Rate Constant for the Reaction of O(^{3}P) with IO at $T = 298$ K

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The rate coefficient for the O(^{3}P) + IO reaction has been measured using the discharge-flow kinetic technique coupled to collision-free mass spectrometric detection at 1 Torr nominal pressure (He). IO is generated by the reaction of O with I_2; IO then decays in the presence of excess atomic oxygen. A one-parameter fitting to a numerical model gives a rate coefficient of $(1.5 \pm 0.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at $T = 298$ K. This result is significantly faster than an earlier estimate but is in good agreement with the only previous study of the reaction which employed laser photolysis combined with absorption spectrophotometry. The present result is compared with those for the reactions O(^{3}P) + XO and X + IO where X = Cl and Br.

Introduction

The suggestions[1,2] that iodine chemistry was potentially important in stratospheric ozone loss generated considerable interest in obtaining kinetic data for reactions of iodine-containing species. This is especially true for reactions of the iodine monoxide radical, IO, which, if present, can participate in ozone destruction cycles. In addition, interest also stemmed from the fact that a paucity of experimental kinetic data exists for the IO radical. The work reported in this study was motivated in part by the fact that the reaction between O(^{3}P) and IO is included in the following catalytic cycle which could be important in the upper stratosphere where there is a larger concentration of O atoms:

$$\mathrm{I} + \mathrm{O_3} \rightarrow \mathrm{IO} + \mathrm{O_2} \tag{1}$$

$$\mathrm{O(^3P)} + \mathrm{IO} \rightarrow \mathrm{I} + \mathrm{O_2} \tag{2}$$

$$\mathrm{O(^3P)} + \mathrm{O_3} \rightarrow 2\mathrm{O_2} \quad \text{(net)}$$

and in part by the fact that only one other measurement of the rate constant for reaction 2 has been reported in the literature.[3] It is presently believed, based on a recent IO atmospheric column abundance measurement,[4] that there is insufficient IO present in the stratosphere for iodine chemistry to be significant in stratospheric ozone destruction. However, this situation is subject to change if iodine compounds gain additional use as fire retardants or fumigants.[5]

Regardless of the role of reaction 2 in stratospheric chemistry, it is desirable to have an independent measure of k_2 using an experimental technique which differs from that employed in the only previous measurement.[3] In the study of Laszlo et al.,[3] laser photolysis of $N_2O/I_2/N_2$ mixtures was combined with visible absorption spectrophotometry to simultaneously monitor the formation of IO and the loss of both IO and I_2. In these experiments it was not possible to isolate reaction 2 from either the IO formation reaction

$$\mathrm{O(^3P)} + \mathrm{I_2} \rightarrow \mathrm{IO} + \mathrm{I} \tag{3}$$

or loss of IO via the self-reaction

$$\mathrm{IO} + \mathrm{IO} \rightarrow \text{products} \tag{4}$$

Accordingly, the system was modeled based on a three-parameter fit: $[\mathrm{O}]_0$, k_2, and k_3. The validity of the fitted $[\mathrm{O}]_0$ and k_3 values was supported by separate measurements of $[\mathrm{O}]_0$ and by agreement of the fitted k_3 value with a previous measurement,[6] respectively. Nevertheless, another measure of k_2 is required.

We have measured the rate constant for reaction 2 at $T = 298$ K using the flow- discharge mass spectrometer technique at low pressures. This provides both an experimental technique which differs from that of Laszlo et al.[3] and a set of experimental conditions that, to a large extent, isolated reaction 2 from both the IO formation and the IO self-reaction loss processes. A comparison is made between the rate coefficients for O(^{3}P) + XO (X = Cl, Br, and I). The rate coefficient for the reaction of O(^{3}P) with IO is also compared with those for the reactions of IO with other atomic species such as Cl and Br.

Experimental Section

Discharge-Flow Reactor. The experiments reported in this study were carried out in a discharge-flow system equipped with mass spectrometric detection of radical and molecular species. The Pyrex flow tube, ~60 cm long and 28 mm in diameter, was Teflon FEP lined to minimize wall losses of radical species. Collision-free sampling was accomplished through a differently pumped region provided with two concentric pinholes placed between the flow tube reactor and the quadrapole mass spectrometer (Extrel, Inc.). Molecular reactants were admitted via a Pyrex movable injector, the position of which could be changed between 2 and 40 cm from the sampling point. Electron impact ionization was used at low electron energies. Ions were detected by an off-axis channeltron multiplier. The channeltron signal output went to a preamp/threshold discriminator, and the peak areas were then measured using a multichannel scaling card in a personal computer. The experimental

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apparatus has been described in detail previously,[7,8] and therefore only the descriptions specific to these experiments are given here.

