Quenching of O(^{1}D$_2$) by Cl$_2$CO: kinetics and O(^{3}P$_J$) yield

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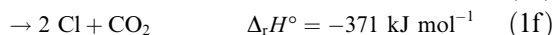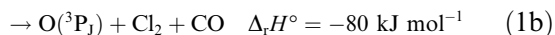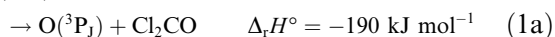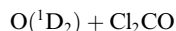Received 23 August 2000; in final form 18 September 2000

Abstract

Absolute rate coefficients (k_1) for the deactivation of electronically excited oxygen atoms, O(^{1}D$_2$), by phosgene (Cl$_2$CO) have been measured as a function of temperature over the range 194–425 K. The results are well described by the Arrhenius expression $k_1(T) = 2.04 \times 10^{-10} \exp(+27/T)$ cm^3 molecule^{-1} s^{-1}. The reported values for $k_1(T)$ are considerably lower than the values currently recommended for use in modeling stratospheric chemistry. The yield of ground state oxygen atoms, O(^{3}P$_J$), is found to be 0.20 ± 0.04. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Phosgene (Cl$_2$CO) is a key intermediate in the atmospheric oxidation of several anthropogenic chlorinated organic compounds including CCl$_4$, C$_2$Cl$_4$, CH$_3$CCl$_3$, CHCl$_3$, and C$_2$HCl$_3$ [1]. Phosgene has a relatively short tropospheric lifetime of about 70 days, with its removal dominated by hydrolysis in cloud water [1]. In the stratosphere, however, phosgene is thought to have a lifetime of several years [1]. The most important sink for stratospheric phosgene is photolysis [1] but, given its rather long lifetime towards photolytic destruction, both heterogeneous loss and reaction with O(^{1}D$_2$) atoms may also make non-negligible contributions to Cl$_2$CO removal. The lifetime of phosgene is sufficiently long that a significant fraction of stratospheric Cl$_2$CO is transported to the troposphere, where it is efficiently destroyed

(see above). Evaluation of the ozone depletion potentials (ODPs) of the phosgene parent compounds requires quantitative knowledge of the fraction of Cl$_2$CO chlorine atoms that are released in the stratosphere, so quantification of the rates and mechanisms of even the minor sinks is important.

The deactivation of O(^{1}D$_2$) by Cl$_2$CO can occur by non-reactive electronic quenching and by several reactive pathways

O(^{1}D$_2$) + Cl$_2$CO

$\rightarrow$ O(^{3}P$_J$) + Cl$_2$CO $\quad \Delta_r H° = -190$ kJ mol^{-1} (1a)

$\rightarrow$ O(^{3}P$_J$) + Cl$_2$ + CO $\quad \Delta_r H° = -80$ kJ mol^{-1} (1b)

$\rightarrow$ ClO + ClCO $\quad \Delta_r H° = -138$ kJ mol^{-1} (1c)

$\rightarrow$ ClO + Cl + CO $\quad \Delta_r H° = -106$ kJ mol^{-1} (1d)

$\rightarrow$ Cl$_2$ + CO$_2$ $\quad \Delta_r H° = -612$ kJ mol^{-1} (1e)

$\rightarrow$ 2 Cl + CO$_2$ $\quad \Delta_r H° = -371$ kJ mol^{-1} (1f)

Two laboratory studies of reaction (1a)–(1f), both of which were carried out during the 1970s, are reported in the literature [2,3]. Fletcher and Husain coupled flash photolysis of O$_3$ with

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time-resolved detection of $O(^1D_2)$ by resonance absorption spectroscopy to obtain the very large rate coefficient $k_1 = (7.1 \pm 0.9) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at $T = 300$ K. The currently recommended value for k_1 for use in stratospheric modeling, 3.6×10^{-10} cm^3 molecule^{-1} s^{-1}, is obtained by scaling the Fletcher and Husain result down by approximately a factor of two to account for a systematic difference between $O(^1D_2)$ rate coefficients obtained by Husain and coworkers (using the resonance absorption detection technique) and $O(^1D_2)$ rate coefficients determined in other laboratories using a variety of other techniques [4]. In addition to the Fletcher and Husain study, Jayanty et al. [3] have studied reaction (1a)–(1f) at 298 K using end product analysis in conjunction with continuous 254 nm photolysis of $O_3/O_2/Cl_2CO/$ N$_2$O mixtures. Jayanty et al. found that CO is a major product of reaction (1a)–(1f) with a yield of approximately 0.8 [3]. They also obtained some relative kinetic data which suggest that k_1 may be significantly slower than the currently recommended [4] value.

