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Kinetics of the $O + O_3$ Reaction*

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Abstract

The gas phase reaction $O + O_3 \rightarrow 2\ O_2$ was studied directly in a flow system under conditions of excess ozone, with O-atoms produced by thermal decomposition of $Ar\text{-}O_3$ mixtures on a Nernst glower, and measurement of the spatial O-atom decay by O + NO chemiluminescence with small, variable NO additions. The rate constant was found to be $(9.6 \pm 0.7) \times 10^{-15}$ cm^3 molecule^{-1} sec^{-1} at 298°K. Over the temperature range 269 to 409°K a rate expression $(1.78 \pm 0.28) \times 10^{-11} \exp[(-4.46 \pm 0.10$ kcal mole$^{-1})/RT]$ is reported. The effects of interference by $O_2\ (^1\Delta_g)$ and product excitation are discussed, and the present results are compared with earlier investigations.

Introduction

A knowledge of the rate constant of the reaction

$$O + O_3 \rightarrow 2\ O_2 \qquad \Delta H^\circ_{298} = -93.7\ \frac{\text{kcal}}{\text{mole}} \qquad 1$$

and of its temperature dependence is essential to an understanding of the photochemistry of the earth's stratosphere and mesosphere. Reaction 1 is one of the main sinks for "odd" oxygen in these regions and is therefore important in determining the vertical profile of atomic oxygen and ozone densities.[1] Recently the photochemical theory of the atmosphere has been extended to include reactions of hydrogen and nitrogen which also contribute to the loss of atmospheric O and O_3.[2,3] Thus a knowledge of the rate of Reaction 1 is also important in determining the roles played by these species and, thereby, indirectly helps assess the magnitude of man-made perturbations such as SST exhaust.[4]

The measurement of its rate constant has been the object of many investigations, yet considerable uncertainty remains as to its activation energy. In the past Glissman and Schumacher[5] and Benson and Axworthy[6] and more recently Intezarova and Kondratiev[7] have inferred k_1 indirectly from studies of the thermal decomposition of ozone which occurs via the mechanism

$$O_3 + M \underset{3}{\overset{2}{\rightleftarrows}} O_2 + O + M$$

$$O_3 + O \xrightarrow{1} 2\ O_2 \quad .$$

Arrhenius parameters for k_1 obtained in this manner, however, are somewhat unreliable because 1) the overall temperature dependence of the reaction scheme is dominated by the endothermicity of Reaction 2 $\Delta H^\circ_{298} = + 25.5$ kcal/mole and 2) there is some uncertainty in the experimentally determined value of k_3 which must be known before k_1 can be extracted. Under shock tube conditions at 800 to 900°K as studied by Jones and Davidson,[8] Reaction 2 is very fast and Reaction 3 can be neglected, but the experimental points show considerable scatter because the large activation energy of Reaction 2 again overshadows that of Reaction 1.

The absorption of red light by ozone (giving only ground state O and O_2) was used by Castellano and Schumacher[9] to obtain k_1 under conditions where Reaction 2 is unimportant, but unfortunately the temperature range covered was very small. Another photolysis study has recently been reported by Krezenski, Simonaitis, and Heicklen[10] in which atomic oxygen was produced by irradiating O_3 above 4300Å and the relative rates of its reactions with OCS and O_3 were determined. A previously measured value for the rate constant of O + OCS was then used to determine k_1 over the temperature range 197 to 299°K.

Early attempts to measure k_1 directly by mixing atomic oxygen and ozone were largely unsuccessful because (1) hydrogenous impurities in discharge flow experiments produced H-atoms whose reaction with O_3 was more than 1000 times faster than Reaction 1 and H was regenerated in the presence of O by the fast reaction $O + OH \rightarrow O_2 + H$; and (2) even in the absence of H, metastable species such as O_2 $(^1\Delta_g)$ were produced which react rapidly with O_3.[11,12] Lundell et al.[13] and Schiff[14] reported k_1 as measured in a flow system where ground state O-atoms were produced in the absence of O_2 by the thermal dissociation of N_2O on a Nernst glower.

This paper describes the direct measurement of k_1 when atomic oxygen was mixed with an excess of ozone in a steady state flow system over the temperature range 269 to 409°k. Ground state atomic oxygen sufficiently free of other labile species was produced by thermally decomposing ozone on a Nernst glower and its disappearance was followed along the reaction tube by photometrically observing the light produced by the reaction $O + NO \rightarrow NO_2 + h\nu$ when small amounts of nitric oxide ($[NO] << [O]$) were added to the flow.

Experimental

The experiments were carried out in a steady state flow system, the main features of which are shown in Figure 1. The central 100 cm of the flow tube (pyrex, 2.540 cm internal diameter, 170 cm total length) is surrounded by a hollow copper cooling jacket through which cold nitrogen gas may be passed to provide uniform cooling. Three cylindrical heating mantles controlled by a solid-state temperature controller (R.I. Controls, model MPRY) directly surround the copper jacket. Six observation ports (each 1/2 inch wide and 4 inches long) along the length of the reaction tube allow measurement of light emission from the tube as function of axial distance. It was found that the temperature of the reaction zone, measured by a movable iron-constantan thermocouple in the flow tube as related to four permanent thermocouples placed along the top of the tube, could be kept constant to better than ± 2°C over the 70 cm reaction length at all temperatures.

The total pressure in the tube was measured both upstream and downstream of the reaction zone through sidearms leading to an electrical pressure transducer (Pace Engineering Co. Model P7, ± 0.1 psi). Gas flows were metered through stainless steel needle valves. The flow rates of the major constituents (except for the M + O_3 flow described below) were measured with Fischer and Porter Tri-Flat flowmeters which were calibrated against a Vol-u-meter (George K. Porter Corp.), a device which accurately measures the volume of a flowing gas by displacement of a mercury sealed piston. Flow rates of NO, NO_2, and M + O_3 were determined by measuring the pressure drop as a function of time in a closed system of known volume.

