Tetramethylbutane.....	471, 482
$\text{C}_4\text{H}_2$		$\text{C}_9\text{H}_{12}$	
Butadiyne.....	474, 501	1,2,3-Trimethylbenzene.....	509
$\text{C}_4\text{H}_6$		1,3,5-Trimethylbenzene.....	509
1,3-Butadiene.....	473, 497, 505	$\text{C}_{10}\text{H}_{14}$	
$\text{C}_4\text{H}_8$		<i>tert</i> -Butylbenzene.....	509
Cyclobutane.....	471, 483, 507	$\text{C}_4\text{N}_2$	
1-Butene.....	473, 495, 505, 506, 508, 509	Dicyanoacetylene.....	509
<i>cis</i> -2-Butene.....	473, 495, 505, 506, 509	$\text{C}_5\text{H}_N$	
<i>trans</i> -2-Butene.....	473, 496, 505, 506, 509	Pyridine.....	501
2-Methylpropene.....	473, 496, 505, 506, 508, 509	$\text{CH}_2\text{O}$	
$\text{C}_4\text{H}_{10}$		Formaldehyde.....	474, 502
<i>n</i> -Butane.....	470, 477, 505, 507	$\text{CHDO}$	
2-Methylpropane.....	482, 509	Monodeuteroformaldehyde.....	475, 503
$\text{C}_5\text{H}_8$		$\text{CH}_4\text{O}$	
Cyclopentene.....	473, 498, 505, 506	Methanol.....	502
$\text{C}_5\text{H}_{10}$		$\text{C}_2\text{H}_2\text{O}$	
Cyclopentane.....	471, 483, 507	Ketene.....	475, 504
Spiropentane.....	471, 483	$\text{C}_2\text{H}_4\text{O}$	
1-Pentene.....	473, 497	Acetaldehyde.....	475, 503, 505, 509
<i>cis</i> -2-Pentene.....	473, 497, 506	Ethylene oxide.....	475, 504, 507
2-Methyl-2-butene.....	473, 497, 505	$\text{C}_2\text{H}_6\text{O}$	
$\text{C}_5\text{H}_{12}$		Ethanol.....	475, 503, 506
<i>n</i> -Pentane.....	471, 478	Dimethyl ether.....	475, 504, 505, 507, 509
2-Methylbutane.....	471, 482	$\text{C}_3\text{H}_6\text{O}$	
2,2-Dimethylpropane.....	471, 478	Propionaldehyde.....	503
$\text{C}_6\text{H}_6$		$\text{C}_3\text{H}_8\text{O}$	
Benzene.....	474, 501, 505, 509	Isopropanol.....	475, 503, 506
$\text{C}_6\text{H}_{10}$		$\text{C}_7\text{H}_8\text{O}$	
Cyclohexene.....	473, 498, 505	Methoxybenzene.....	509
$\text{C}_6\text{H}_{12}$		$\text{CH}_3\text{F}$	
Cyclohexane.....	471, 484, 507	Fluoromethane.....	492
1-Hexene.....	473, 497, 506	$\text{CH}_2\text{F}_2$	
2,3-Dimethyl-2-butene.....	473, 497, 505	Difluoromethane.....	492
$\text{C}_6\text{H}_{14}$		$\text{CHF}_3$	
<i>n</i> -Hexane.....	471, 478	Trifluoromethane.....	492, 505
2,3-Dimethylbutane.....	471, 478	$\text{C}_2\text{H}_2\text{F}$	
$\text{C}_7\text{H}_8$		Fluoroethylene.....	473, 498, 507
Toluene.....	474, 501, 505, 509	$\text{C}_2\text{H}_2\text{F}_2$	
$\text{C}_7\text{H}_{14}$		1,1-Difluoroethylene.....	473, 498, 507
Cycloheptane.....	472, 484		

	Page		Page
1,2-Difluoroethylene.....	473, 498	C <sub>2</sub> H <sub>3</sub> Cl	
cis-1,2-Difluoroethylene.....	498, 507	Chloroethylene.....	473, 498
