After being purged with CO_2 gas, the tube was closed off with a gum stopper and then irradiated under magnetic stirring at >290 nm using a 500-W high pressure mercury arc lamp. For homogeneous runs, the DMF solution of OPP-3 (5×10^{-3} M) was used. The gaseous and liquid products were analyzed by GLC and HPLC.

Pulse Radiolysis. A 3-mL DMF solution of OPP-3 (5×10^{-3} M) was placed in a quartz cell (4 mL). After being purged with argon gas under cooling on an ice bath, the cell was closed off with a gum stopper and CO_2 gas was added and then measured by the pulse radiolysis technique before and after the introduction of CO_2 as reported.[17b,26]

Laser Flash Photolysis. A DMF solution containing OPP-*n* (*n* = 3–5) and TEA (1 M) was placed in a quartz cell and then degassed: [OPP-3] = 1.0×10^{-5} M, [OPP-4] = 2.4×10^{-6} M, [OPP-5] = 2.0×10^{-6} M. Measurements were conducted by means of an eximer laser under conditions similar to those already reported.[17b]

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Temperature Dependence and Mechanism of the Reaction between O(^{3}P) and Chlorine Dioxide

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Second-order rate constants for the decay of O(^{3}P) in excess chlorine dioxide, k_{II}, were measured by flash photolysis–atomic resonance fluorescence as a function of total pressure (20–600 Torr argon) and temperature (248–312 K). It was found that (1) k_{II} is pressure dependent with a value, k_b, that is nonzero at zero pressure and (2) both the third-order rate constant $(dk_{II}/d[M])_{[M]=0} = k_o$, and k_b have negative temperature dependences. These results are consistent with an association reaction leading to an intermediate having two decomposition channels: O + OClO $\leftrightarrow$ ClO_3^* (1, 2); ClO_3^* + M $\rightarrow$ ClO_3 + M (3); ClO_3^* $\rightarrow$ ClO + O_2^* (4), with $E_{02} > E_{04}$. The measured k_o values were used in conjunction with Troe's expression for unimolecular decomposition rates in the low-pressure limit to derive a critical energy for ClO_3 of 10 700 cm^{-1}, which leads to $\Delta H_f(ClO_3) = 51.9 \pm 5$ kcal/mol. This is ~4 kcal/mol smaller than the value derived in our previous room temperature study of this reaction.

Introduction

We have recently investigated the photochemical decomposition of chlorine dioxide at 308 nm.[2] The primary process

$$OClO + h\nu \rightarrow O(^3P) + ClO^*(v) \qquad (5)$$

is followed by fast reactions of both product species with OClO. A kinetic study of the ensuing reaction between ground-state oxygen atoms and chlorine dioxide at 298 K, reaction A

$$O(^3P) + OClO \rightarrow \text{products} \qquad (A)$$

revealed a positive rate dependence of k_{II} (the observed bimolecular rate constant) on inert gas pressure extrapolating to a finite value k_b at zero pressure.[2] These observations were rationalized in terms of the following mechanism:

$$O + OClO \leftrightarrow ClO_3^* \qquad (1,2)$$

$$M + ClO_3^* \rightarrow ClO_3 + M \qquad (3)$$

$$O + OClO \rightarrow ClO + O_2 \qquad (6)$$

in which an association path, steps 1–3, accounts for the pressure dependence of k_{II} and a direct O atom transfer reaction, step 6, for the constant contribution to the overall rates k_b (see below). However, we also argued that the decomposition of excited chlorine trioxide, ClO_3^*, along a second channel, reaction 4, provides an

$$ClO_3^* \rightarrow ClO + O_2 \qquad (4)$$

alternative explanation for the pressure-independent term which is kinetically indistinguishable from step 6 in experiments which monitor the decay of O(^{3}P).

Previous studies of the kinetics of reaction A were carried out by Bemand et al. at low pressures and at room temperature and do not provide additional information on the above issues.[3] Considering the potential importance of reactions of chlorine oxides with reactive atmospheric species in the mechanism of the chlorine-induced destruction of stratospheric ozone,[4] we decided to investigate the effect of temperature on the kinetics of this system. In this paper we report measurements of k_{II} as a function of total pressure in the range 248–312 K. The observed negative temperature dependence of the third-order rate constant $k_o \equiv (dk_{II})/d[M])_{[M]=0}$ establishes the competition between reactions 2 and 3 as the source of pressure effects in reaction A. We found that the bimolecular rate constant extrapolated to zero pressure, k_b, also has a negative temperature dependence. This effect, if confirmed, would imply that the ClO product arises from the decomposition of the ClO_3 intermediate (reaction 4) rather than metathesis (reaction 6).