Approximately 5% ozone in molecular oxygen was generated by passing pure O_2 (Baker extra dry) at atmospheric pressure through a Welsbach Siemens type ozonizer (Model T-408). The ozone was then selectively trapped in a U-tube containing 500g of silica gel (Davison 6-12 mesh) cooled to -78°C from which it was eluted by a carrier gas (Ar or O_2). The partial pressure of O_3 over the silica gel and thus the percentage of ozone in a given flow could be increased by raising the temperature of the silica gel trap. The ozone concentration was determined by its optical absorption of the 2537Å line of mercury in a quartz cell of 4.75 cm path length.

Atomic oxygen was produced by thermally decomposing ozone on a hot Nernst glower in a modification of a method first reported by Lundell, et al.[13] At room temperature the glower resistance is high, but when preheated to about 600°C by a flame it becomes conductive and can be further heated by passing electrical current through it. For this reason a housing was constructed (Figure 1) so that the glower could be removed, heated to dull red heat with a torch and then reinserted into the system. The glower housing was also equipped with a water cooling jacket. The negative temperature coefficient of resistance required that a current limiting ballast resistance, consisting of three 100 watt tungsten light bulbs in parallel, be wired in series with the glower.

The atomic oxygen concentration was measured before each experiment by an NO_2 titration.[15] Nitrogen dioxide obtained from Matheson at a stated purity of 99.5% was condensed at -78°C and pumped. Following a trap to trap distillation the center portion of the distillate, a white crystalline solid at -78°C, was used. Matheson nitric oxide with a stated purity of 98.5% was further purified by passing it slowly at atmospheric pressure through a 1 meter long absorption tube filled with Mikohbite

(G. Frederick Smith Chemical Co.) to remove higher oxides of nitrogen. This was followed by repeated distillation at 77°K.

The optical detection system was designed to measure the relative intensity of the O-NO chemilumenescence as a function of axial distance along the reaction tube at very low intensities. A dry-ice cooled end-window photomultiplier tube (EMR 541E-01-14) was mounted on a platform which could be moved parallel to the flow tube along two stainless steel tracks over a distance of about 70 cm. Pulse counting was used, pulses were amplified by two Keithley pulse amplifiers (Model 111), fed into an E.G.G. pulse height discriminator (Model T 101) and summed over a preset time interval, usually 1 to 10 seconds, by a Hewlett-Packard electronic counter (Model 5245L). The lower threshold on the discriminator was normally set at 75 mV. Counting rates ranged from 200 to 10,000 counts/sec and dark current contributed about 20 counts/sec. The relative position of the photomultiplier was determined using a linear 10 turn potentiometer attached to a pulley which reeled up a nylon cord connected to the platform. A battery across the potentiometer produced a voltage proportional to the traversal distance. The axial resolution of the optical system along the flow tube was determined by two vertical slits, 2 mm wide and 2.3 cm apart which defined an emitting length of 1.5 cm in the tube. A Corning color filter (C.S. 4-97) placed between the slits transmitted light from 4000 to about 6000Å and discriminated against most of the red NO + O_3 emission.

Experimental Procedure and Results

The experimental procedure involved measuring the spatial decay of atomic oxygen in the presence of an excess of ozone. Light from the chemiluminescent reaction $O + NO \rightarrow NO_2 + h\nu$ produced by the addition of a small amount of nitric oxide was used as an indicator for atomic oxygen. The emission intensity is proportional to the atom density, because any NO_2 formed by the reaction of O and NO is rapidly destroyed by the reaction

$$NO_2 + O \rightarrow NO + O_2 \qquad 4$$

which regenerates NO. The sensitivity of the optical detection system is such that the amount of NO required was responsible for a negligible loss of atomic oxygen by direct reaction. It is the reaction of nitric oxide and ozone, however, which limits the amount of NO which can be used. This reaction proceeds with a rate constant of 9.5×10^{-13} $\exp(-2.46/RT)$ cm^3 $molec.^{-1}$ sec^{-1} (1.6×10^{-14} at 298°K)[16] and when followed by Reaction 4 is kinetically equivalent to the reaction of O and O_3.

A parallel chemiluminescent reaction between NO and O_3 produces electronically excited NO_2 and weakly emits a red glow at wavelengths greater than 6000Å.[16] Due to the transmission of the Corning color filter mounted on the movable platform and the response of the photopultiplier, however, the signal from this reaction contributed negligibly to the observed air afterglow signal.

The important chemical reactions are

$$O + O_3 \rightarrow 2\ O_2 \qquad 1$$

$$O + \text{wall} \overset{k_w}{\rightarrow} 1/2\ O_2 + \text{wall} \qquad 2$$

$$O + O_2 + M \rightarrow O_3 + M \qquad 3$$

$$NO_2 + O \rightarrow NO + O_2 \qquad 4$$

$$O + NO + M \rightarrow NO_2 + M \qquad 5$$

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad 6$$

Reaction 3 could be neglected, because it is a slow three body reaction and $[O_2]$ was low, as could Reaction 5, because [NO] had to be kept very small. The kinetic expression for the disappearance of atomic oxygen is

$$-\frac{d[O]}{dt} = -\bar{v}\frac{dI}{dx} = k_w[O] + k_1[O_3][O] + k_3[NO_2][O]$$

where $\bar{v}$ is the average flow velocity assumed to be constant along the length of the reaction tube, and I is the intensity of the O + NO chemiluminescence. Because $[O_3] >> [O]$, the ozone concentration remained approximately constant and Reaction 1 was pseudo first order in [O], so that

$$-\bar{v}\frac{d\ln I}{dx} = k_w + k_1[O_3] + k_4[NO_2] \quad .$$

Small NO flows were used in order to minimize the effect of Reactions 4 and 6 on the overall kinetics. The disappearance of O was found to be first order for NO flows varied over a factor of 10 and the first order rate constants obtained from plots of lnI versus x were found to increase with increasing NO partial pressure. This dependence of slope on [NO] can be illustrated by assuming NO_2 to be in steady state, even though this is a reasonable assumption only at the beginning of the reaction ozone where [O] is relatively high. Substitution of $[NO_2]_{s.s.} = \frac{k_6[O_3][NO]}{k_4[O]}$ into the expression for O-atom disappearance gives

$$k^* \equiv -\bar{v}\,\frac{d\ln I}{dx} = k_w + k_1[O_3] + k_6[O_3]\,\frac{[NO]}{[O]} \quad .$$