trans-1,2-Difluoroethylene.....	498, 507	C <sub>2</sub> H <sub>5</sub> Cl	
C <sub>2</sub> HF <sub>3</sub>		Chloroethane.....	472, 487
Trifluoroethylene.....	498, 508	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	
C <sub>2</sub> F <sub>4</sub>		1,2-Dichloroethane.....	492
Tetrafluoroethylene.....	473, 498, 506, 508, 509	C <sub>3</sub> H <sub>7</sub> Cl	
C <sub>3</sub> H <sub>5</sub> F		2-Chloropropane.....	472, 488
2-Fluoropropene.....	474, 499, 508	C <sub>3</sub> H <sub>9</sub> Cl	
3-Fluoropropene.....	474, 499, 508	2-Chlorobutane.....	472, 489
C <sub>3</sub> H <sub>4</sub> F <sub>2</sub>		1-Chloro-2-methylpropane.....	472, 489
1,1-Difluoropropene.....	474, 499, 508	2-Chloro-2-methylpropane.....	472, 490
C <sub>3</sub> H <sub>3</sub> F <sub>3</sub>		C <sub>3</sub> H <sub>11</sub> Cl	
3,3,3-Trifluoropropene.....	474, 499, 508	1-Chloro-2,2-dimethylpropane.....	472, 491
C <sub>3</sub> F <sub>6</sub>		C <sub>4</sub> H <sub>5</sub> Cl	
Hexafluoropropene.....	474, 499, 506, 507	Chlorobenzene.....	474, 501
C <sub>4</sub> H <sub>7</sub> F		C <sub>4</sub> H <sub>15</sub> Cl	
4-Fluoro-1-butene.....	474, 499, 508	1-Chloroheptane.....	472, 492
C <sub>4</sub> H <sub>5</sub> F <sub>3</sub>		CCl <sub>2</sub> O	
2-Trifluoromethylpropene.....	474, 499, 508	Dichloroformaldehyde.....	475, 503
1,1,2-Trifluoro-1-butene.....	474, 499, 508	C <sub>2</sub> F <sub>3</sub> Cl	
C <sub>4</sub> F <sub>6</sub>		Trifluorochloroethylene.....	499, 509
1,3-Hexafluorobutadiene.....	474, 499, 506, 507	C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub>	
C <sub>6</sub> H <sub>5</sub> F		1,1-Difluoro-2,2-dichloroethylene.....	499, 509
Fluorobenzene.....	474, 501, 509	C <sub>2</sub> H <sub>3</sub> Br	
C <sub>7</sub> H <sub>5</sub> F <sub>3</sub>		Bromomethane.....	472, 486, 505
Trifluoromethylbenzene.....	509	C <sub>2</sub> H <sub>5</sub> Br	
CF <sub>2</sub> O		Bromoethylene.....	473, 498
Difluoroformaldehyde.....	503	C <sub>2</sub> H <sub>9</sub> Br	
CH <sub>3</sub> Cl		Bromoethane.....	472, 487
Chloromethane.....	472, 485, 505	C <sub>3</sub> H <sub>7</sub> Br	
CHCl <sub>3</sub>		2-Bromopropane.....	472, 488
Trichloromethane.....	492	C <sub>4</sub> H <sub>9</sub> Br	
CCl <sub>4</sub>		1-Bromobutane.....	472, 490
Tetrachloromethane.....	472, 486	1-Bromo-2-methylpropane.....	472, 491

## 6. Author Index to Bibliography

Ai, H. C.....	188	Braun, W.....	104
Allen, E. R.....	5	Brennen, W.....	36, 201
Amichai, O.....	162	Brown, J. M.....	29
Arrington, C. A.....	36, 201	Browne, W. G.....	91
Ashmore, P. G.....	133		
Atkinson, R.....	128, 150	Cadle, R. D.....	5, 50
Avery, H. E.....	110, 165	Callear, A. B.....	24
