A LASER FLASH PHOTOLYSIS–RESONANCE FLUORESCENCE KINETIC STUDY: REACTION OF O(^{3}P) WITH O$_3$

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The laser flash photolysis of ozone at ≈ 6000 Å has been used to generate a clean kinetic source of ground state atomic oxygen, O(^{3}P). The decay of O(^{3}P) due to reaction with O$_3$ was monitored via resonance fluorescence at 1300 Å, under static reaction cell conditions. Over the temperature range of 220–353° K, the bimolecular rate constant, k_1, could be expressed in Arrhenius form as: $k_1 = (2.02 \pm 0.19) \times 10^{-11} \exp[-(4522 \pm 210 \text{ kcal/mole})/RT]$. Units are in cm^3 molec^{-1} sec^{-1}. A comparison of the results from this work with other recent investigations, indicates that the reliability of k_1 is now probably as good as 10–15% over nearly 300 degrees.

1. Introduction

The reaction

$$O(^3P) + O_3 \rightarrow O_2 + O_2 \tag{1}$$

has been the subject of numerous investigations over the last 15 years [1–7]. In most of these studies a major problem has been the generation of ground state atomic oxygen in the absence of metastable oxygen species (e.g., O$_2$($^1\Delta_g$), O(^{1}D) and O$_2$($^1\Sigma_g$)). In the present investigation, we have eliminated this problem by utilizing the high radiation intensities and spectral selectivity available from dye lasers. Ground state atomic oxygen was produced by the laser flash photolysis of ozone in the Chappius band at wavelengths between 5900 and 6200 Å. In this wavelength region, the energy available necessarily limits the oxygen species formed to ground state O(^{3}P) and O$_2$($^3\Sigma_g^-$). The means of detection of O(^{3}P) was that of resonance fluorescence.

2. Experimental

The flash photolysis–resonance fluorescence technique has been discussed in detail previously [8,9]. The only major change in the original system was the substituting of a Synergetics Chromobeam 1070 dye laser for the conventional spark discharge flash lamp. In these experiments, the dye laser was operated in the 5900–6200 Å region of the spectrum, using the dye rhodamine 6G. The laser flash photolysis of a mixture of ozone and diluent gas (Ar of N$_2$) typically produced from 10^{11}–10^{13} ground state atomic oxygen atoms per cm^3 in the reaction cell. A small fraction of these atoms was continuously excited by an atomic oxygen resonance lamp [10], and the decay of oxygen atoms in the mixture was monitored by following the fluorescence of the atomic oxygen resonance radiation. This fluorescence signal was recorded on a multichannel analyzer, and multiple laser flashes were then used to generate one kinetic decay curve. The reaction mixture was changed several times in the course of an experiment to prevent any significant depletion of O$_3$.

Because of the recognizable O$_3$ decomposition on the surface of a metal reaction cell, an all-glass reaction vessel [11] was employed in this study. Only at tem-

peratures of 240°K and below was the metal reaction cell used. At this temperature and below, no significant difference could be observed in the results from the metal and glass vessels.

To investigate the possible problem caused by the thermal decomposition of ozone at high temperatures, a careful study was made of the ozone concentration as a function of time and temperature. In these experiments, the ozone concentration was monitored via UV spectrophotometry. At 298 and 378°K, the thermal decomposition of ozone in a Pyrex glass vessel was found to proceed at rates of 0.06 and 1.5% per minute. The rates of thermal decomposition of ozone at both 298 and 378°K were determined at ozone pressures of 150 mtorr, 1 torr, and 3 torr. These results were later used to correct the ozone concentration whenever appropriate.

The argon used in this work was Matheson Ultra-High Purity Gold Label (99.999%). The nitrogen was Air Products Ultra-High Purity and was also 99.999% pure. These two diluent gases were used without further purification. The ozone used throughout these experiments was generated by passing pure O_2 (Matheson) through an ozonator which produced ozone at a rate of about 10 gram per hour. The O_3 was then collected and stored in a U-trap containing about 350 gram of silica gel (12–16 mesh, Fisher Scientific Co.) at the temperature of dry ice–trichloroethylene ($\approx -80°C$). Before each experiment, the ozone was purified by continuously pumping while at $\approx -80°C$. The purified O_3 was then monitored with a Cary 15 UV spectrophotometer to ensure a minimum purity of 94%.