For a given set of experimental conditions, I was measured as a function of distance along the reaction zone (x) for each of several fixed NO additions. For each P_{NO}, lnI was plotted against x and k* calculated from the slope. Values of $\frac{k^*-k_w}{[O_3]}$ were then plotted against the partial pressure of NO and extrapolated linearly to $P_{NO} = 0$ using a least squares computer fit. The first order heterogeneous wall recombination rate constant, k_w, was determined before and after each experiment by measuring the O-atom decay, as described above, with the ozone flow turned off (an argon flow substituted for the Ar + O_3 flow). Figures 2 and 3 illustrate this procedure for a typical set of experimental conditions (Table 1).

An essential prerequisite to this study was an oxygen atom source which generated a sufficient number of atoms free of metastable energetic species which react with ozone. While workable amounts of atomic oxygen can be produced by the thermal dissociation of O_2, O_3 or N_2O on a Nernst glower, the applicability of each of these gases to this particular system was judged from the actual data obtained in the measurement of the rate constant.

Lundell et al.[13] had used the Nernst glower dissociation of nitrous oxide as an atom source in the measurement of k_1. When medically pure N_2O (Union Carbide Corp., Linde Div.) was passed over the glower on this apparatus, however, a bright greenish-yellow glow was observed along the reaction tube. This glow, which increased in intensity as the glower temperature was raised, was presumably due to the O + NO chemiluminescence where NO was produced by the reaction $O + N_2O \rightarrow 2NO$ in the immediate vicinity of the glower. The ratio of nitric oxide to atomic oxygen was found to decrease with decreasing glower temperature, but even at the lowest attainable glower temperatures the NO concentration was still too large to be practical in this experiment.

Atomic oxygen could also be produced by the thermal dissociation of pure O_2. By operating the glower at the relatively high temperature of 2300° to 2400°K, from 1 to 5×10^{-3} torr atomic oxygen could be produced at total flow tube pressures of 1 to 2 torr. A series of measurements of k_1 were made using this atom source but the values were found to exhibit great scatter, ranging from 1.6 to 4.6×10^{-15} cm^3 $molec.^{-1}$ sec^{-1}. A correlation was found between the magnitude of k_1 and the glower temperature, i.e. the measured rate constant was larger at lower glower temperatures. Another series of experiments were performed in which O was generated by passing a flow of argon and a small amount of O_2 (as little as 5% of that used in the pure O_2 case) over the glower. It was found that this method gave workable amounts of atomic oxygen, but the rate constants measured still showed considerable scatter, ranging from 1.6 to 7.4×10^{-15} cm^3 $molec^{-1}$ sec^{-1}. A general trend, however, was observed, i.e. measured values of k_1 increased as the flow of O_2 being dissociated was decreased. This method could also not be used to arrive at a reasonable value of k_1, because at the lower oxygen flows the atomic oxygen concentrations dropped below workable levels.

The third method of O-atom production was the thermal decomposition of ozone in an excess of argon. In a typical experiment 1.8×10^{-3} atm cm^3 sec^{-1} atomic oxygen was produced by flowing 3.6×10^{-2} atm cm^3 sec^{-1} ozone and 2.5 atm cm^3 sec^{-1} argon over the glower at a temperature of 2100°K. Evidence that the ozone was effectively destroyed by the glower comes from the fact that there was no observed increase in the measured k_w's since any ozone which might survive the thermal dissociator and pass into the flow tube would contribute to the observed O-atom decay in both the k_w and k^* measurements, although it would not contribute to the calculated k_1. Values of k_1 measured in this manner are listed along with experimental conditions in Table 2. The lnI versus x plots were linear (e.g. see Figure 3) and the k_1 values $(\frac{k^*-k_w}{[O_3]}$ extrapolated to $P_{NO} = 0)$ were consistent for a variety of experimental conditions. The average value at 298°K was found to be $k_1 = 9.6 \pm (\sigma = 0.7) \times 10^{-15}$ cm^3 $molec.^{-1}$ sec^{-1}. It was then measured over the temperature range 269 to 409°K as shown in Table 3 and in Figure 4. From a least squares fit of the data, the Arrhenius expression is $k_1 = 1.78 \pm (\sigma = .28) \times 10^{-11} \exp[-4.46 \pm (\sigma = .10)/RT]$ cm^3 $molecule^{-1}$ sec^{-1} where σ is a single standard deviation.

Discussion

An explanation of the results obtained when the thermal dissociation of O_2 was used to produce atomic oxygen can be made in terms of metastable O_2 ($^1\Delta_g$) formed in the atom source. This species undergoes reaction with ozone[17] by

$$O_2\ (^1\Delta_g) + O_3 \rightarrow 2\ O_2 + O \qquad 7$$

and has the effect of increasing atomic oxygen along the tube, thus causing an underestimation in the observed value of k_1, and had led to the abandonment of discharge atom sources for such studies.[11]

The actual amount of O_2 ($^1\Delta_g$) present was not measured and is likely to be a function of the glower temperature, the amount of oxygen flowing over the glower and the total pressure. The scatter in these measurements, therefore, was probably due to the presence of varying amounts of O_2 ($^1\Delta_g$) produced under differing experimental conditions. This would also explain the trend of higher observed values of k_1 with lower glower temperatures and with smaller amounts of O_2 being dissociated, because both of these conditions should have the effect of reducing the amount of O_2 ($^1\Delta_g$) produced. In the case of the thermal dissociation of ozone, on the other hand, not only is the glower temperature (2100°K) lower than the O_2 case, but the amount of O_2 present is also small. An upper limit of the O_2 ($^1\Delta_g$) concentration can be calculated by assuming full thermal equilibrium between the glower and the gas flowing over it. The ratio of metastable O_2 ($^1\Delta_g$) to ground state O_2 ($^3\Sigma_g^-$) equals (2/3) $\exp(-\Delta E/kT)$ in good approximation, which at 2100°K is about 3×10^{-3}