In this Letter, we report the results of a kinetic and mechanistic study of reaction (1a)–(1f). Total rate coefficients for $O(^1D_2)$ removal by Cl_2CO, k_1, are reported as a function of temperature for the first time, and the first measurement of the yield of $O(^3P_J)$ is also reported. We find that the rate coefficient for deactivation of $O(^1D_2)$ by Cl_2CO is about a factor of 1.6 slower than previously thought.

2. Experimental approach

The experimental approach is similar to the one we have employed in several previous studies of $O(^1D_2)$ reactions of atmospheric interest [5–9], although the data acquisition and analysis methods are improved over those employed in the earlier studies. The experiments involve time-resolved detection of $O(^3P_J)$ by atomic resonance fluorescence spectroscopy following laser flash photolysis of $O_3/Cl_2CO/He$ and $O_3/N_2/He$ mixtures. An apparatus diagram is published elsewhere [10]. Some experimental details that are particularly relevant to this study are given below.

A jacketed, Pyrex reaction cell with an internal volume of approximately 160 cm^3 was used in all experiments. The cell was maintained at a constant temperature (± 1 K) by circulating either ethylene glycol (for $T > 298$ K) or 1:1 ethanol–methanol (for $T < 298$ K) through the outer jacket. $O(^1D_2)$ atoms were produced by 266 nm photolysis of O_3. Fourth harmonic radiation from a Quanta Ray Model DCR-2A Nd:YAG laser served as the photolytic light source. Fluences utilized in this study ranged from 12 to 36 mJ cm^{-2}, and the laser pulse width was 6 ns (FWHM). An atomic resonance lamp, situated perpendicular to the photolysis laser, excited ground state $O(^3P_J)$ atoms in the reaction cell; these atoms are produced with a small quantum yield via O_3 photodissociation and are also produced as a product of $O(^1D_2)$ deactivation. Radiation was coupled out of the lamp through a MgF$_2$ window and into the reaction cell through a MgF$_2$ lens. The region between the lamp and the reaction cell was purged with N$_2$. Fluorescence was collected by a CaF$_2$ lens on the axis normal to both the photolysis laser beam and the resonance lamp beam and imaged onto the photocathode of a solar blind photomultiplier. Signals were processed using photon-counting techniques in conjunction with multichannel scaling. The multichannel scaler sweep was pre-triggered in order to allow a pre-flash baseline to be obtained. All experiments were carried out under 'slow flow' conditions with a linear flow rate through the reactor of about 25 cm s^{-1}. Since the laser repetition rate was 10 Hz, the gas mixture within the detection volume was replenished between laser pulses.
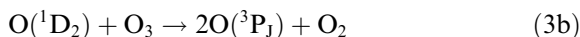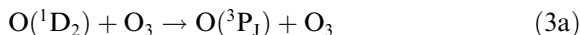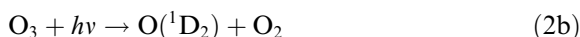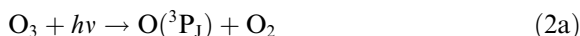
Ozone and phosgene were flowed into the reaction cell from 12-L Pyrex bulbs containing dilute mixtures in helium buffer gas, while helium and nitrogen were flowed directly from their high-pressure storage tanks. The concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates and the total pressure. The mole fractions of ozone and phosgene in their storage bulbs were checked frequently by UV photometry. Atomic line sources were used as the photometric light sources, and the monitoring wavelengths

were 253.7 nm (Hg line) for O_3 and 228.8 nm (Cd line) for Cl_2CO. The room temperature absorption cross-sections that were employed to convert measured absorbances to concentrations were 1.144×10^{-17} cm^2 for O_3 at 253.7 nm [11–16] and 1.31×10^{-19} cm^2 for Cl_2CO at 228.8 nm [17].

Research grade helium (>99.9999% purity) was used as the buffer gas (the total pressure was 20 Torr in most experiments) and in the preparation of all gas mixtures. The minimum purities of the other gases were: N_2 – 99.999%; O_2 – 99.997%; Cl_2CO – 99.0% (liquid phase in the storage cylinder). Ozone was prepared by passing O_2 through a commercial ozonizer; the O_3 was trapped on silica gel at 196 K and excess O_2 was removed by pumping. Cl_2CO samples were transferred from their cylinders into 12-l storage bulbs and degassed repeatedly at 77 K before use.

