

# Absolute Rate Constants for the Reaction $O + O_2 + M \rightarrow O_3 + M$ over the Temperature Range 200–346°K

by Robert E. Huie,<sup>1,2</sup>

*University of Maryland, College Park, Maryland 20740 and National Bureau of Standards, Washington, D. C. 20234*

John T. Herron,<sup>2</sup>

*National Bureau of Standards, Washington, D. C. 20234*

and Douglas D. Davis\*<sup>3</sup>

*Chemistry Department, University of Maryland, College Park, Maryland 20740 (Received March 20, 1972)*

*Publication costs assisted by The Petroleum Research Fund*

Using the technique of flash photolysis–resonance fluorescence, absolute rate constants have been measured for the reaction  $O + O_2 + M \rightarrow O_3 + M$ . For the case of  $M = Ar$  the temperature range covered was 200–346°K, and the total pressure was varied from 50 to 500 Torr. Over the indicated temperature range, an Arrhenius plot of the data yielded the expression  $k_{Ar} = (6.57 \pm 0.59) \times 10^{-35} \exp[(1014 \pm 46 \text{ cal mol}^{-1})/RT] \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ . A comparison of the third-order rate constants for  $M = He, Ar,$  and  $N_2$  gave the relative efficiencies for these three gases as 0.92:1.0:1.6 at 298°K. At 218°K, the efficiencies of Ar to  $N_2$  were in the ratio of 1.0:1.7. The reported rate measurements indicate that the rate of production of stratospheric ozone could be nearly a factor of 2 lower than that estimated from previously reported values of the third-order rate constant.

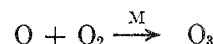
The reaction of atomic oxygen,  $O(^3P)$ , with molecular oxygen is the only important ozone forming reaction in both the troposphere and stratosphere. In order to understand either photochemical air pollution<sup>4</sup> or the ozone balance in the stratosphere,<sup>5–7</sup> the rate constant for this reaction must be known accurately. The need for kinetic information on reactions important in stratospheric chemistry has been emphasized by the recent suggestion that nitrogen oxides emitted by supersonic aircraft might significantly reduce the ozone concentration in the stratosphere.<sup>5,8</sup>

The atomic oxygen–molecular oxygen reaction has been the subject of many studies in recent years,<sup>9–20</sup> the data prior to mid-1967 having been reviewed by Johnston.<sup>20</sup> At room temperature, several techniques have been applied to the study of this reaction and a wide range of experimental parameters covered. The temperature dependence of this reaction, however, has been determined only in experiments using flow systems at low total pressure, with the atomic oxygen decay being followed by the air afterglow reaction<sup>9,10</sup>



In both of these studies, care was taken to prevent the introduction of extraneous active species into the reaction zone which might contribute to the decay of atomic oxygen. As is the case in nearly all flow systems, however, the measured O atom decay might have been influenced by reactions occurring on the walls of the reactor.

Since



is of such importance in stratospheric chemistry and since its rate constant needs to be well established at

(1) This research carried out at the University of Maryland is part of a thesis to be submitted to the Faculty of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Supported in part by the Climatic Impact Assessment Program, Office of the Secretary, Department of Transportation.

(3) Acknowledgment is made by this author to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(4) P. A. Leighton, "Photochemistry of Air Pollution," Academic Press, New York, N. Y., 1961.

(5) M. Nicolet, *J. Geophys. Res.*, **70**, 679 (1965).

(6) P. J. Crutzen, *Quart. J. Roy. Meteorol. Soc.*, **96**, 320 (1970).

(7) P. J. Crutzen, *J. Geophys. Res.*, **76**, 7311 (1971).

(8) H. Johnston, *Science*, **173**, 517 (1971).

(9) M. A. A. Clyne, D. J. McKenney, and B. A. Thrush, *Trans. Faraday Soc.*, **61**, 2701 (1965).

(10) M. F. R. Mulcahy and D. J. Williams, *ibid.*, **64**, 59 (1968).