($\Delta E = 7918.1\ cm^{-1}$). The amount of ozone dissociated was fairly constant in these experiments and corresponds to about 1.5×10^{-2} torr O_2 in the flow tube. The upper limit of $[O_2\ (^1\Delta_g)]$ is therefore about 5×10^{-5} torr or $[O_2\ (^1\Delta_g)]/[O] \simeq 0.1$. To estimate the perturbation on the measured value of k_1 caused by this amount of metastable oxygen a computer program was written which integrates the differential rate equations for Reactions 1 and 7. [O], $[O_3]$ and $[O_2\ (^1\Delta_g)]$ were calculated as functions of x for given flow velocity, initial concentrations and rate constants. Using typical values for these and $k_7 = 3.4\times10^{-15}\ cm^3$ $molec^{-1} sec^{-1}$,[17] a comparison of derived values of k_1 when $[O_2\ (^1\Delta_g)] = 0$ and $[O_2\ (^1\Delta_g)]/[O] = 0.1$ showed that the maximum possible error was about 8%. It is also clear from the relatively close range of k_1 obtained at higher glower temperatures and in O_2 carrier gas that much less $O_2\ (^1\Delta_g)$ is formed than corresponds to thermodynamic equilibrium.

Figure 5 shows the agreement between the present data and most of the data from previous investigations. The points measured by Krezenski et al.[10] whose temperature range, 197 to 299°K, is complementary to that of this work, fall nicely on the line calculated from the present data. It is also useful to summarize the Arrhenius expressions reported by various investigators in Table 4. The entry by Johnston[18] represents a careful evaluation and recalculation of all published work prior to 1967 and is in good agreement with the most recent experimental studies.

The possibility that excited molecular oxygen formed in the highly exothermic Reaction 1 is responsible for the further decomposition of ozone by

$$O_2\ (\text{excit.}) + O_3 \rightarrow 2\ O_2 + O \qquad 8$$

must be considered for both vibrational and electronic excitation. McGrath and Norrish[19] found vibrationally excited molecular oxygen in the electronic ground state during the ultraviolet flash photoysis of ozone by observing the Schumann-Runge absorption spectrum. There was some question, however, as to the origin of this excitation.[20] Under their experimental conditions it could have been produced by the reaction of O_3 with either $O(^3P)$ or $O(^1D)$. In a recent study, Ellis, McGarvey and McGrath[21] have shown that it is the reaction of $O(^3P)$ with ozone which produces the vibrational excitation. They flash-photolyzed ozone at wavelengths longer than 5700Å so that only ground state molecular and atomic oxygen were energetically accessible. The vibrational intensity distribution of O_2^v appeared identical to that observed by McGrath and Norrish, i.e. bands with $v'' = 12$ to 16 were observed in absorption with an apparent maximum intensity at $v'' = 13$. Evidence that Reaction 1 produces vibrationally excited molecular oxygen had also been given by Jones et al[8] the shock tube thermal decomposition of O_3 between 700 and 900°K where a Schumann-Runge absorption spectrum was observed similar to that obtained by McGrath and Norrish under conditions where only $O(^3P)$ was being produced.

In light of the fact that vibrationally excited nitrogen has been shown to decompose ozone,[22] it is plausible that vibrationally excited oxygen formed in Reaction 1 is also capable of decomposing ozone. Several experimental studies, however, have shown that this is not the case. Fitzsimmons and Bair[23] measured the time variation of vibrationally excited states of oxygen from v" = 13 to 19 formed by secondary processes in the ultraviolet flash photoysis of ozone. They analyzed their results in therms of stepwise deactivation mechanism where vibrational energy is lost one quantum at a time. The observed rate of decay of O_2^v was consistent with this model, and the relaxation rate constants for transfer of vibrational energy between ozone and excited oxygen were found to be large. No evidence was obtained for the efficient simultaneous transfer of six or more vibrational quanta which would be required to decompose ozone. On the contrary, all recent work on the quantum yield of ozone photolysis has disproved the occurence of energy chains due to O_2^v.[9,24] This evidence against energy chains has been obtained from studies of the photolysis of ozone with red light where the observed quantum yield in pure O_3 of 2.0 ± 5% sets an upper limit of 1.05 for the chain length at room temperature.[9] Also, the shock tube decomposition of ozone was interpreted without assuming that Reaction 8 occurs.[8] Assuming a 20% error in shock tube experiments, Johnston[18] was able to set an upper limit of 1.2 on chain length at 800°K. It thus seems well established that the rate expression does refer to the elementary reaction (1) uncomplicated by subsequent steps involving excited O_2, and that this excitation is mainly vibrational, i.e. that the reaction produces little if any O_2 ($^1\Delta_g$ or $^1\Sigma_g^+$).

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Table 1

Experimental Conditions for Typical O + O_3 Measurement

P_{TOTAL}=1.48 torr

F_{TOTAL}=5.47 $\frac{cm^3}{sec}$

$\bar{v}$=554 $\frac{cm}{sec}$

$P_{a.o.}$=3.4x10^{-4} torr

P_{O_3}=4.94x10^{-2} torr

k_w=2.6 sec^{-1}

Figure 2 line No.	P_{NO} (torr)	$-\bar{v}\frac{k^*}{dx}$ (sec^{-1})	$\frac{k^*-k_w}{[O_3]}$ (torr^{-1} sec^{-1})
1	3.56×10^{-5}	19.9	350
2	7.46×10^{-5}	22.0	393
3	1.69×10^{-5}	19.0	332
4	4.37×10^{-5}	20.3	358
5	2.29×10^{-5}	19.4	340
6	1.23×10^{-4}	26.4	482
7	5.82×10^{-5}	22.4	401