Avramenko, L. I.....	2,	Camaggi, G.....	156
	6, 8, 31, 40, 41, 43, 47, 54, 57, 116, 131	Carr, R. W., Jr.....	82
Ayling, A. B.....	96	Castellion, G. A.....	172
Azatyan, V. V.....	1, 61, 62, 64, 68, 74, 119	Christie, M. I.....	66
Bader, R. F. W.....	123	Chu, J. C.....	188
Bayes, K. D.....	151, 179, 180	Clark, A. H.....	91
Benson, S. W.....	139, 195	Clough, P. N.....	107, 152
Bergomi, A.....	156	Cohen, N.....	22
Bonanno, R. A.....	187	Collins, B. M.....	66
Boocock, G.....	45	Connor, J.....	106
Bradley, J. N.....	86	Creek, D. M.....	173

Cvetanovic, R. J.....	11,	Ikawa, T.....	122
14, 20, 23, 26, 27, 28, 39, 45, 46, 52, 59, 63, 97, 98, 110, 112, 120, 121, 127, 128, 134, 138, 150, 194			
Daby, E. E.....	85, 87	Jaffe, S.....	189, 190
Dalby, F. W.....	155	James, G. S.....	89
Davis, D.....	77, 104, 118, 130, 166, 168, 201	Jarvie, J. M. S.....	20
Dean, A. M.....	105	Jennings, K. R.....	44, 79, 83
deHaas, N.....	9, 25, 75, 80, 183	Jonathan, N.....	92, 174, 175
DeMore, W. B.....	198	Jones, G. R. H.....	52
Doyle, L. C.....	121, 138	Jones, G. W.....	56, 70, 71, 176
Dryer, F. L.....	181	Jones, I. T. N.....	179, 180
Dzotsenidze, Z. G.....	65	Klemm, R. B.....	201
Elias, L.....	10, 19	Kanofsky, J. R.....	177, 178, 191
Endow, N.....	17	Kasimovskaya, R. R.....	137
Eusuf, M.....	171	Kato, A.....	39, 59
Fair, R. W.....	106	Kaufman, F.....	100, 117
Fenimore, C. P.....	56, 70, 71, 176	Kaufman, M.....	101
Fish, A.....	145	Kawasaki, H.....	49
Foner, S. N.....	157	Keith, J.....	189
Fontijn, A.....	161	Kistiakowsky, G. B.....	38, 105
Ford, W.....	17	Klein, R.....	103, 113, 114, 115, 132, 193
Frazier, G. C., Jr.....	73	Knight, V.....	18, 154
Froben, F. W.....	84	Kolb, C. E.....	101
Gaedtke, H.....	182	Kolesnikova, R. V.....	2, 6, 8, 31, 40, 41, 43, 47, 54, 57, 116, 131
Gangi, R. A.....	123	Kooyman, W. J.....	73
Gay, I. D.....	82	Kurylo, M. J.....	104, 149
Glänzer, K.....	182	Kuznetsova, N. L.....	6, 43, 54
Glass, G. P.....	36, 38, 82, 89	Kuwa, M.....	122
Glassman, I.....	181	Lau, H. H.....	142
Gollnick, K.....	169	Lee, J.-H.....	187
Gozzo, F.....	156	LeFevre, H. F.....	141
Grant, R. C. S.....	190	Leppin, E.....	169
Gray, P.....	160, 167	Liu, Y. S.....	185
Greene, F. D.....	142	Lucas, D.....	177, 178
Greig, G.....	200	Luther, K.....	182
Grovenstein, E., Jr.....	90	Mani, I.....	67
Gutman, D.....	177, 178, 191	Marsh, G.....	58
Haller, I.....	184	Mayer, S. W.....	69
Heath, S. J.....	165	McFarlane, R. A.....	185
Heicklen, J.....	12, 13, 15, 16, 18, 21, 22, 58, 129, 140, 154	McMillan, G. R.....	144
Herron, J. T.....	60, 76, 77, 78, 99, 102, 104, 118, 130, 163, 166, 168, 202	Meagher, J. F.....	141