Experimental Section

The kinetics of the reaction between O atoms and OClO was studied using time-resolved atomic oxygen resonance fluorescence measurements following the laser flash photolysis of chlorine

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dioxide, reaction 5, in a temperature-controlled flow cell. The details of the experimental setup have been presented elsewhere and only a brief description will be given here.[2,4] The photolysis source was a XeCl excimer laser (Lumonics TE 860-2) operating at 308 nm, whose output (25–50 mJ/pulse) could be attenuated by means of fine mesh metal screens. In order to minimize secondary reactions, the smallest flash energies compatible with acceptable fluorescence signal to noise ratios were used in these experiments. The fluorescence cell was equipped with MgF_2 windows for transmission of 130-nm radiation produced by an atomic oxygen low-pressure resonance lamp. A solar blind photomultiplier tube (Hamamatsu R1459P), perpendicular to both the laser beam and the output of the resonance lamp, was used to detect the fluorescence emission of oxygen atoms from the irradiated volume. The electrical signals from the photomultiplier were discriminated, counted, and then processed by a multichannel digital averager (Nicolet 1170). Accumulated signals from 30 to 4000 photolysis cycles, depending on the experimental conditions, were acquired by a personal computer and numerically analyzed.

Chlorine dioxide was prepared by passage of 5% Cl_2/He through slightly moist $NaClO_2$ (Eastman) and trapped at 195 K. Products more volatile than OClO such as Cl_2 were pumped off. A slow flow of helium carried OClO (vapor pressure ~1 Torr at 195 K) into the flow system through a fine metering valve. With this procedure, products which are less volatile than OClO, including water, remain in the trap. This procedure is known to produce OClO with no detectable impurities as determined by ultraviolet absorption (ref 5). Further dilution with argon (Matheson, UHP), the bath gas, was performed at this point. This mixture traversed a 50-cm-long, 3.5-cm-diameter, silica cell fitted with Suprasil windows and folded optics (optical path length 1 m) before entering the fluorescence cell. The OClO concentration was determined using an on-line double-beam spectrophotometer (Cary 219) optically coupled to the above cylindrical cell, which was maintained at room temperature. Recently published values of the absorption cross sections of OClO at 0.25-nm resolution were used in the data analysis.[5] Ratios of cross sections taken from different parts of the recorded spectra always were in excellent agreement with the data in ref 5. This rules out the presence of impurities absorbing in this region.

Experimental temperatures were controlled by circulation of cooled methanol or heated water through the jacket of the fluorescence cell; cell temperatures were monitored with a pair of iron/constantan thermocouples. Temperature fluctuations over the course of an experimental run were smaller than 1 K.

Results and Discussion

Kinetic Results. As in our previous study (ref 2, Figures 1 and 2), the rates of oxygen atom decay in excess OClO, reaction A, followed first-order kinetics under all conditions. Taking into account our previous observations at 298 K[2] regarding the dependence of these rates on laser flash intensities, all experiments were conducted at fluences resulting in $[O]_0 < 0.001$ [OClO] with $[O]_0$ in the range $(1{-}10) \times 10^{11}$ atoms/cm^3. Under these conditions it is estimated that secondary reactions of O with ClO and ClO_3 will result in errors no greater than ~10%.[2] The pseudo-first-order rate constants, $k_I = -d \ln [O]/dt$, obtained at values of [OClO] in the range $(0.08{-}1.2) \times 10^{15}$ molecules/cm^3 were converted into second-order rate constants k_{II} using the relationship $k_I = k_X + k_{II}[OClO]$; k_X represents first-order O atom losses due to diffusion and/or reaction with carrier gas impurities. As in the our previous study at 298 K,[2] plots of k_I vs [OClO] were linear. At all temperatures and pressures, k_X contributed less than 20% to k_I at the lowest OClO concentrations used. The results obtained at 248, 273, and 312 K at total pressures between 20 and 600 Torr argon are shown in Table I and Figure 1. The bimolecular rate constant, k_{II}, shows the same qualitative dependence upon [M] as found in the earlier study at 298 K.