(11) G. M. Meaburn, D. Perner, J. LeCalve, and M. Bourene, *J. Phys. Chem.*, **72**, 3920 (1968).

(12) F. Kaufman and J. R. Kelso, *J. Chem. Phys.*, **46**, 4541 (1967).

(13) F. Stuhl and H. Niki, *ibid.*, **55**, 3943 (1971).

(14) R. J. Donovan, D. Husain, and L. J. Kirsch, *Trans. Faraday Soc.*, **66**, 2551 (1970).

(15) H. Hippler and J. Troe, *Ber. Bunsenges. Phys. Chem.*, **75**, 27 (1971).

(16) T. G. Slinger and G. Black, *J. Chem. Phys.*, **53**, 3717 (1970).

(17) P. D. Francis, *Brit. J. Appl. Phys.*, 1717 (1969).

(18) M. C. Sauer, *J. Phys. Chem.*, **71**, 3311 (1967).

temperatures and pressures corresponding to stratospheric conditions, we have undertaken a flash photolysis-resonance fluorescence study of this reaction over a wide temperature and pressure range and under conditions in which neither secondary reactions nor wall reactions were important.

### Experimental Section

The apparatus and technique have been discussed in detail previously.<sup>21,22</sup> In these experiments a mixture of a few Torr of molecular oxygen and a diluent gas (helium, argon, or nitrogen) was flash photolyzed above  $\lambda$  1050 Å, producing on the order of 0.05 to 0.005 mTorr of atomic oxygen. A small portion of the atomic oxygen was continuously excited by an atomic oxygen resonance lamp and the decay of atomic oxygen in the mixture was monitored by following the fluorescence of the atomic oxygen resonance radiation. The fluorescence signal was recorded on a multichannel analyzer, and multiple flashes (>100) were used to generate one kinetic decay curve (see Figure 1). The reaction mixture was changed several times in the course of an experiment to prevent ozone accumulation. The first-order rate constant was determined from a plot of the logarithm of the count rate, corrected for background, against channel number, or time. A good linear fit was found over at least a full decade change in the count rate.

The second-order rate constant at a particular total pressure was calculated from the slope of a plot of this first-order rate constant against the molecular oxygen pressure as shown in Figure 2. In a few cases, when only one or two data points were taken at a given temperature and pressure, a zero intercept was assumed. Finally, the third-order rate constant was derived by dividing the second-order rate constant by the total pressure of the diluent gas. With argon and nitrogen as third bodies, the third-order rate constant at 298°K and around 220°K was also calculated from the slope of a plot of the second-order rate constant against total pressure, as shown in Figure 3. When the inert gas pressure was 100 Torr or less, the contribution to the measured rate from the reaction  $O + O_2 + O_2 \rightarrow O_3 + O_2$  became significant. In those cases, the rate of the reaction with oxygen as the third body was calculated using the rate expression for argon at higher pressures from the present work, and the relative third body efficiencies given by Kaufman and Kelso.<sup>12</sup> This value was then subtracted from the total measured first-order rate. At worst, this correction amounted to about 15% of the total first-order rate constant.

The gases used in this study were Matheson Gold Label<sup>23</sup> helium, argon, and oxygen, and Air Products Ultra-high Purity<sup>23</sup> nitrogen (all better than 99.9% stated purity). All were used without further purification. In the preparation of the gas mixtures, low pressures (1–6 Torr) were measured on a dibutyl