3. Results and discussion

The reaction of $O(^3P)$ with O_3 was studied over an

Table 1
Rate measurements on the reaction $O(^3P) + O_3 \rightarrow O_2 + O_2$

T (°K)	O_3 (mtorr)	Diluent Ar(torr)	Reaction cell	Laser flash energy (mJ)	First order k_1 (sec^{-1})	Bimolecular $k_{bi} \times 10^{-15}$ (cm^3 molecule^{-1} sec^{-1})
220	120	150	brass	15	20	0.6 ± 0.11
	1164	150	brass	15	50	
240	192	150	brass	50	31	
	384	150	brass	50	47	
	672	150	brass	50	60	
	672	150	brass	15	62	
	768	150	brass	50	66	
	1344	150	brass	15	110	1.66 ± 0.15
266	237.5	180	glass	50	55	
	475	180	glass	50	76	
	665	180	glass	50	104	
	665	180	glass	15	110	
	950	180	glass	15	144	
	1330	180	glass	15	200	3.72 ± 0.23
298	47	50	glass	50	60	
	235	50	glass	50	142	
	470	50	glass	50	217	
	940	50	glass	15	370	10.6 ± 0.64
	235	300	glass	50	80	
	470	300	glass	50	185	
	940	300	glass	15	325	10.3 ± 1.01
	470	50 (N_2)	glass	50	182	11.3 ± 0.60
353	134.2	50	glass	50	270	
	312	50	glass	50	380	
	626	50	glass	50	640	27.8 ± 2.86
	94	50 (N_2)	glass	50	115	

ozone concentration range of 50–1400 mtorr, and a temperature range of 220–353°K. The results of this study are presented in table 1. It should be noted that the bimolecular rate constant was obtained from the slope of a plot of the pseudo-first order rate constant, k_1, versus ozone concentration at various temperatures (see fig. 1). The intercept in fig. 1 represents the rate of loss of atomic oxygen from the sampling zone of the reaction vessel, due to diffusion.

At room temperature (298°K), the bimolecular rate constant for the reaction $O(^3P) + O_3$ was found to be $(1.06 \pm 0.064) \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1}. At this temperature, the total pressure (Ar) was varied by a factor of six with no change in the resulting rate constant being observed. Also, a change from Ar to N_2 as the diluent gas showed no effect on the rate constant within the experimental uncertainty ($\approx \pm 7\%$). These observations would tend to rule out any possible kinetic influence of the metastable species, $O_2(^1\Sigma_g^+)$. However, more importantly is the fact that the O_3 was flash photolyzed at $\lambda \geq 6000$ Å which directly rules out the possible formation of both the metastables, $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$. At 220°K, the rate constant was found to be equal to $(6.0 \pm 1.1) \times 10^{-16}$ cm^3 molecule^{-1} sec^{-1}. The uncertainty in this measurement was determined to be approximately $\pm 20\%$.

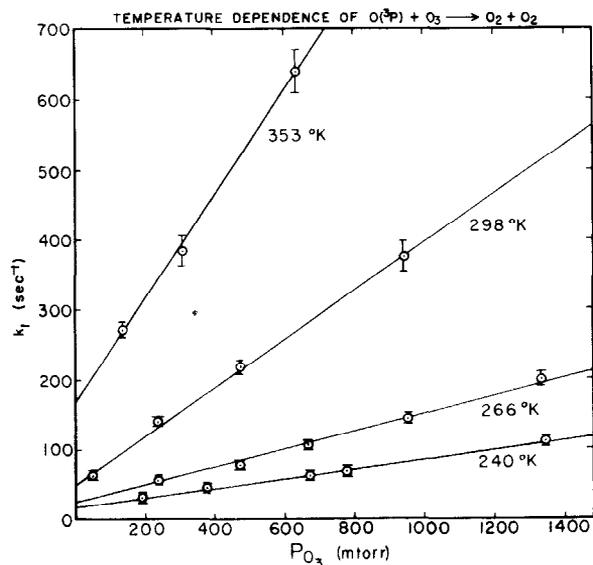Fig. 2. Arrhenius plot for the reaction $O(^3P) + O_3 \rightarrow O_2 + O_2$.

Over the temperature range 353–220°K, a fit of the rate data to the Arrhenius expression (fig. 2) gave the rate expression:

$$k_1(\text{cm}^3\text{molecule}^{-1}\text{sec}^{-1}) = (2.02 \pm 0.19) \times 10^{-11}$$

$$\times \exp[-(4522 \pm 210 \text{ cal/mole})/RT].$$

The above error limits were determined from a least-square fit to all of the data. An examination of the uncertainty in the rate constant for this reaction using the maximum and minimum slope procedure indicated that the rate constant, k_1, was at worst reliable to about a factor of ± 1.8 outside the temperature range that was studied (220–353°K).