TABLE I: Rate Constants as a Function of Temperature and Pressure

T/K	pressure/ Torr[a]	$10^{12}k_{II}$/ cm^3 molecule^{-1} s^{-1} [b]
248	20	0.62
	26	0.54
	43	0.66
	74	1.06
	116	1.16
	179	1.66
	307	2.17
	459	2.51
	601	3.20
273	21	0.46
	41	0.50
	101	0.95
	204	1.22
	302	1.61
	400	2.21
	502	2.37
	610	2.46
312	21	0.32
	50	0.31
	71	0.47
	112	0.64
	210	0.91
	312	1.36
	458	1.70
	618	2.21

[a] Argon. [b] Estimated uncertainties (random plus systematic) are ±20% at the 95% confidence level (see text).

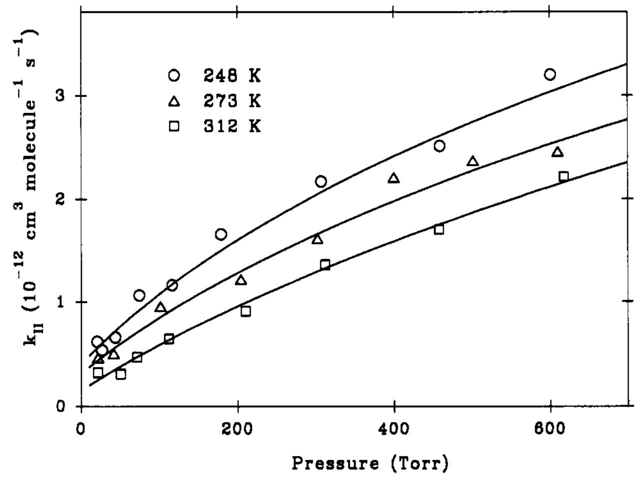

Figure 1. k_{II} vs argon pressure at 248, 273, and 312 K. Solid curves calculated from eqs 7 and 8 using the parameters in Appendix 1.

The average precision of the kinetic measurements at a given temperature and pressure was ±7% (2σ) as determined from the uncertainties in the slopes of the plots of k_I vs [OClO]. Combining this with other systematic uncertainties (OClO cross section, pressure, secondary chemistry) results in an estimated uncertainty of ±20% for individual rate constant determinations at the 95% confidence level.

At each temperature, the observed rate coefficients can be expressed as the sum of a constant term and a pressure-dependent contribution:

$$k_{II} = k_b + k_\infty G(M) \tag{7}$$

where k_b is the intercept, $0 < G(M) < 1$ a falloff function of total gas density M, and k_∞ the high-pressure limiting rate constant. In principle the curves drawn through the experimental points at each temperature could be characterized by their intercept k_b, slope at $[M] = 0$, k_0, asymptotic value of k_{II} at $[M] \rightarrow \infty$, k_∞, and their curvature at the midpoint. It is more instructive, however, to describe the observed behavior in terms of the elementary processes of association, vibrational deactivation, and unimolecular dissociation.

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TABLE II: Kinetic Parameters for the Reaction $O(^3P) + OClO \rightarrow$ Products[a]

T/K	$10^{31}k_0$	$10^{11}k_\infty$	$10^{13}k_b$	β	F_c	N
248	2.34 ± 0.35	2.5 ± 1.0	4.0 ± 2.0	0.56	0.503	1.084
273	2.00 ± 0.30	2.5 ± 1.0	3.1 ± 1.6	0.52	0.483	1.104
312	1.80 ± 0.27	3.5 ± 1.5	1.5 ± 0.8	0.50	0.453	1.134

[a] Parameters are defined in eqs 7 and 8. Rate constants in units of cm^3 molecule^{-1} s^{-1} for k_∞ and k_b and cm^6 molecule^{-2} s^{-1} for k_0. Uncertainties are $\pm 2\sigma$ determined by varying β, F_c, and N within expected limits.

Discussion

Estimated Lower Limit of A_6. If the intercept of the plots of Figure 1 corresponded to a truly bimolecular reaction between O atoms and OClO proceeding through an independent transition state such as reaction 6, then its A factor should be not smaller than $\sim 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. This lower limit follows from assigning to the tightest possible transition state of reaction 6 the structure of the peroxy form of ClO_3, OClOO, for which we estimate $S^\circ \approx 300$ J K^{-1} mol^{-1} at 298 K.[6] The extrapolated value of k_b deduced by Colussi,[2] $(1.6 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (more than 1 order of magnitude smaller than the estimated minimum value of A_b), implies a positive activation energy $E_6 >$ 5.7 kJ/mol. This does not seem to be the case, however, since visual inspection of Figure 1 reveals that k_b apparently decreases, rather than increases, with temperature, i.e., that $E_b < 0$.