All experiments were performed with nominal flow tube pressures of 1 Torr (He) and with linear flow velocities in the range 2422−2485 cm s^{-1}. In the calculations of the linear flow velocity, the plug flow assumption was made. The flow velocity is calculated from the gas constant, temperature, cross-sectional area of the flow tube, total gas flow, and total pressure. Gas flows were measured and controlled by electronic flow meters (MKS). A sidearm, at the upstream end of the flow tube, contained a microwave discharge (<70 W, 2450 MHz) for the production of atomic species.

Production of O and IO. Atomic oxygen was produced at the upstream end of the flow reactor by passing molecular oxygen diluted in helium through a microwave discharge. Typically, 5.5 ± 1.0% of the O_2 was dissociated in the discharge. Absolute O atom concentrations were determined via the reaction

$$O(^3P) + NO_2 \rightarrow NO + O_2 \qquad (5)$$

$$k_5 = 9.7 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{(ref 9)}$$

With NO_2 in excess, the O atom concentration was determined by measuring the decrease in the NO_2^+ signal ($m/z = 46$) when the discharge was initiated. The dilute NO_2/He mixture was admitted via the movable injector. The position of the injector was chosen to ensure that reaction 5 went to completion and that the position was close to the middle of the decay range for IO under reaction conditions. At an electron energy of 15 eV, dissociative ionization of NO_2 was small and does not affect the determination of the fractional decrease in the NO_2 signal. The absolute O concentration is given by $[O] = [NO_2]_{\text{disc. off}} - [NO_2]_{\text{disc. on}} \equiv \Delta NO_2\ \text{signal} \times [NO_2]_{\text{disc. off}}$. Resultant oxygen atom concentrations were in the range $1.79 \times 10^{12} \le [O]_0 \le 1.77 \times 10^{13}$ molecules cm^{-3}. The details of the precautions taken to avoid systematic errors in the determinations of the concentrations of atomic species have been discussed previously.[8]

Molecular iodine, highly diluted in helium, was admitted into the flow tube via a Pyrex movable injector. At the tip of the injector iodine oxide radicals were produced in the flow tube via the rapid reaction 3 [$k_3 = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; refs 3 and 6]. With [O] in excess over $[I_2]$, I_2 is completely consumed and stoichiometrically converted to IO; hence $[IO]_0 = [I_2]_0$. The initial I_2 concentration and hence $[IO]_0$ were in the range $(4.12-9.94) \times 10^{11}$ molecules cm^{-3}. The mass spectrometer was calibrated for I_2 by flowing a known mixture of I_2 and helium into the flow reactor through the movable injector. In a typical experiment, however, helium was flowed through a trap containing iodine crystals and held at a constant temperature of 293 K. The helium flow rate through the trap was adjusted to obtain the desired I_2 concentration.

IO was monitored mass spectrometrically at $m/z = 143$ using an ionization energy of 20 eV. IO was detected at a concentration of about 7×10^9 molecules cm^{-3} at S/N = 1. The ratio of IO signal to background at the beginning of the decay was typically between 25:1 and 90:1.

Two experiments, each at a different ionization energy but at reagent concentrations similar to those used in the kinetic studies, attempted to detect the association product of reaction 2, OIO, at $m/z = 159$. At IE = 15 and 19 eV, OIO was not detected as a product of reaction 2 since the net signal was not statistically above the background signal.

Materials. The main carrier gas, helium (Air Products, 99.999%), was passed through a trap held at $T = 77$ K before entering the flow system. Nitrogen dioxide (Matheson, 99.5%) used in the titration of O atoms was purified by adding excess O_2 followed by degassing at 77 K. A small correction was made to the NO_2 flow rate to account for the rapid dissociation of the N_2O_4 dimer. Oxygen (Matheson, 99.9%) was used as purchased. Iodine (Fisher Scientific, resublimed) was degassed at 77 K and used without further purification.

Results

The experiments reported in this study were carried out at 298 K under pseudo-first-order conditions with the atomic oxygen concentration in excess over the concentration of IO. Experimental values of $[O]_0/[IO]_0$ were between approximately 3 and 30. The pseudo-first-order rate constant k_{obs} is given by

$$\ln\{[IO]_0/[IO]_t\} = k_{obs}t \qquad (6)$$

or rewritten

$$\ln[IO]_t = -k_{obs}t + \ln[IO]_0 \qquad (7)$$

where t is determined from the flow velocity and distance between the tip of the movable injector and the sampling pinhole. A plot of ln(IO signal) versus time (t) will yield k_{obs} as the slope. The obtained pseudo-first-order rate constants were then corrected for axial diffusion of IO in the helium carrier gas to give k_{cor}, according to the method described by Lewis et al.[10] Diffusion corrections ranged from 2 to 13% of k_{obs}. A stoichiometric correction to $[O]_0$ was made to account for depletion of O during the formation of IO via reaction 3 and the decay of IO via reaction 2.