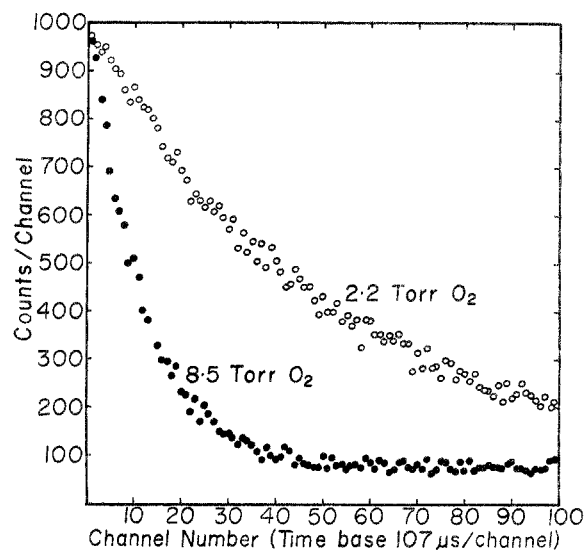


Figure 1. Typical  $O(^3P)$  atom decay curves: flash intensity, 31 J and total pressure, 250 Torr.

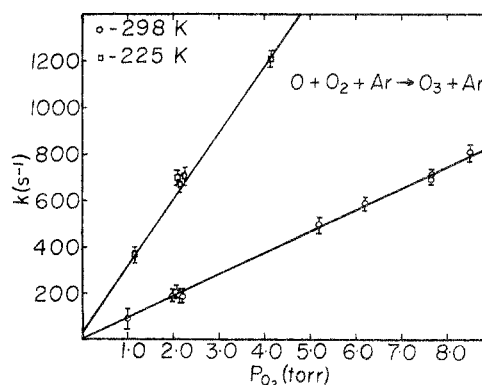


Figure 2. Plot of the experimentally measured first-order rate constant as a function of the  $O_2$  pressure: total pressure, 250 Torr.

phthalate manometer and higher pressures were measured on a two-turn Bourdon gauge. The precision to which various gas mixtures could be made up was determined to be  $\sim 3\%$ .

### Results and Discussion

The results of the present study are presented in Tables I–III. The stated error limits were derived

(19) M. C. Sauer and L. M. Dorfman, *J. Amer. Chem. Soc.*, **87**, 3801 (1965).

(20) H. S. Johnston, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U. S.)*, **20** (1968).

(21) D. D. Davis, A. M. Bass, and W. Braun, *Int. J. Chem. Kinet.*, **2**, 101 (1970).

(22) D. D. Davis, R. E. Huie, J. T. Herron, M. J. Kurylo, and W. Braun, *J. Chem. Phys.*, **56**, 4868 (1972).

(23) Certain commercial instruments and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

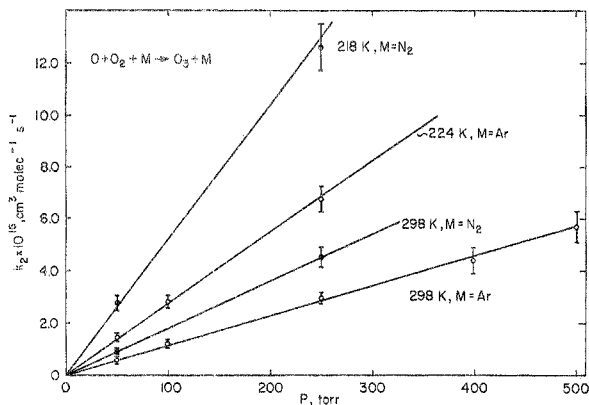


Figure 3. Plot of the second-order rate constants as a function of the total pressure.

**Table I:** Rate Measurements on the Reaction  $O + O_2 + He \rightarrow O_3 + He$  at 298°K

O <sub>2</sub> , Torr, <sup>a</sup>	He, Torr <sup>b</sup>	Flash energy, <sup>c</sup> J	First-order rate constant, sec <sup>-1</sup>	Third-order rate constant × 10 <sup>14</sup> cm <sup>6</sup> molecule <sup>-2</sup> sec <sup>-1</sup>
1.00	250	92	113	
1.00	250	100	113	
1.25	250	39	114	
2.00	250	100	182	
2.53	250	39	258	
5.00	250	92	428	
5.00	250	100	456	
6.20	250	39	578	3.33 ± 0.2

<sup>a</sup> 1 Torr = 9.65/T × 10<sup>18</sup> molecules cm<sup>-3</sup>. <sup>b</sup> Pressures greater than 100 Torr are the total pressure M + O<sub>2</sub>, others are pressures of M alone. <sup>c</sup> A flash energy of 80 J corresponds to about 1.5 × 10<sup>-13</sup> photons/cm<sup>2</sup> at the reaction cell (λ < 1800 Å).