Another potential problem in this as well as other studies of the reaction of $O(^3P)$ with O_3 is the formation of excited molecular oxygen (O_3^*) due to the high exothermicity of reaction (1). This could possibly lead to secondary reactions of the type,

$$O_2^* + O_3 \rightarrow 2O_2 + O. \tag{2}$$

Recent studies [12, 13] however, have produced evidence which suggests that under our experimental conditions the form of the excitation resulting from reaction (1) is vibrational. Furthermore, although the

Fig. 1. Plot of the pseudo first order rate constant versus the ozone pressure at various temperatures.

transfer of vibrational energy between ozone and vibrationally excited oxygen has been found to have a large cross section, it appears to be inefficient in causing the decomposition of ozone [14]. Other recent work [15, 16], involving the photolysis of ozone at $\lambda > 5000$ Å, has shown the quantum yield for O_3 decomposition to be 2.0 ± 0.1. This would set an upper limit of 1.05 for the chain length resulting from vibrationally excited molecular oxygen. It would appear, therefore, that all evidence to date strongly supports the conclusion: that under the experimental conditions of this study, the secondary production of $O(^3P)$ via reaction (2) was of negligible importance.

The only other secondary reactions which need to be considered in this study are

$$O(^3P) + O(^3P) + M \rightarrow O_2 + M, \tag{3}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M. \tag{4}$$
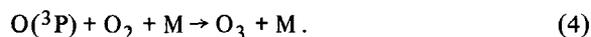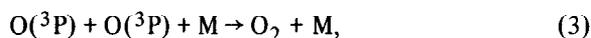
However, the contributions of these two reactions to the overall decay of O atoms should have been very small since the rate constants for these processes are small; and, in addition, the concentration of $O(^3P)$ was kept reasonably low in this investigation. In fact, calculations show that these processes were negligible ($< 2\%$) when compared with the overall rate constant for the primary reaction, $O(^3P) + O_3$.

A final problem area that was explored in this study of reaction (1) was the question of the linearity between the fluorescence signal observed and the atomic oxygen concentration sampled. In order to define this region of linearity, experiments were carried out in which the flash intensity (and thus the O atom concentration) was varied by factors of three and five. At partial pressures of 300 and 700 mtorr of ozone, a comparison of the full flash intensity (≈ 50 mJ) with one third flash intensity revealed that the values of the rate constant were invariant within the experimental error, indicating that the fluorescence signal was linearly dependent upon the atom concentration at these ozone pressures. On the other hand, at O_3 pressures of ≈ 1000 and 1400 mtorr, the experimental rate constants obtained at full flash intensity were found to be $\approx 15-25\%$ lower than the rate constants at one third flash intensity. Reducing the laser intensity to one fifth of its original value resulted in no measurable change in the k values when compared with the one third flash intensity results. Therefore, in

all experiments involving O_3 concentrations above 700 mtorr, flash intensities no higher than ≈ 15 mJ were employed.

A comparison of the present results with those of earlier studies is given in table 2. In the earlier high temperature thermal decomposition studies of the reaction $O(^3P) + O_3$, Jones and Davidson [3], and Benson and Axworthy [1] both obtained activation energies which were about 25% higher than that observed in this study. Moreover, the rate constants calculated from both their Arrhenius expressions at 298 and 220°K differ from those in this study by about 55% and 75%, respectively. In the case of the work by Benson and Axworthy, it appears likely that much of the disagreement on the value of k_1 could be related to an incorrect value being assigned to the activation energy of the process [17]

$$O_3 + M \rightarrow O + O_2 + M. \tag{5}$$

A more recent ozone thermal decomposition study by Intezarova and Kondratiev [2] resulted in an activation energy $\approx 17\%$ lower than in this study. The rate constant calculated from their Arrhenius expression at room temperature agrees reasonably well with the data of the present study ($\approx 10\%$). However, the rate constant calculated at 220°K differs from this work by $\approx 45\%$. It should be noted that these authors did not make a direct measurement of the value of k_1 but rather measured the ratio k_1/k_6,

$$O_2 + O + M \rightarrow O_3 + M. \tag{6}$$

The value of k_6 was in turn calculated from the equilibrium constant $k = k_5/k_6$ and some averaged value of k_5. Considering the indirect manner in which k_1 was established one must consider the agreement between this work and ref. [2] to be quite good.