3. Results and discussion

Most experiments were carried out under pseudo first-order conditions with O_3, Cl_2CO, and N_2 in excess over oxygen atoms (see Table 1). In reaction mixtures containing O_3, Cl_2CO, and He, the processes that control the temporal evolution of $O(^3P_J)$ are reaction (1a)–(1f) and the following:

$$O_3 + h\nu \rightarrow O(^3P_J) + O_2 \tag{2a}$$

$$O_3 + h\nu \rightarrow O(^1D_2) + O_2 \tag{2b}$$

$$O(^1D_2) + O_3 \rightarrow O(^3P_J) + O_3 \tag{3a}$$

$$O(^1D_2) + O_3 \rightarrow 2O(^3P_J) + O_2 \tag{3b}$$

$$O(^1D_2) + O_3 \rightarrow 2O_2 \tag{3c}$$

$$O(^1D_2) + \text{impurities}$$
$$\rightarrow O(^3P_J) + \text{other products} \tag{4}$$

In the presence of N_2, production of $O(^3P_J)$ also occurs via the following process:

$$O(^1D_2) + N_2 \rightarrow O(^3P_J) + N_2 \tag{5}$$
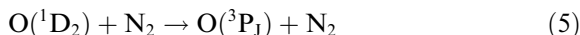
The temporal profile of the $O(^3P_J)$ fluorescence following the laser flash is described by the following expression:

Table 1
Summary of kinetic data for the reaction $O(^1D_2) + Cl_2CO \rightarrow$ products[a]

T[b]	$[O_3]$[b]	$[O]_0$[b,c]	$[Cl_2CO]$[b]	Number of experiments[d]	Range of k_a[b]	$k_1(T)$[b,e]	$(k_{1a} + k_{1b})/k_1$[e,f]
194	13	6.0	0–1010	6	3380–27500	2.35 ± 0.06	0.229 ± 0.025
208	59	9.0	0–714	9	3510–20200	2.34 ± 0.14	0.288 ± 0.064
249	60	9.3	0–901	7	3440–25600	2.27 ± 0.08	0.217 ± 0.094
297	12	5.6	0–2470	7	2810–57100	2.19 ± 0.05	0.209 ± 0.080
298	75	12	0–1260	20	3390–31600	2.22 ± 0.06	0.207 ± 0.023
354	50	7.9	0–952	7	3140–24300	2.23 ± 0.12	0.204 ± 0.039
429	34	5.2	0–431	3	2490–11700	2.14 ± 0.06	0.191 ± 0.060
429	57	8.8	0–771	6	3660–20700	2.12 ± 0.19	0.216 ± 0.074

[a] The pressure was 20 Torr and the buffer gas was helium in all experiments.
[b] Units are T (K); Concentrations (10^{11} molecules cm^{-3}); k_a(s^{-1}); k_1(10^{-10} cm^3 molecule^{-1} s^{-1}).
[c] Determined from the laser fluence, O_3 concentration, and an estimate of the laser beam cross-sectional area.
[d] Experiment $\equiv$ the measurement of a single $O(^3P_J)$ temporal profile.
[e] Uncertainties are 2σ and represent precision only.
[f] These values are the ones determined from plots of $\beta^* k_a / \beta$ versus $[Cl_2CO]$.

$$S_t = \{k_a/(k_d - k_a)\}A\{\exp(-k_a t) - \exp(-k_d t)\}$$
$$+ B\exp(-k_d t). \tag{I}$$

In Eq. (I), S_t is the fluorescence signal at time t after the laser flash, k_a the pseudo first-order rate coefficient for $O(^3P_J)$ appearance, k_d the rate coefficient for $O(^3P_J)$ decay (assumed to be first-order), and the parameters A and B are related to the concentrations of $O(^1D_2)$ and $O(^3P_J)$ produced by the laser flash.

$$A = C\Phi\big[O(^1D_2)\big]_0, \tag{II}$$
$$B = C\big[O(^3P_J)\big]_0. \tag{III}$$

In Eqs. (II) and (III), C is the proportionality constant that relates the resonance fluorescence signal to the $O(^3P_J)$ concentration and Φ is the number of $O(^3P_J)$ produced per $O(^1D_2)$ destroyed. If the reaction mixture contains O_3, He, and Cl_2CO, then

$$k_a = k_1[Cl_2CO] + k_a^0. \tag{IV}$$

In Eq. (IV), k_a^0 is the pseudo first-order rate coefficient for $O(^3P_J)$ appearance in the absence of Cl_2CO. Ground state oxygen atoms are unreactive towards He, Cl_2CO, and N_2, and react very slowly with O_3 [4]. Hence, under the experimental conditions employed in this study, $k_a \gg k_d$. As a result, the assumption that k_d is a first-order rate coefficient, while not strictly correct, does not compromise the accuracy with which the parameters of interest (k_a and Φ) can be determined.