**Table II:** Rate Measurements on the Reaction  $O + O_2 + N_2 \rightarrow O_3 + N_2$

T, °K	O <sub>2</sub> , Torr <sup>b</sup>	N <sub>2</sub> , Torr <sup>b</sup>	Flash energy, <sup>c</sup> J	First-order rate constant, sec <sup>-1</sup>	Third-order rate constant × 10 <sup>14</sup> cm <sup>6</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
218	1.54	50	39	210	
	4.72	50	45	645	12.5 ± 0.9
	7.1	50	37	1037	
	1.31	250	45	667	
	2.38	250	45	1390	11.4 ± 1.2
221	2.88	50	51	334	11.9 ± 0.9
	298	1.03	50	48	40
298	1.42	50	26	59	
	2.79	50	37	117	5.71 ± 0.6
	4.31	50	28	165	
	7.1	50	37	261	
	1.11	250	45	169	
	1.94	250	48	288	5.57 ± 0.6
	2.49	250	39	326	
	4.43	250	39	654	

<sup>a-c</sup> See corresponding footnotes in Table I.

**Table III:** Rate Measurements on the Reaction  $O + O_2 + Ar \rightarrow O_3 + Ar$

T, °K	O <sub>2</sub> , Torr <sup>a</sup>	Ar, Torr <sup>b</sup>	Flash energy, <sup>c</sup> J	First-order rate constant, sec <sup>-1</sup>	Third-order rate constant × 10 <sup>14</sup> cm <sup>6</sup> molecule <sup>-2</sup> sec <sup>-1</sup>	
200	1.17	150	29	333		
	2.54	150	29	773		
221	1.61	50	31	126		
	2.91	50	31	206		
	3.14	50	34	236		
	4.41	50	34	322		
	4.83	50	31	373	6.62 ± 0.6	
225	1.17	250	31	369		
	2.09	250	13	699		
	2.14	250	100	668		
	2.24	250	29	704		
	4.16	250	29	1210	6.30 ± 0.5	
227	1.71	100	39	206		
	4.03	100	42	492	6.54 ± 0.7	
247	1.01	250	39	206		
	1.98	250	31	362		
265	4.16	250	34	514	5.01 ± 0.4	
	0.75	250	54	125		
	1.64	250	54	241		
298	4.50	250	58	678	4.44 ± 0.4	
	1.46	50	39	42		
	2.36	50	31	60		
	2.95	50	34	75		
	4.40	50	31	111		
	4.60	50	29	115		
	6.93	50	31	187	4.09 ± 0.3	
	0.71	98	29	35		
	2.08	98	29	96		
	3.67	98	29	159	3.76 ± 0.4	
346	1.00	250	58	95		
	2.00	250	100	192		
	2.06	250	11	202		
	2.12	250	48	196		
	2.20	250	31	184		
	5.20	250	26	497		
	6.20	250	31	592		
	7.66	250	8	714		
	7.66	250	93	695		
	8.50	250	31	814	3.67 ± 0.2	
	3.80	400	29	540	3.40 ± 0.4	
	2.07	500	29	375		
	3.20	500	26	596	3.51 ± 0.4	
	346	2.60	250	29	150	
		4.88	250	29	273	
7.71		250	29	433	2.82 ± 0.3	

<sup>a-c</sup> See corresponding footnotes in Table I.