In a study by Krezenski et al. [4], the rate constant for the $O(^3P) + O_3$ reaction was determined from a measurement of the rate constant ratio k_7/k_1 for the competitive reactions

$$O(^3P) + OCS \rightarrow CO + SO, \tag{7}$$
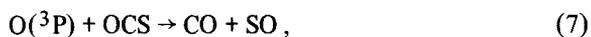
and (1). In this system, the rate constant ratio k_7/k_1 was obtained by following the rate of formation of CO and CO_2. The carbon dioxide was formed from the reaction of O_3 with CO. The rate constant k_1 was then determined using the known rate constant for reaction (7). Since ozone was photolyzed at $\lambda > 4300$ Å,

Table 2
A summary of rate data on the reaction $O(^3P) + O_3 \rightarrow 2 O_2$

$T(^\circ K)$	k_{bi} (cm^{3}molecule^{-1}sec^{-1})	Method	Reference
298	10.6 $\times 10^{-15}$	laser flash photolysis—	this work (1972)
220	0.6 $\times 10^{-15}$	resonance fluorescence	
353–220	2.02 $\times 10^{-11}$ exp($-4522/RT$)		
769–910	4.9 $\times 10^{-11}$ exp($-5600/RT$)	shock wave decomposition	
298	3.9 $\times 10^{-15}$ a)	of O_3	ref. [3] (1962)
220	0.15 $\times 10^{-15}$ a)		
373–473	5.6 $\times 10^{-11}$ exp($-5700/RT$)	thermal decomposition	ref. [1] (1965)
298	4.2 $\times 10^{-15}$ a)		
220	0.13 $\times 10^{-15}$ a)		
409–449	0.48 $\times 10^{-11}$ exp($-3700/RT$)	thermal decomposition	
298	11.0 $\times 10^{-15}$ a)	at constant flow rate and constant mole	
220	1.08 $\times 10^{-15}$ a)	fraction of O_3	ref. [2] (1967)
197–299	1.2 $\times 10^{-11}$ exp($-4300/RT$)	photolysis $\lambda > 4300$ Å	
298	9.4 $\times 10^{-15}$ a)	of O_3 in O_3/OCS mixture $\phi(CO)/\phi(CO_2)$	
220	0.67 $\times 10^{-15}$ a)	measured	ref. [4] (1972)
300	3.2 $\times 10^{-11}$ exp($-4500/RT$)	flow system calorimetric detection of O atoms	ref. [6] (1972)
300	13.0 $\times 10^{-15}$	flash photolysis—atomic absorption spectroscopy	ref. [5] (1972)
269–409	1.05 $\times 10^{-11}$ exp($-4310/RT$)	flow system with O + NO	
298	7.5 $\times 10^{-15}$	chemiluminescence	ref. [7] (1972)
220	0.58 $\times 10^{-15}$ a)		
—	2.0 $\times 10^{-11}$ exp($-4820/RT$)	preferred value	ref. [18] (1972)
298	9.0 $\times 10^{-15}$ a)		
220	0.67 $\times 10^{-15}$ a)		

a) Calculated from the corresponding Arrhenius expression.

the production of ground state oxygen atoms and molecules was ensured. The uncertainties in their rate data were essentially the experimental errors in obtaining the ratio of k_1/k_7 plus kinetic complications resulting from the further reactions of SO. The rate constants measured by Krezenski et al. [4] at 298 and 220°K agree with the values of this study to within 12%.

Husain et al. [5] used the flash photolysis—resonance absorption technique to study the reaction $O(^3P) + O_3$ at 300°K. In these experiments, ozone was flash photolyzed at $\lambda > 2000$ Å. This resulted in both excited oxygen atoms and oxygen molecules being formed in their system, and may explain why the room temperature data of these authors is about 20% higher than the value obtained in this study.

Lundell et al. [6] have reported a temperature dependence study of reaction (1) over a temperature range of 273–343°K. In this investigation, ground state atomic oxygen was produced in the absence of O_2 via the decomposition of N_2O on a "Nernst" glower. The decay of the atomic oxygen was moni-

tored under flow conditions. Over the indicated temperature range these workers found E_1 = 4.5 kcal/mole, in excellent agreement with the results from this study.

In the most recent temperature dependent study of reaction (1), McCrumb and Kaufman [7] employed a flow system in which atomic oxygen was again produced by thermal decomposition of O_3. Detection of the O atoms was via the O + NO chemiluminescence reaction. Their values for the rate constant at both 298 and 200°K agree with the values of the present study within $\approx$ 25%. These workers conducted a careful evaluation of the possible wall reactions and secondary reactions as well as the effects of the species $O_2(^1\Delta_g)$ on their O + NO chemiluminescence detecting technique.

The Arrhenius expression derived in this study is in good agreement with the recent expression recommended by the National Bureau of Standards Chemical Kinetics Data Survey [18]. The activation energy for the reaction $O(^3P) + O_3$ derived from this study agrees with the recommended values within $\approx$ 10%. The values of the absolute rate constants at 298 and 220°K, calculated from the recommended Arrhenius expression, agree with the experimental values obtained in this study to within 20% (see table 2).

Considering the good agreement between the results of several recent investigations [4, 6, 7] and those reported here, the rate constant for reaction (1) is now probably of an accuracy approaching the 10 to 15% level over at least 300 degrees.

Acknowledgement

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