Some typical $O(^3P_J)$ temporal profiles, observed following laser flash photolysis of $O_3/Cl_2CO/He$ mixtures, are shown in Fig. 1. Bi-molecular rate coefficients for the collisional removal of $O(^1D_2)$ by Cl_2CO, $k_1(T)$, are obtained from the variation of k_a with $[Cl_2CO]$ at constant concentrations of O_3 and He. Typical data are shown in Fig. 2. The results of all experiments are summarized in Table 1 and an Arrhenius plot for reaction (1a)–(1f) is shown in Fig. 3. The following Arrhenius expression is derived from the data:

$$k_1(T) = (2.04 \pm 0.08) \times 10^{-10}$$
$$\times \exp\{(27 \pm 11)/T\}\ cm^3\ molecule^{-1}\ s^{-1}.$$

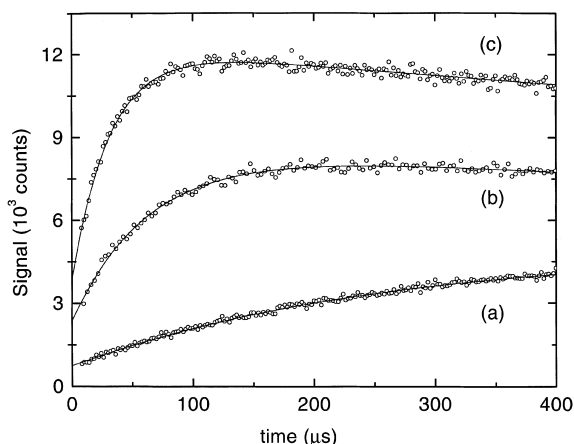Uncertainties in the above expression are 2σ and represent precision only (all data points weighted

Fig. 1. Typical $O(^3P_J)$ appearance temporal profiles. The photolysis laser fired at time $= 0$. Experimental conditions – $T = 298$ K; $[O_3] = 7.5 \times 10^{12}$ molecules cm^{-3}; $[Cl_2CO]$ in units of 10^{13} molecules cm^{-3}: (a) 0; (b) 5.49; (c) 12.6. Number of laser shots averaged: (a) 2000; (b) 5000; (c) 10,000. Solid lines are obtained from least-squares analyses that give the following best fit parameters – k_a in units of s^{-1}: (a) 3390; (b) 15,400; (c) 31,600; k_d in units of s^{-1}: (a) 217; (b) 291; (c) 304. A: (a) 4740; (b) 6230; (c) 8360. B: (a) 760; (b) 2370; (c) 3880.
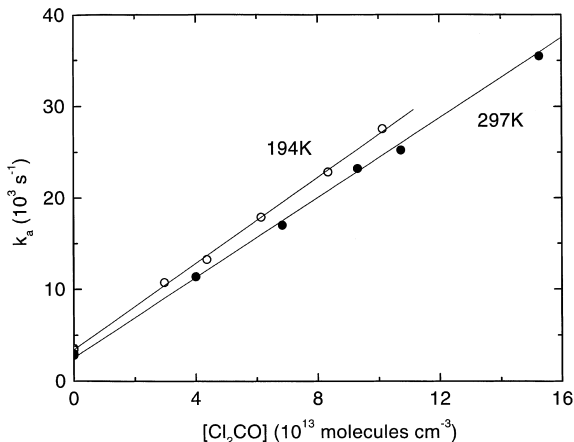

Fig. 2. Plots of k_a versus $[Cl_2CO]$ for data obtained at two different temperatures. Solid lines are obtained from linear least-squares analyses and give the following bimolecular rate coefficients in units of 10^{-10} cm^3 molecule^{-1} s^{-1}: 2.35 at 194 K and 2.19 at 297 K.