k_1 = 305 torr^{-1} sec^{-1} = 9.4 x 10^{-15} cm^3 molec.$^{-1}$ sec^{-1}

Table 2

Experimental Measurements of k_1 at 298°K

Flow	Total Pressure	Flow Velocity	Atomic Oxygen Partial Pressure	Ozone Partial Pressure	k_w	k_1
$\frac{\text{Atm cm}^3}{\text{sec}}$	Torr	cm/sec	Torr	Torr	sec^{-1}	$\frac{\text{cm}^3}{\text{molec. sec}}$
4.00	1.19	504		5.50×10^{-2}	2.2	1.07×10^{-14}
4.00	1.19	504	4.8×10^{-4}	3.48×10^{-2}	1.5	0.95×10^{-14}
4.37	1.96	334	5.2×10^{-4}	7.33×10^{-2}	2.5	1.03×10^{-14}
4.37	1.30	504	5.4×10^{-4}	3.70×10^{-2}	1.6	1.03×10^{-14}
5.49	1.52	542	5.3×10^{-4}	1.25×10^{-2}	2.7	0.84×10^{-14}
3.62	1.16	468	5.9×10^{-4}	5.8×10^{-2}	2.1	0.96×10^{-14}
2.71	1.94	210		1.87×10^{-2}	2.6	0.83×10^{-14}
5.70	1.52	563	3.5×10^{-4}	2.62×10^{-2}	2.5	1.00×10^{-14}
6.50	1.67	584	4.34×10^{-4}	2.46×10^{-2}	2.2	1.02×10^{-14}
5.47	1.48	554	3.40×10^{-4}	4.94×10^{-2}	2.6	0.95×10^{-14}
5.91	1.55	572	4.2×10^{-4}	2.79×10^{-2}	3.0	0.92×10^{-14}

Table 3

Experimental Measurements of k_1 Temperature Dependence

Temperature °K	Flow $\frac{\text{Atm cm}^3}{\text{sec}}$	Pressure Torr	Flow Velocity cm/sec	Atomic Oxygen Partial Pressure Torr	Ozone Partial Pressure Torr	k_w sec^{-1}	k_1 $\frac{\text{cm}^3}{\text{molec. sec}}$
269	5.09	1.55	492	3.85×10^{-4}	4.40×10^{-2}	1.9	3.68×10^{-15}
273	5.19	1.57	540	4.32×10^{-4}	1.30×10^{-2}	2.0	4.24×10^{-15}
296	3.64	1.13	459	3.1×10^{-4}	4.73×10^{-2}	2.2	9.25×10^{-15}
296	4.76	1.36	525		8.40×10^{-2}	1.3	1.06×10^{-14}
314	7.05	1.71	619	4.70×10^{-4}	2.10×10^{-2}	4.0	1.43×10^{-14}
330	6.31	1.52	623	3.7×10^{-4}	2.94×10^{-2}	3.5	2.02×10^{-14}
338	7.37	1.67	662	4.3×10^{-4}	2.63×10^{-2}	4.0	2.66×10^{-14}
347	7.80	1.71	685		2.05×10^{-2}	6.9	2.58×10^{-14}
359	7.36	1.60	690	4.52×10^{-4}	1.49×10^{-2}	4.5	3.40×10^{-14}
363	7.92	1.67	711		2.70×10^{-2}	6.6	3.83×10^{-14}
378	6.96	1.52	688	5.3×10^{-4}	1.25×10^{-2}	7.0	4.48×10^{-14}
384	8.63	1.71	758		1.86×10^{-2}	11.0	5.24×10^{-14}
388	7.96	1.60	746	4.52×10^{-4}	1.53×10^{-2}	7.5	5.31×10^{-14}
409	8.39	1.60	786	4.52×10^{-4}	1.63×10^{-2}	11.0	6.92×10^{-14}

Table 4

Arrhenius Expressions for $O + O_3 \rightarrow 2\ O_2$

Investigator	Reference	A 10^{-11} cm^3 $molec.^{-1}$ sec^{-1}	E kcal $mole^{-1}$
Benson and Axworthy	10	5.6	5.7
Intezarova and Kondratiev	7	0.48	3.7
Johnston	18	2.00	4.79
Schiff	14	3.2	4.5
Krezenski et al	10	1.2	4.3
This work		1.78 ± 0.28	4.46 ± 0.10