$$[O]_{mean} = [O]_0 - {}^1/_2[I_2]_0 - {}^1/_2[IO]_0 \qquad (8)$$

However, with stoichiometric conversion of I_2 to IO, $[IO]_0 = [I_2]_0$. Equation 8 then reduces to

$$[O]_{mean} = [O]_0 - [I_2]_0 \qquad (9)$$

The stoichiometric correction ranged from 3 to 37% of $[O]_0$. The corrected pseudo-first-order rate constant k_{corr} is related to the bimolecular rate constant k_2 by

$$k_{corr} = k_2[O]_{mean} + k_w \qquad (10)$$

where $[O]_{mean}$ is calculated from eq 9 and k_w represents the loss of IO on the wall of the flow reactor.

$$IO \rightarrow \text{first-order decay} \qquad (11)$$

A summary of experimental conditions is shown in Table 1. The initial O atom concentration was varied by a factor of 10. Following eq 10, a plot of the corrected rate constant versus the mean O atom concentration should yield a straight line with the slope equal to k_2 and intercept equal to k_w. A linear least-squares analysis of the data yielded a bimolecular rate coefficient of $k_2 = (1.2 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and a wall loss of $k_w = 28 \pm 101$ s^{-1}, indicating a negligible wall loss for IO. The quoted uncertainty is two standard deviations and is statistical only. The resulting low wall loss for IO is consistent with the observations of Bedjanian et al.[11,12]

However, a simple pseudo-first-order analysis may be inadequate if the primary O + IO reaction is not sufficiently isolated from the secondary IO self-reaction or from formation

TABLE 1: Summary of Kinetic Data for the Reaction O(^{3}P) + IO[a]

$[O]_0$, 10^{13} molecules cm^{-3}	$[I_2]_0$, 10^{11} molecules cm^{-3}	k_2, 10^{-10} cm^3 molecule^{-1} s^{-1}
1.77	7.82	2.07
1.49	7.15	1.86
1.32	4.12	1.86
1.14	7.15	1.66
1.00	9.94	1.10
0.76	6.62	1.20
0.76	6.62	1.50
0.70	4.12	0.91
0.28	8.23	2.26
0.18	6.60	0.93

[a] $\langle k_2 \rangle = (1.53 \pm 0.48) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

TABLE 2: Chemical System and Rate Constants Used in the Numerical Model

no.	reaction	k(298 K)[a]	ref
2	$O(^3P) + IO \rightarrow I + O_2$	fitted	this study
3	$O(^3P) + I_2 \rightarrow IO + I$	1.4×10^{-10}	9
4a	$IO + IO \rightarrow I + I + O_2$	7.6×10^{-11}	9, 3, 13
4b	$IO + IO \rightarrow I_2 + O_2$	4.0×10^{-12}	9, 3, 13
11	$IO \rightarrow$ first-order decay	28[b]	this study

[a] Rate constant units are cm^3 molecule^{-1} s^{-1} except where noted. [b] Units are s^{-1}.

of IO via the reaction O + I_2. In both cases, the effect will be most significant at the lower values of $[O]_0$. To quantify the effect of both the IO self-reaction (reaction 4) and IO formation process via reaction 3, k_2 was determined by one-parameter fitting of the net IO signal decays to a numerical simulation (FACSIMILE program)[14] of the reaction system. The mechanism consisted of reactions given in Table 2. Inputs to the model included the initial atomic oxygen concentration, $[O]_0$, which was determined in the separate aforementioned atomic O titration experiments, and the initial iodine concentration, $[I_2]_0$. The mass spectrometer IO signal calibration was determined from extrapolation of the linear plot of ln IO signal vs time to the intercept at $t = 0$ and the known $[IO]_0 = [I_2]_0$. Table 1 summarizes the modeling results for the 10 independent kinetic experiments performed. An example of the model fit to an experimentally observed IO decay is shown in Figure 1. The resulting mean value for k_2(298 K) with 1σ statistical uncertainty is $k_2 = (1.5 \pm 0.5) \times 10^{-10}$ cm^3 molecules^{-1} s^{-1}. To allow for systematic errors in the $[O]_0$ and the I_2 and IO signal calibration, we add an additional ±15% uncertainty to obtain the rate constant

$$k_2(T = 298\ \text{K}) = (1.5 \pm 0.7) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

This is the preferred result. The alternate value from the pseudo-first-order analysis is consistent with the preferred value within the quoted uncertainty.