The above analysis suggests that establishing the sign of the temperature dependence of k_b might be a crucial test of the actual mechanism of the "bimolecular" channel of reaction A. In the following section we attempt to reduce the dimensions of the problem by analyzing the pressure dependence of $G(M,T)$ in terms of existing theory rather than empirically.

Pressure Falloff of k_{II} and the Temperature Dependences of k_0 and k_b. Following Troe we have adopted the functional form[7]

$$G(M) = \{r[M]/(1 + r[M])\}F_c^{\{1+[\log\,(r[M])/N]^2\}^{-1}} \qquad (8)$$

where $r = k_0/k_\infty$, $F_c = F_{cs}F_{cw}$ is the so-called broadening factor, and N is the width factor. These parameters, which can be calculated according to the rules derived by Luther and Troe,[8,9] are a function of the vibrational frequencies of ClO_3, its Lennard-Jones parameters, the height of the barrier E_0 for the decomposition of ClO_3 (reaction 2), and temperature. The definitions of the several factors involved in this calculation and the numerical values of the input parameters are given in Appendix 1.

A complete a priori evaluation of the k_0 at different temperatures requires, in addition, the value of the average amount of internal energy exchanged in deactivating collisions $\langle \Delta E \rangle$.[7] Here we have assumed that the collision efficiency, β, is 0.5 for argon at 312 K, which leads to $\langle \Delta E \rangle = 400$ cm^{-1}, independent of temperature, and, in conjunction with the measured value of k_0 (Table II), to $E_0 = 10\,700$ cm^{-1}. This value of β is consistent with the derived values of β for other third-order association reactions which fall in the range $0.3 < \beta < 0.7$.[9,10] Notice that this value of the critical energy of reaction 2 is $\sim$1300 cm^{-1} larger than the one derived in ref 2 using $\beta = 0.76$; we found that in this energy region a 1400 cm^{-1} increase of E_0 duplicates the value of k_0. This value of E_0 leads to $\Delta H_f(ClO_3) = 51.9 \pm 5$ kcal/mol, where the stated error limits include estimated errors in the calculation as well as the uncertainty in ΔH_f(OClO).

In order to parametrize eqs 7 and 8, we observed that the results for k_{II} at 312 K as a function of pressure (Figure 1) display the least scatter of the three temperatures for which there are data and that the initial slope, k_0, reaches its smallest value; hence, extrapolation of k_{II} to [M] = 0 involves the least error. We therefore directly fitted the low-pressure results at 312 K with $k_0 = 1.8 \times 10^{-31}$ cm^6 molecule^{-2} s^{-1}, which extrapolates to k_b = 1.5×10^{-13} cm^3 molecule^{-1} s^{-1}. Then using eqs 7 and 8 with F_c = 0.453, N = 1.134, we extended the fit to the entire range using k_∞ as the adjustable parameter. The fit is very sensitive to k_0 and k_b but much less sensitive to k_∞ at this temperature; the fit also depends on k_b in a manner quite different from k_∞. Thus, whereas the former introduces a pressure-independent shift the latter only affects the data at the higher pressures. In other words, all points are effectively used in determining k_b, most points are used for k_0, and only the ones at the highest pressures affect k_∞. Notice that our experiments were conducted much closer to the low-pressure limit than the high-pressure limit (the smallest k_{II} values in Table I are less than 50% larger than k_b, and the largest are a factor of 10 smaller than k_∞).