Hikita, T.....	72	Mearns, A. M.....	197
Hippler, H.....	182	Melliar-Smith, C. M.....	173
Hoffmann, R.....	170	Meng-yuan, T.....	1, 61, 68
Hoyermann, K.....	33, 37	Meyer, J. A.....	94
Hudson, R. L.....	157	Michael, J. V.....	36, 38
Hughes, A. N.....	132	Mitchell, R. C.....	111
Huié, R. E.....	60, 76, 77, 102, 104, 118, 130, 166, 168, 202	Mori, S.....	48, 49
		Morris, A.....	174
		Morris, A. J.....	197
		Morris, E. D., Jr.....	159
		Mosher, A. J.....	90
		Moss, S. J.....	44, 79, 83, 146
		Mulcahy, M. F. R.....	158

Nalbandyan, A. B.	1, 61, 64, 65, 68, 74, 81, 119	Smith, I. W. M.	24, 55
Neagu, V.	170	Smith, W. N.	142
Neumann, M. C.	92	Sorokina, M. F.	41
Niki, H.	34, 35, 36, 38, 51, 82, 85, 87, 124, 125, 126, 159	Steacie, E. W. R.	153
Noyes, W. A., Jr.	172	Stedman, D. H.	159
O'Donovan, J. T.	53	Stockburger, L., III	129
Oganesyan, K. T.	65	Strausz, O. P.	106
Oishi, K.	48	Stuckey, W. K.	12, 21
Okuda, M.	174	Stuhl, F.	124, 125, 126
O'Neal, H. E.	139	Style, D. W. G.	160
Oprandi, V.	156	Sullivan, J. O.	30
Orlov, V. M.	136		
Osterholtz, F. D.	142	Takezaki, Y.	48, 49
Othmer, D. F.	188	Tanaka, C.	72
Padiva, A.	143	Terao, T.	186
Papadopoulos, C.	133	Thrush, B. A.	29, 95, 107, 152
Parsamyan, N. I.	64, 81	Thynne, J. C. J.	167, 200
Penzhorn, R. D.	78	Timmons, R. B.	141, 187
Pethard, M. R.	158	Treinin, A.	162
Pimentel, G. C.	184	Troe, J.	182
Ponomarev, A. N.	135, 136, 137	Tse, R. S.	86
Poonzag, K.	187	Tsuchiya, F.	122
Porter, R. P.	91	Tsuchiya, S.	72
Postnikov, L. M.	131	Ts'ui, M.-Y.	119
Potter, A. E., Jr.	3, 4	Tberman, W. J. R.	32
Powers, J. W.	50	Tyler, B. J.	133
Pravilov, A. M.	93		
Preston, K. F.	97	Ung, A. Y.-M.	42
Quickett, K. A.	175	Van Rooselaar, A.	106
Ring, D. F.	138	Verlin, J. D.	91
Sachyan, G. A.	65	Vilesov, F. I.	93
Sakai, N.	186		
Sato, S.	26, 27, 28, 134	Wagner, H. G.	33, 37, 171
Sauer, C., Jr.	67	Walker, R. E.	109
Saunders, D.	13, 15, 16	Walling, C.	143
Savinova, G. I.	2, 8, 31, 40, 47, 57	Wan, C. C.	170
Savitz, M. R.	142	Warnneck, P.	30
Scala, A. A.	88	Weinstock, B.	34, 85, 87
Scheer, M. D.	103, 113, 114, 115, 132, 193	Westenberg, A. A.	9, 25, 75, 80, 183
Schieler, L.	69	Williams, A.	108
Schiff, H. I.	10, 42	Williams, D. J.	96
Schwartz, S. E.	107	Williamson, D. G.	148, 151
Setser, D. W.	94, 196	Wilson, W. E., Jr.	53
Shaw, R.	167	Wolfrum, J.	33, 37
Shida, S.	186	Wolga, G. T.	185
Silakhtaryan, N. T.	74	Wong, E. L.	3, 4
Simons, J. P.	111	Wright, F. J.	7, 147
Smith, D. B.	108	Wu, W.-T.	88
Smith, D. S.	174	Yamazaki, H.	120
		Zanet, P. M.	142

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