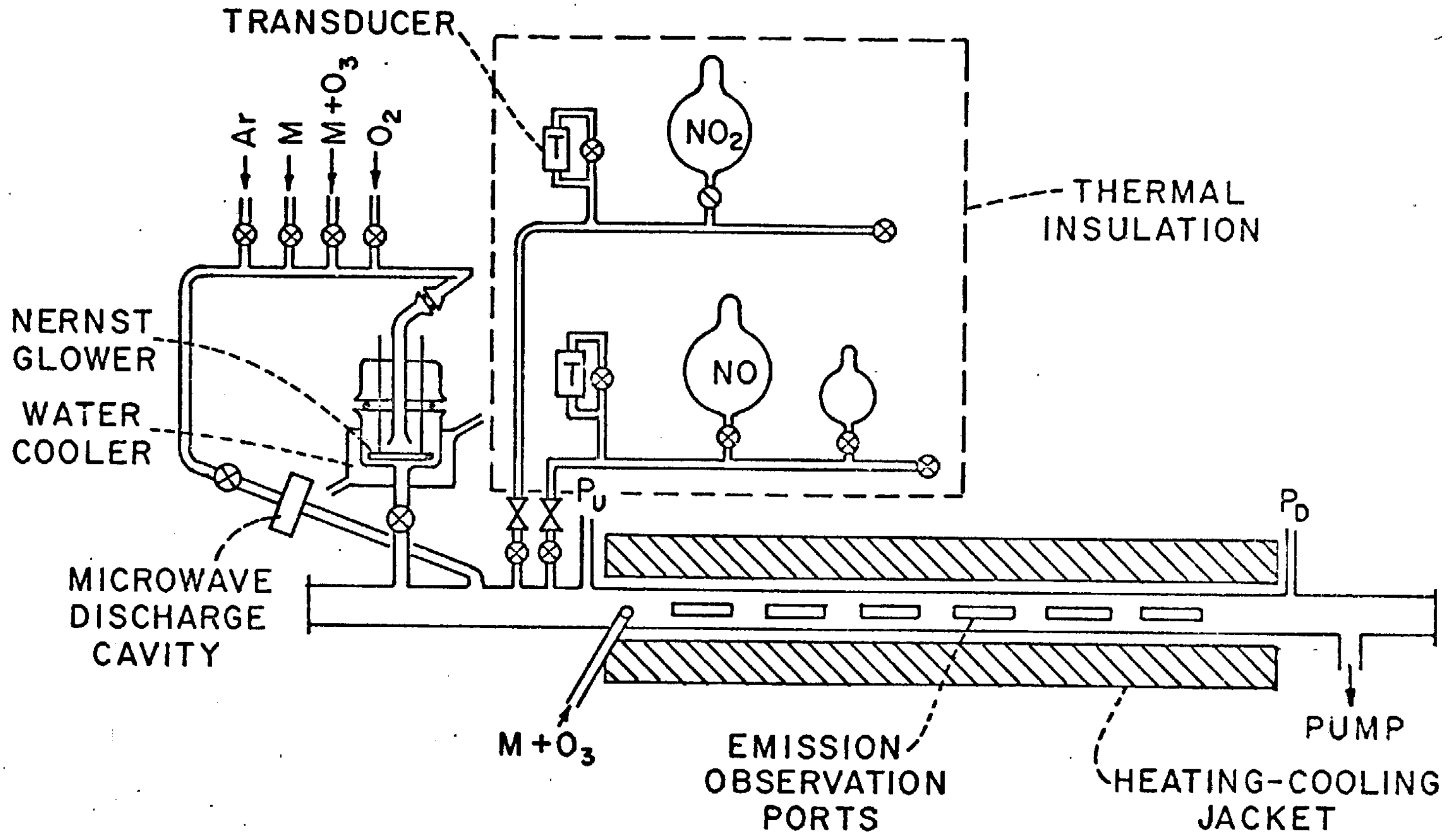

Figure 1

Diagram of flow system

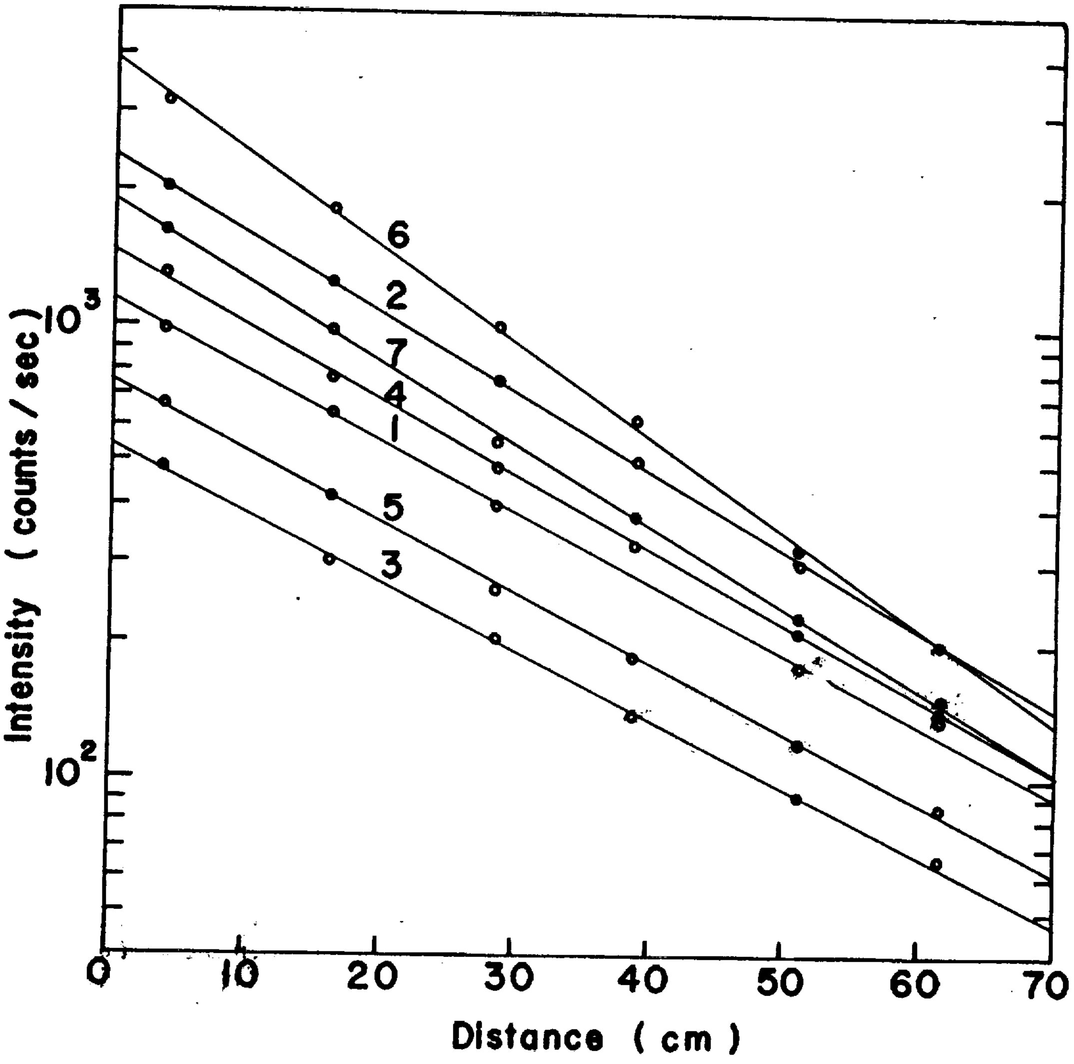

Figure 2

Decay of O(^{3}P) as a function of x for different NO partial pressures. Experimental conditions given in Table 1.