equally). The uncertainties in the above expression refer to the Arrhenius parameters only. We believe that systematic errors in the determination of k_1 are small, and conservatively estimate the absolute
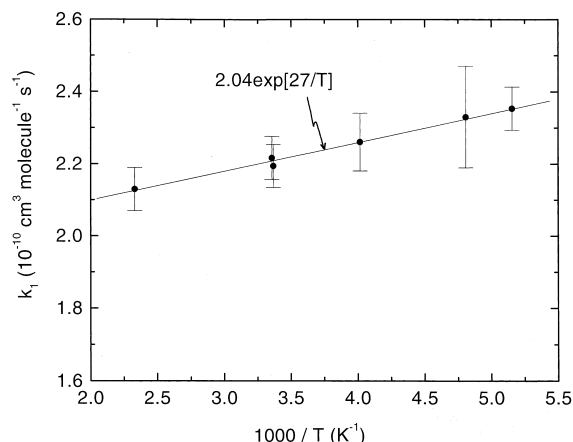
Fig. 3. Arrhenius plot for the reaction $O(^1D_2) + Cl_2CO \rightarrow$ products. The solid line is obtained from a least-squares analysis and gives the Arrhenius expression shown in the figure.

accuracy of each reported rate coefficient to be $\pm 15\%$ at the 95% confidence level. Assumed contributions to the overall uncertainty are precision, uncertainty in the Cl_2CO absorption cross-section (estimated to be $\pm 5\%$), and small systematic errors in temperature, pressure, and mass flow rates.

The kinetic data shown in Fig. 1 provide information not only about the value of k_1, the total rate coefficient for $O(^1D_2)$ removal by Cl_2CO, but also about $k_{1a} + k_{1b}$, the rate coefficient for $O(^1D_2)$ deactivation to $O(^3P_J)$. To evaluate $k_{1a} + k_{1b}$, we first define the parameter β to be the ratio of $O(^3P_J)$ produced by photolysis to that produced by $O(^1D_2)$ deactivation. It can be shown that since

$$\beta = B/A \qquad (V)$$

then

$$\beta^*\{(k_a/\beta) - (k_a^0/\beta^0)\} = (k_{1a} + k_{1b})[Cl_2CO]. \qquad (VI)$$

In Eq. (VI), β^0 is the value of β in the absence of Cl_2CO and β^* is the value of β in the limit where $O(^1D_2)$ is converted to $O(^3P_J)$ with unit yield. The value of β^* can be determined by applying Eq. (VI) to data obtained with N_2 replacing Cl_2CO as the reactant (and recognizing that $k_a[N_2] = k_a - k_a^0$). From data obtained using $O_3/N_2/He$ mixtures (which will be published elsewhere), we obtain $\beta^* = 0.123 \pm 0.019$ independent of temperature

(error is 2σ). Assuming that the total O_3 photodissociation quantum yield at 266 nm is unity, the parameter β^* is related to $\Phi_{O(^3P)}$, the quantum yield for $O(^3P)$ production from O_3 photolysis at 266 nm, as follows:

$$\Phi_{O(^3P)} = \beta^*/(1 + \beta^*). \qquad (VII)$$

Hence, our data give $\Phi_{O(^3P)} = 0.110 \pm 0.017$, a result that agrees very well with the literature value of 0.12 ± 0.02 [18]. A plot of $\beta^* k_a/\beta$ versus $[Cl_2CO]$ for data obtained at 298 K is shown in Fig. 4; the slope gives $k_{1a} + k_{1b} = (4.53 \pm 0.41) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (error is 2σ, precision only). From the data shown in Fig. 4, the branching ratio for conversion of $O(^1D_2)$ to $O(^3P_J)$, i.e., $(k_{1a} + k_{1b})/k_1$, is found to be 0.208 ± 0.033. Data analogous to that shown in Fig. 4 were obtained at each temperature investigated, and for more than one data set at some temperatures; the results are summarized in Table 1. Although there appears to be a slight tendency for the measured yield to decrease with increasing temperature, the uncertainty in most measured yields is larger than the differences between yields measured at the temperature extremes of our study. Hence, we prefer to take a weighted average of all measured yields to obtain $(k_{1a} + k_{1b})/k_1 = 0.217 \pm 0.040$ independent of temperature, where the uncertainty is two standard deviations of the weighted mean.
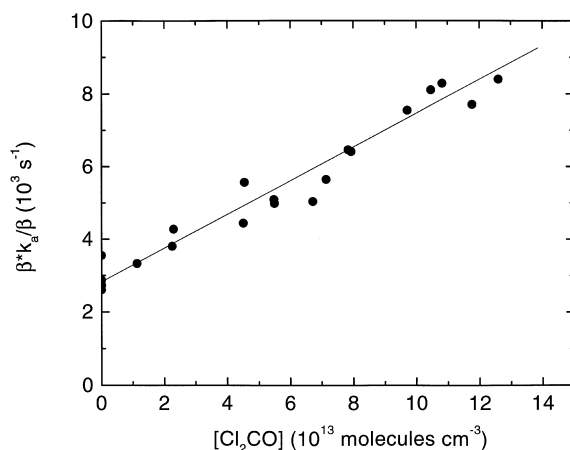