from a consideration of the maximum and minimum slopes which could be fit through the points plotted in Figure 2 (*k* (sec<sup>-1</sup>) vs. *P*<sub>O<sub>2</sub></sub>). The uncertainty in each of the first-order rate constants plotted in Figure 2 was ~5%. In all cases, the standard deviation derived from a least-squares treatment of the data was less than the error limit derived from a consideration of maximum and minimum slopes. The rate constant for the reaction  $O + O_2 + He \rightarrow O_3 + He$  was determined in this

work only at room temperature and 250 Torr pressure (Table I). Its value under these conditions was  $3.33 \pm 0.2 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ . Since nitrogen is a more efficient quencher of the oxygen resonance fluorescence radiation than helium or argon, rate measurements using this gas were found to be more difficult than those involving He or Ar as the third body. Due to the importance of the reaction  $\text{O} + \text{O}_2 + \text{N}_2 \rightarrow \text{O}_3 + \text{N}_2$ , however, rate constant measurements were carried out both at 218 and 298°K and at 50 and 250 Torr total pressure (Table II). The respective third-order  $k$  values at these two temperatures, calculated from the slopes in Figure 3, were  $11.7 \pm 1.2 \times 10^{-34}$  and  $5.63 \pm 0.77 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ . For the reaction  $\text{O} + \text{O}_2 + \text{Ar} \rightarrow \text{O}_3 + \text{Ar}$ , rate measurements were made over the temperature range 200–346°K and over a pressure range 50–500 Torr. These data are presented in Table III and in the form of an Arrhenius plot in Figure 4. The third-order rate constants calculated from the slopes in Figure 3 were  $3.47 \pm 0.3 \times 10^{-34}$  and  $6.36 \pm 0.72 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$  at 298°K and about 224°K. A fit of the third-order rate constants from Table III to the Arrhenius equation gave the expression  $k_{\text{Ar}} = (6.57 \pm 0.59) \times 10^{-35} \exp[(1014 \pm 46 \text{ cal mol}^{-1})/RT] \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ . The stated uncertainties are the standard errors of the least-squares fit to the data. From a consideration of the maximum and minimum slopes which could be fit through the error bars of each point in Figure 4, the indicated uncertainties in A and E were  $\pm 180 \text{ cal/mol}$  and  $\pm 2.15 \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ , respectively. A comparison of the third-order rate constants for M = He, Ar, and N<sub>2</sub> gave the relative efficiencies of these three gases for deactivation as 0.92:1.0:1.6 at 298°K. At 218°K, the efficiencies of Ar to N<sub>2</sub> were in the ratio 1.0:1.7.

At the lower oxygen pressures used in this work, the absorption of the flash lamp radiation by molecular oxygen in the reaction zone was low, resulting in only a small initial concentration gradient for the oxygen atoms. At higher oxygen pressures, this gradient became larger, thus possibly leading to spurious kinetic results. As illustrated in Figure 2, however, the first-order rate constants were directly proportional to the O<sub>2</sub> pressure over the entire experimental range, demonstrating that no effects on the rate measurements resulted from oxygen atom concentration gradients in the reaction zone.

Another possible source of error in this study, which has been discussed previously,<sup>22</sup> concerns the production of electronically excited oxygen atoms in the flash photolysis of molecular oxygen. In these experiments, a minimum of a 200- $\mu\text{sec}$  delay was employed between the flash photolysis of the reaction mixture and the atom concentration measurements used in determining the rate constants. At the pressures used in this study, the 200- $\mu\text{sec}$  delay would ensure that all atoms

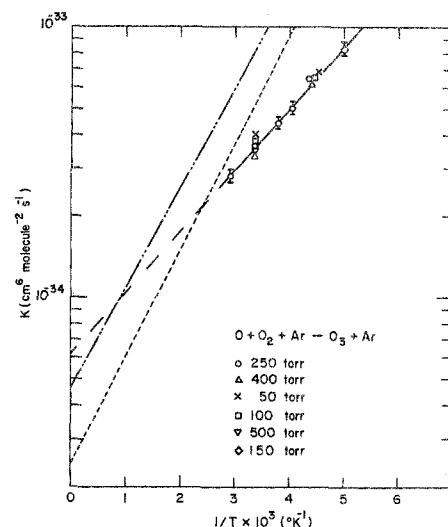


Figure 4. Arrhenius plot of the third-order rate constant for the reaction of atomic oxygen with O<sub>2</sub>: (—) represents values taken from ref 10 and (---) represents values taken from ref 9.