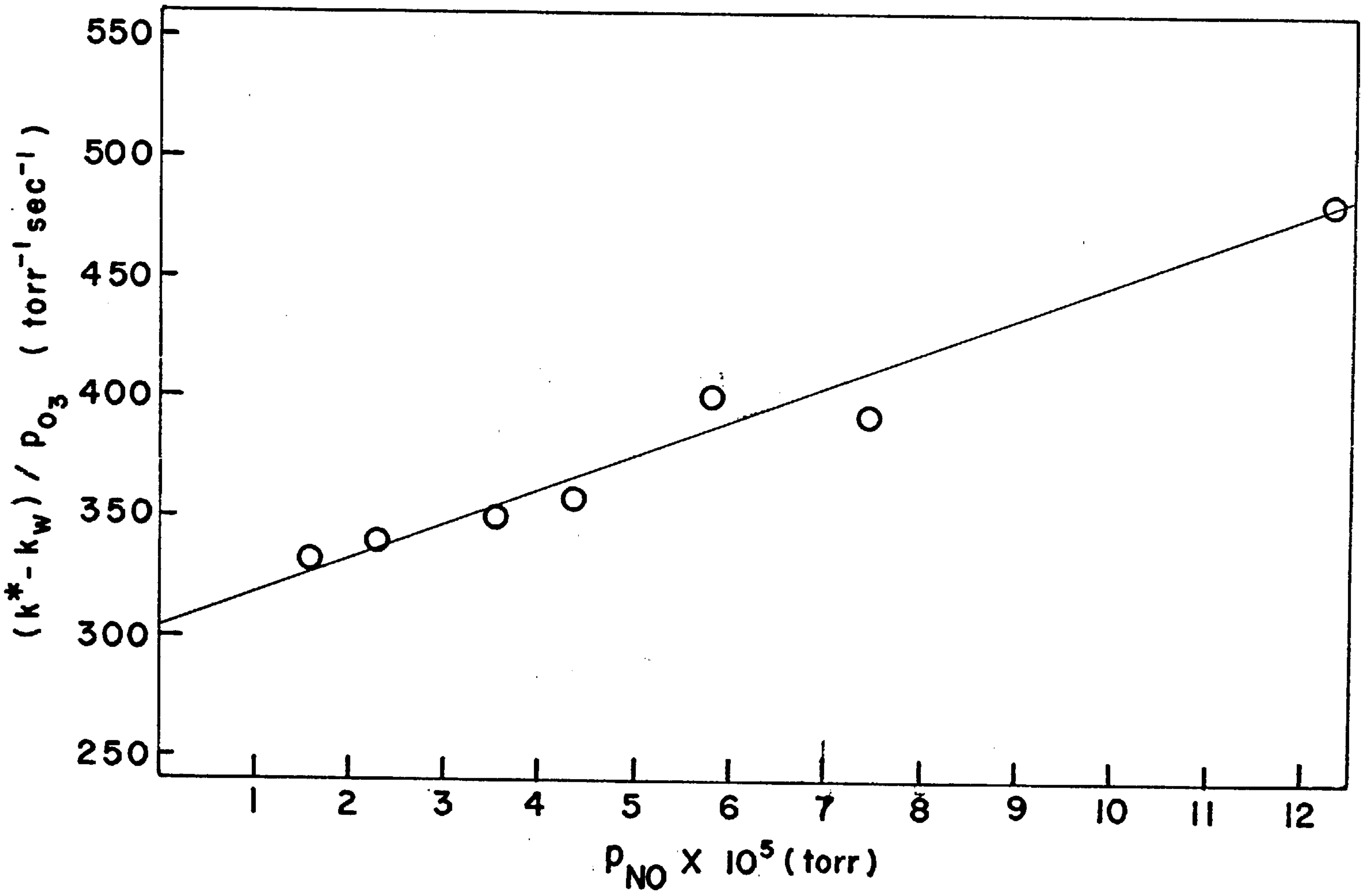

Figure 3

Extrapolation of $\frac{k^* - k_W}{P_{O_3}}$ to $P_{NO} = 0$. Experimental conditions given in Table 1.