Several experiments were attempted at $T = 225$ K, but they were stymied by a 20-fold decrease in $[I_2]$. This observation was unexpected since the $[I_2]$ was well below the equilibrium vapor pressure of I_2 at 225 K. Bedjanian et al.[11] have also observed unexpected condensation of I_2 at $T < 288$ K on flow tube walls. The decrease in $[I_2]$ resulted in a corresponding decrease in [IO], and consequently, no signal was observed at $m/z = 143$ amu.

Additional experiments were attempted at $T = 400$ K. Although IO signal could be detected at this temperature, reliable values for k_{obs} could not be determined because the results were highly variable.

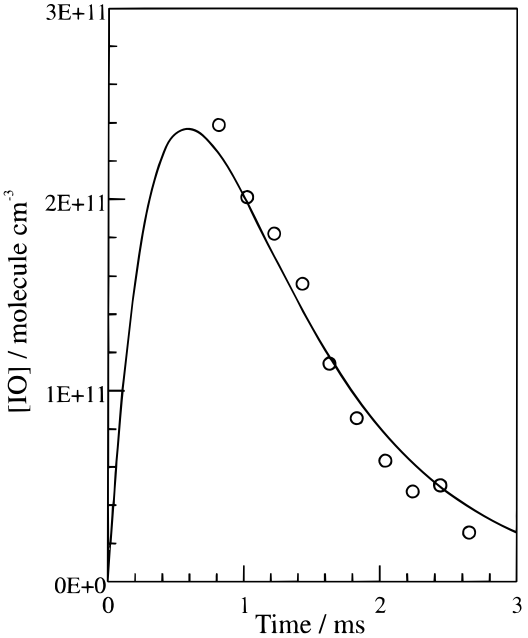

Figure 1. Example of the experimentally determined decay of IO (open circles) with reaction time and the model fit (solid line) to the formation and decay of IO. $[O]_0 = 1.14 \times 10^{13}$ molecules cm^{-3} and fitted $k_2 = 1.66 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

TABLE 3: Rate Coefficients for O(^{3}P) + XO and for X + IO Radical−Atom Reactions at $T = 298$ K

reaction	rate coefficient[a]	ref
$O(^3P) + IO$	15	this study
$O(^3P) + BrO$	4.1	9
$O(^3P) + ClO$	3.8	9
Cl + IO	4.4	11
Br + IO	2.2	17

[a] Units are 10^{-11} cm^3 molecule^{-1} s^{-1}.

Discussion

There has been only one previous determination of the O(^{3}P) + IO rate coefficient by Laszlo *et al.*[3] which employed the laser flash photolysis−visible absorption technique performed at $T = 295 \pm 2$ K and in 200 Torr of N_2 buffer gas. Laszlo et al.[3] reported a rate coefficient of $(1.2 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, in good agreement with the study reported here. The two studies represent a comparison of rate data for an elementary reaction obtained under different experimental conditions using different experimental techniques. Prior to this study and the Laszlo et al.[3] study, there was an estimate of $k_2 = 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} by Atkinson et al.,[15] which was probably accurate to within a factor of 3. The lower limit of the present value is at the upper limit of this estimate. The low estimated value for k_2 was used in the model calculations of Solomon et al.[1,2] since there were no experimental values available at that time. The reaction O(^{3}P) + IO may be involved in laboratory studies of the spectroscopy and kinetics of the IO radical. When this occurs, a knowledge of the rate constant is required to correct for the occurrence of the reaction. For example, in the determination of the IO absorption cross section at $\lambda = 427.2$ nm using photolysis of N_2O/CF_3I, Harwood et al.[16] made a small but quantifiable correction to the measured IO cross section to allow for consumption of IO via reaction with O(^{3}P).

A comparison of the present result for the O(^{3}P) + IO rate coefficient with published results[9,11,17] for the O(^{3}P) + XO and X + IO (X = Cl, Br) atom−radical reactions is shown in Table

3. In both comparisons, k_2 is considerably faster by a factor of 3 or more than the corresponding halogen oxide or atomic halogen reactions. However, it is not unexpected that the rate constant for the atom−radical reaction O + IO is at least comparable to that for the related atom−molecule reaction O + I_2 (3) where $k_3 = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. For the corresponding bromine reactions, k(O + BrO)[9,18] is twice k(O + Br_2).[19] Since k_2 is near the hard-sphere collision rate, little or no temperature dependence is expected. Thus, the present value of $k_2 = (1.5 \pm 0.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} is appropriate for use in atmospheric models.

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