If $\langle \Delta E \rangle$ is indeed independent of temperature down to 248 K, then theory provides the values of β and, therefore, of k_0, F_c, and N at 248 K as well as the exponent n in the expression

$$k_0(T)/k_0(300) = (T/300)^{-n} \qquad (9)$$

In this manner we obtain k_0(248 K) = 2.34×10^{-31} cm^6 molecule^{-2} s^{-1} and a value of $n = 1.14$ (see Appendix 1). On the other hand the best fit of experimental results (Table II) leads to the following expressions:

$$k_0(T) = 1.86 \times 10^{-31}\ (T/300)^{-1.12}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1} \qquad (10)$$

$$k_b(T) = 1.86 \times 10^{-13}\ (T/300)^{-4.35}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \qquad (11)$$

More importantly for the following discussion, this procedure imposes a realistic upper bound to k_0 of $<2.94 \times 10^{-31}$ cm^6 molecule^{-2} s^{-1} at 248 K, a value derived from the condition n = 1.14 ± 1, where the error limits on n represent a measure of the predictive power of this approach as applied to many other cases.[9,10] This condition translates into a maximum downward correction of only -4.7×10^{-14} cm^3 molecule^{-1} s^{-1} to the value of k_b(248 K) = 4.0×10^{-13} cm^3 molecule^{-1} s^{-1}. In other words, the data in Table I and Figure 1 and the "best" parameters in Appendix 1 support a negative temperature dependence for k_b. In order to reverse or substantially reduce the temperature dependence of k_b, a value of k_0 at 248 K would be required, which is significantly larger than that derived from the extrapolation of the falloff data. This in turn would require values of $n > 4$, which are inconsistent with both our data and the theoretical estimation of k_0. The present results, therefore, appear to rule out reaction 6 as an independent bimolecular elementary reaction.

An alternative explanation is that the constant contribution to the overall rate arises instead from the decomposition of ClO_3^*, reactions 1–4. This scheme leads to the following expressions:

$$k_{II} = k_1(k_4 + k_3[M])/(k_2 + k_4 + k_3[M]) \qquad (12)$$

$$k_b = k_1k_4/(k_2 + k_4) \qquad (13)$$

$$k_0 = k_1k_3/(k_2 + k_4) \qquad (14)$$

$$k_\infty = k_1 \qquad (15)$$

From the above relations and $k_3 = \beta Z = 1.7 \times 10^{-10}$ (see Appendix 1), $k_b = 1.5 \times 10^{-13}$, $k_0 = 1.8 \times 10^{-31}$, and $k_\infty = 3.5 \times 10^{-11}$ (all in units of cm^3 molecule^{-1} s^{-1}) at 312 K, we obtain $k_2 = 3.21 \times 10^{10}$ s^{-1} and $k_4 = 1.4 \times 10^8$ s^{-1}. Also from k_∞ and $\Delta S_1 = -141$ J K^{-1} mol^{-1}, we obtain a value of 7×10^{15} s^{-1} for A_2, which is in the expected range for the high-pressure A factor of an atom fission reaction.[6] On the basis of the estimated A factor for the three-center elimination of O_2 in reaction 4, $A_4 = 1 \times 10^{13}$ s^{-1},[6] it is also apparent that the ratio k_2/k_4 is largely accounted for by A_2/A_4 and therefore that the entrance and exit barriers

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$E_2 = E_0$ and E_4 have similar values although, as follows from eq 13, the negative temperature dependence of k_b requires that $E_2 > E_4$. Considering that present results only yield extrapolated values of k_b, a more quantitative description of the potential energy surface of this system should be based on the RRKM analysis of direct low-pressure experiments.[11,12]

Potential Sources of Systematic Error. There are several potential sources of systematic error which should be considered. Reactions which cause the secondary removal of atomic oxygen are the most likely because of measured rate constants that are too large. This has been discussed in detail by Colussi.[2] For secondary chemistry to be important, however, the ratio $[O]_o/[OClO]$ must be considerably larger than in the present experiments. Under such conditions, and on the basis of the mechanism outlined in ref 2, numerical modeling of the atomic oxygen concentration reveals that substantially faster rates can be achieved via autocatalysis.

Another potential source of error in the determination of k_{II} is spectral interference due to fluorescence from vibrationally excited ClO produced in the photolysis of OClO.[13,14] We have recently shown that some vibronic transitions connecting vibrational overtones of the ground (X) state of ClO with its G and H Rydberg states are nearly resonant with the 130.6-nm O atom line and possess sizable Franck–Condon factors.[15] On the basis of the vacuum ultraviolet spectrum of ClO reported by Basco and Morse,[16] we were able to calculate that the energies of the transitions: $G(v'=11) \leftarrow X(v''=10)$ (76 569.6 cm^{-1}), $G(v'=5) \leftarrow X(v''=3)$ (76 552.5 cm^{-1}), and $H(v'=4) \leftarrow X(v''=2)$ (76 555.4 cm^{-1}) are within 20 cm^{-1} of the 130.6029-nm (76 568.0-cm^{-1}) line. Interestingly, enough no active transitions originating in ClO(X,$v''=0$), i.e., in thermalized ClO, were found. The sensitivity of ClO* detection by VUV fluorescence induced by these means is, however, ~10-fold smaller than for O atoms. The absolute contribution of ClO fluorescence to overall O atom signals is expected to be minor, consistent with the fact that $\phi_O \approx 1$.[2,15]