produced by the flash were in the ground electronic state and at thermal equilibrium. In the experiments employing He or Ar as the inert gas, most of the O(<sup>1</sup>D) produced by the flash would be quenched by O<sub>2</sub>, producing O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>).<sup>24</sup> The excited molecular oxygen could then react with the ozone produced by the O + O<sub>2</sub> + M reaction to regenerate atomic oxygen.<sup>25</sup> Since the concentrations of both O<sub>3</sub> and O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) would be proportional to the flash intensity, any contribution from this reaction would be strongly dependent upon the flash intensity. To investigate the possibility that this reaction could have influenced the observed O atom decay, or that any other secondary reactions could have been important, the flash intensity was varied over about a factor of 10 at both 298 and 225°K (see Table III and Figure 2). The observed invariance of the first-order rate constant with flash intensity demonstrates that the rate of atom loss was not being influenced by secondary reactions involving O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) and O<sub>3</sub> or any other secondary processes such as O + O<sub>3</sub> → 2O<sub>2</sub> and O + O + M → O<sub>2</sub> + M.

Since the third-order rate constant was obtained from the slopes of the first-order rate against the molecular oxygen partial pressure at a fixed total pressure, the results are independent of any impurities in the inert gas. Additionally, lack of significant dependence of the third-order rate constant on total pressure indicates that no impurity capable of a rapid second-order reaction with atomic oxygen was present in the molecular oxygen. (As indicated earlier, ultrahigh purity gases were used throughout this study.) Other possible systematic errors associated with the use of the

(24) R. J. Donovan and D. Husain, *Chem. Rev.*, **70**, 489 (1970).

(25) T. P. Izod and R. P. Wayne, *Proc. Roy. Soc., Ser. A*, **308**, 81 (1968).

Table IV: A Summary of Rate Data on the Reaction  $O + O_2 + M \rightarrow O_3 + M$ 