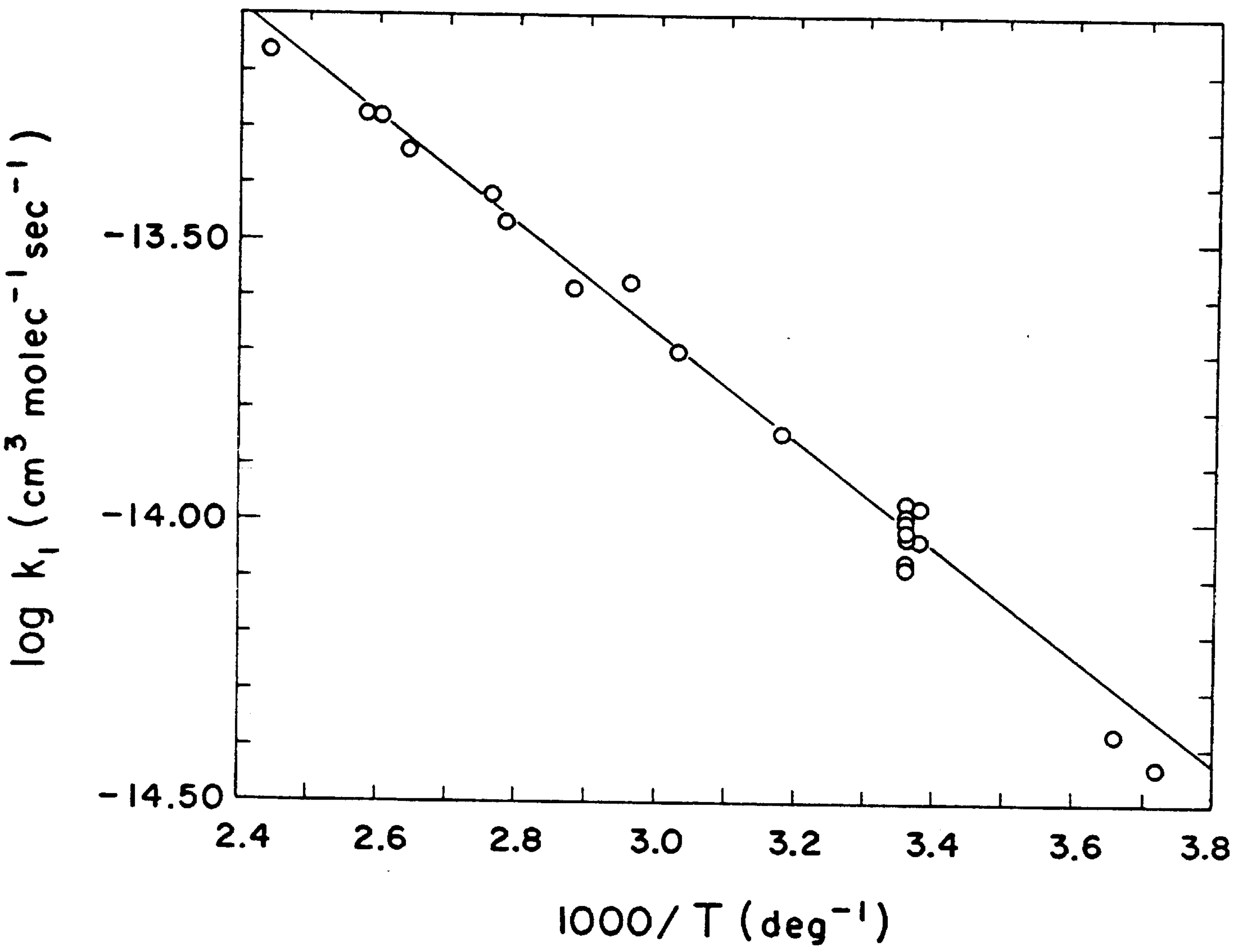

Figure 4

Arrhenius plot of k_1. Data from Tables 2 and 3.

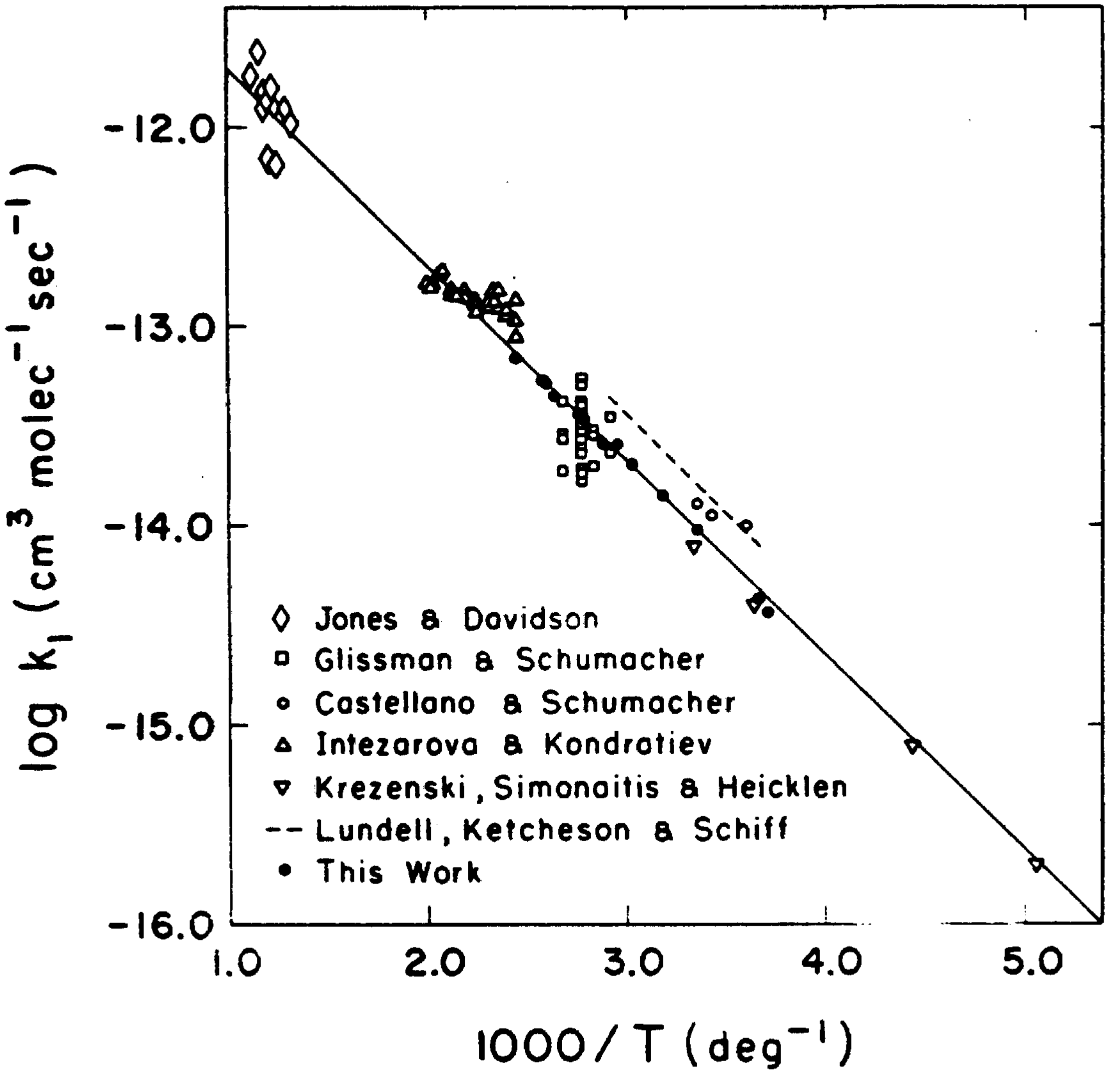

Figure 5

Summary graph of k_1 temperature dependence. Line is least squares fit to present work, $k_1 = 1.78 \times 10^{-11} \exp(-4.46/RT)$.