The fate of ClO* in these systems includes deactivation by argon or OClO as well as chemical reaction with OClO. The latter is an association in the falloff region, and therefore, its rate will also be a function of total pressure, vanishing at $[M] = 0$.[17] Our method of deriving k_{II} is insensitive to the rate of deactivation of ClO* by argon. Vibrational quenching of ClO* by OClO, however, will contribute to k_{II} at all values of [M]. Since the intrinsic rate of reaction A at zero pressure is slow, even small contributions of ClO* to the fluorescence signal would lead to faster initial rates of O atom decay, i.e., to a magnification of k_b. The magnitude of this effect is difficult to estimate, and no corrections to the data have been made.

Comparison with Other Measurements of k_b. In addition to the original work of Bemand et al., two recent, still unpublished, studies of the kinetics of reaction A at low pressures (<5 Torr) carried out in discharge flow reactors using O atom resonance fluorescence detection have been reported.[11,12] They represent direct measurements of k_b and therefore should be compared with the present results.

Toohey[12] obtained a value of $k_b \approx 5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K, i.e., nearly a factor of 3 smaller than our measurements. A proposal was made in this experiment for still another product channel forming ClOO + O. In another study, Gleason et al.[11] determined a somewhat larger value of k_b(298 K), 1.0×10^{-13} cm^3 molecule^{-1} s^{-1}. A non-Arrhenius temperature dependence was observed; the rate coefficients decreased with temperature over the range 400–225 K, increasing at lower temperatures. These studies point out the disparity in the results reported for k_b, not only between the low-pressure and extrapolated high-pressure experiments but also between the discharge flow studies themselves.

Conclusions

The temperature and pressure dependences of the rate of reaction between O atoms and chlorine dioxide confirm the occurrence of an association reaction, possibly leading to ClO_3, as the dominant process at stratospheric conditions.[18] On the basis of present results, we conclude that the reaction channel which produces $ClO + O_2$ (which predominates as the low-pressure limit is approached) results from the decomposition of a long-lived ClO_3* intermediate and not by direct abstraction.

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Appendix 1

(1) Definitions.

$$k_o = \beta Z_{LJ}[\rho(E_o)kT/Q_v] \exp\{[(\Delta H_2 - E_o)/kT] + [\Delta S_1/k]\}(R'T)F$$

$$Z_{LJ} = 8.1 \times 10^{-10}[(T/1000)(20/\mu)]^{1/2}(\sigma/5)^2\Omega$$

$$\Omega = [0.697 + 0.5185 \log (T/\epsilon)]^{-1}$$

$$F = F_E F_{anh} F_{rot}$$

$$\beta/(1 - \sqrt{\beta}) = \langle \Delta E \rangle / F_E RT$$

$$F_c = F_{sc}\beta^{0.14}$$

where β is the collision efficiency, ρ the density of harmonic states at E_o calculated in the Whitten–Rabinovich approximation, μ the reduced mass of ClO_3/Ar in amu, σ and ϵ the Lennard-Jones parameters of the pair in Å and K, respectively. The definitions of the F factors were taken from ref 8.

(2) Input Data.

vibrational frequencies of ClO_3 (ref. 2):

$$1270, 1024, 1080, 580, 544, 486 \text{ cm}^{-1}$$

$$S°(ClO_3) = 277 \text{ J K}^{-1} \text{ mol}^{-1} \text{ (298 K)}$$

$$\Delta H_2 - E_o = 457 \text{ cm}^{-1} \text{ (298 K)}$$

$$\sigma = 4.1 \text{ Å} \quad \epsilon/k = 211 \text{ K} \quad E_o = 10\,700 \text{ cm}^{-1}$$

$$\beta = 0.5 \text{ (312 K)}$$

Registry No. O, 17778-80-2; OClO, 10049-04-4; ClO_3, 13932-10-0.

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