$T, ^\circ K$	M	$k, \text{cm}^3 \text{molecule}^{-2} \text{sec}^{-1}$	Method	Ref		
298	He	$3.33 \times 10^{-34}$	Flash photolysis-resonance fluorescence	This work		
298	Ar	$3.63 \times 10^{-34}$				
200-346	Ar	$6.57 \times 10^{-35} \exp(1014 \text{ cal mol}^{-1}/RT)$				
218	N <sub>2</sub>	$11.7 \times 10^{-34}$				
298	N <sub>2</sub>	$5.63 \times 10^{-34}$	Discharge flow	9		
188-373	Ar	$2.44 \times 10^{-35} \exp(1800 \text{ cal mol}^{-1}/RT)$				
213-386	Ar	$4.7 \times 10^{-35} \exp(1680 \text{ cal mol}^{-1}/RT)$	Thermal decomposition-flow	10		
298	CO <sub>2</sub>	$23 \times 10^{-34}$				
298	O <sub>2</sub>	$9.0 \times 10^{-34}$	Pulse radiolysis	11		
298	He	$6.33 \times 10^{-34}$				
298	CO <sub>2</sub>	$10.2 \times 10^{-34}$				
298	N <sub>2</sub> O	$8.84 \times 10^{-34}$				
298	CO	$4.42 \times 10^{-34}$				
298	He	$4 \times 10^{-34}$			Thermal decomposition-flow	12
298	Ar	$4 \times 10^{-34}$				
298	O <sub>2</sub>	$6.5 \times 10^{-34}$				
298	N <sub>2</sub>	$5.6 \times 10^{-34}$				
298	CO <sub>2</sub>	$15 \times 10^{-34}$				
298	N <sub>2</sub> O	$15 \times 10^{-34}$	Flash photolysis-chemi- luminescence	13		
298	CF <sub>4</sub>	$16 \times 10^{-34}$				
298	SF <sub>6</sub>	$34 \times 10^{-34}$	Flash photolysis-absorption	14		
298	H <sub>2</sub> O	$60 \times 10^{-34}$				
298	O <sub>2</sub>	$6.4 \times 10^{-34}$				
298	N <sub>2</sub>	$5.4 \times 10^{-34}$				
298	CO	$6.7 \times 10^{-34}$				
298	He	$4.6 \times 10^{-34}$				
298	Ar	$5.0 \times 10^{-34}$				
298	Kr	$4.9 \times 10^{-34}$				
298	N <sub>2</sub>	$8 \times 10^{-34}$			Photolysis relative to O + NO <sub>2</sub>	15
298	Ar	$4.4 \times 10^{-34}$				
298	N <sub>2</sub>	$7.0 \times 10^{-34}$	Flash photolysis-resonance fluorescence	16		
298	O <sub>2</sub>	$1.24 \times 10^{-34}$				
298	Ar	$2.28 \times 10^{-34}$	Discharge flow	17		
298	Ar	$2.48 \times 10^{-34}$				
298	Ar	$2.48 \times 10^{-34}$	Pulse radiolysis	18		
298	CO <sub>2</sub>	$11.5 \times 10^{-34}$				
298	N <sub>2</sub> O	$9.6 \times 10^{-34}$	Pulse radiolysis	19		
298	He	$1.92 \times 10^{-34}$				
298	O <sub>3</sub>	$4.63 \times 10^{-35} \exp(2100 \text{ cal mol}^{-1}/RT)$	$K_{eq}$ (review)	20		
298	Ar	$1.16 \times 10^{-35} \exp(2100 \text{ cal mol}^{-1}/RT)$				
298	O <sub>3</sub>	$8.14 \times 10^{-35} \exp(890 \text{ cal mol}^{-1}/RT)$	$K_{eq}$ (review)	28		

resonance fluorescence technique have been discussed more fully elsewhere.<sup>22</sup>

In Table IV, the results of the present work are summarized along with rate measurements reported by other workers. Excluded are those discharge flow measurements which were carried out under conditions where the effects of active impurities and metastable molecular oxygen species could have significantly influenced the final results.<sup>26</sup> Most of the earlier kinetic investigations on the system  $O + O_2 + M \rightarrow O_3 + M$  were carried out at a single temperature, 298°K. In three of these studies, oxygen atoms were produced *via* flash photolysis and loss of atomic oxygen was then followed either by  $O + NO$  chemiluminescence (Stuhl and Niki),<sup>13</sup> kinetic absorption spectroscopy (Donovan, Husain, and Kirsch),<sup>14</sup> or resonance fluorescence (Slanger and Black).<sup>18</sup> These results are seen to

agree with the present data to within 30%. In two reported pulse radiolysis studies by Sauer<sup>18</sup> and Sauer and Dorfman,<sup>19</sup> the reaction was followed by monitoring the formation of ozone. The rate constants determined at 298°K were about 50% lower than those measured in this work. In another study, Hippler and Troe<sup>15</sup> used the photolysis of NO<sub>2</sub> at 3660 Å as a means of determining the rate constant for the reaction  $O + O_2 + N_2 \rightarrow O_3 + N_2$  relative to the process  $O + NO_2 \rightarrow NO + O_2$ . In this study the extent of the ozone-producing reaction was determined by measuring the quantum yield for destruction of NO<sub>2</sub> with and without added O<sub>2</sub>. The results from this investigation were about 40% higher than reported here for N<sub>2</sub> as a third body. In both of the latter studies, the experimental

(26) F. Kaufman and J. R. Kelso, *J. Chem. Phys.*, **40**, 1162 (1964).

uncertainties associated with the techniques were sufficiently large as to explain the difference between their results and the present measurements. In an extensive study by Kaufman and Kelso<sup>12</sup> a flow system was employed in which the thermal decomposition of ozone was the atom source and detection of the atoms was by means of chemiluminescence. The agreement between the results of this study and those reported here for the third body gases He, Ar, and N<sub>2</sub> is seen to be within 10%.

As noted in the introduction, the only previous direct data on the temperature dependence of the rate of reaction of atomic oxygen with molecular oxygen are derived from flow system studies. Clyne, McKenney, and Thrush<sup>9</sup> studied the reaction in a plug-flow reactor, using a microwave discharge in oxygen as an atom source. The decay of the oxygen atoms down the reactor was determined by monitoring the chemiluminescence from the reaction  $O + NO \rightarrow NO_2 + h\nu$ . At room temperature, the results of these authors are in reasonable agreement with the present work ( $\pm 15\%$ ). At lower temperatures, however, their data diverge from the present results and are about a factor of 3 higher at 220°K. Mulcahy and Williams<sup>10</sup> also used the  $O + NO$  chemiluminescence to follow the atom concentration, but used the thermal decomposition of ozone as an atom source and carried out the study in a bulb reactor. These authors report a third-order rate constant for Ar which is a factor of 2 higher than the present results at 298°K and a factor of 3 higher at 220°K. In neither study were sufficient data given to allow a detailed discussion of the results. Although specific reasons for the discrepancies between the above studies of the temperature dependence of the  $O + O_2$  reaction and the results of this work cannot be given at present, some possibilities can be considered. In both studies, heterogeneous reactions involving the walls of the reaction vessels are possible sources of error; whereas, in the present work, the reaction time is much shorter than the time for diffusion to the walls. Since wall reactions would be expected to be more important at low temperatures,<sup>27</sup> this could also contribute the stronger temperature dependence observed in these flow studies. Additionally, the results of Mulcahy and Williams<sup>10</sup> depend on the assumption of perfect mixing in their bulb reactor, which if in error could possibly

explain why their results were also higher than those of Clyne, *et al.*<sup>9</sup>

In the review of Johnston<sup>20</sup> on the kinetics of neutral oxygen species, the recommended value for the reaction of atomic oxygen with molecular oxygen was derived from the equilibrium constant and the recommended rate constant for the reverse reaction. The preexponential term obtained by this method is a factor of 5 lower than from the present study, and the exponential term is a factor of 2 higher. At 220°K, this results in a rate constant a factor of 2 higher than reported here. This discrepancy, however, is probably not as unreasonable as it first appears. For example, the ozone bond strength used by Johnston was 24.8 kcal mol<sup>-1</sup>, and the activation energy used for the reverse reaction was 22.7 kcal mol<sup>-1</sup>. An error of 5% in either of these values would be sufficient to account for the observed difference in the exponential factors.

Benson and Axworthy,<sup>28</sup> in an earlier review of ozone decomposition, also derived a value for the recombination rate constant. Their value of the rate constant for the  $O + O_2 + M \rightarrow O_3 + M$  reaction was also based on the rate constant for the reverse reaction and the equilibrium constant. The Arrhenius parameters so derived are not extremely different from those reported here, although at stratospheric temperatures the calculated rate constant is a factor of 1.5 lower than that measured in this work.

In the present work, the rate constant for the reaction of atomic oxygen with molecular oxygen as a function of temperature has been determined in a static system free of the possible uncertainties associated with wall reactions. Rate constants have been measured at temperatures and pressures corresponding to stratospheric conditions. The reported rate measurements indicate that the rate of production of stratospheric ozone could be nearly a factor of 2 lower than that estimated from previously reported values of the third-order rate constant. This could be of considerable importance in estimating the magnitude of possible ozone destruction mechanisms necessary to explain the observed ozone profiles.

(27) J. T. Herron and R. E. Huie, *J. Phys. Chem.*, **73**, 3327 (1969).

(28) S. W. Benson and A. E. Axworthy, *J. Chem. Phys.*, **42**, 2614 (1965).