Fig. 4. Plot of $\beta^* k_a/\beta$ versus $[Cl_2CO]$ for data obtained at 298 K. The solid line is obtained from a linear least-squares analysis; its slope gives $k_{1a} + k_{1b} = 4.53 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

A slightly less direct, but potentially more precise determination of $(k_{1a} + k_{1b})/k_1$ was performed at room temperature only using reaction mixtures where Cl_2CO was added in sufficient quantity to completely dominate $O(^1D_2)$ removal. Experiments were carried out such that the $O(^3P_J)$ appearance was essentially instantaneous but the $O(^3P_J)$ decay was temporally resolved. The signal at time t' ($\equiv$ a time shortly after the laser fired when $O(^3P_J)$ formation had gone to completion but no appreciable decay had occurred) could be determined very accurately and represented $O(^3P_J)$ produced both by direct photolysis and by $O(^1D_2)$ deactivation. A single determination of an $O(^3P_J)$ yield involved back-to-back experiments, where the signal at $t = t'$ was determined with N_2 as the dominant $O(^1D_2)$ quencher (signal $\equiv S_{N2}$), then with Cl_2CO as the dominant quencher (signal $\equiv S_{Cl2CO}$). Signals were normalized for $[O_3]$ and total laser fluence. In addition, it was necessary to correct S_{Cl2CO} (but not S_{N_2}) for absorption of resonance lamp radiation and fluorescence by Cl_2CO. This was done by constructing an S_{Cl2CO} versus $[Cl_2CO]$ calibration curve from a series of experiments with constant $[O]_0$. A majority of experiments with Cl_2CO as the dominant quencher employed $[Cl_2CO] \sim 1.2 \times 10^{15}$ molecules cm^{-3}; at this concentration, the fluorescence signal per unit concentration of $O(^3P_J)$ was a factor of 1.50 lower than it was with no Cl_2CO present in the reaction mixture. The observed signal reduction resulting from addition of Cl_2CO to the reaction mixture is approximately that expected based on the reaction cell geometry and the known (low resolution) absorption cross-section for Cl_2CO at 130 nm, i.e., $\sim 5 \times 10^{-17}$ cm^2 [19]. Since $O(^1D_2)$ deactivation by N_2 produces $O(^3P_J)$ with unit yield, $(k_{1a} + k_{1b})/k_1$ could be determined from the following relationship [7]:

$$(k_{1a} + k_{1b})/k_1 = \{(S_{Cl_2CO}/S_{N_2}) - \Phi_{O(^3P)}\} \\ \times \{1 - \Phi_{O(^3P)}\}^{-1}. \qquad \text{(VIII)}$$

Using $\Phi_{O(^3P)} = 0.110 \pm 0.017$ (see above), we obtain $(k_{1a} + k_{1b})/k_1 = 0.185 \pm 0.035$. The branching ratios obtained by the two methods are in reasonable agreement. Giving equal weighting to each of the two determinations, we report

$(k_{1a} + k_{1b})/k_1 = 0.20 \pm 0.04$.

We find that k_1 is about a factor of 1.6 slower than the currently recommended value [4], and that a small but significant fraction of $O(^1D_2)$ removed by Cl_2CO produces $O(^3P_J)$. Depending on whether $O(^3P_J)$ formation occurs via channel (1a) or channel (1b), production of $O(^3P_J)$ may or may not result in destruction of Cl_2CO. Further studies will be required to resolve this issue.

The only other direct measurement of k_1 reported to date was carried out by Fletcher and Husain [2] using time-resolved atomic resonance absorption spectroscopy to monitor $O(^1D_2)$. These investigators obtained a rate coefficient (7.1×10^{-10} cm^3 molecule^{-1} s^{-1}) that is much faster than the one obtained in our study. Many rate coefficients for $O(^1D_2)$ reactions reported by Husain and co-workers are larger than those obtained in other laboratories by about a factor 2 [4]. This factor is believed to be the result of an error in the determination of γ, an empirically determined parameter that relates the measured absorbance to the $O(^1D_2)$ concentration [7]. Correction of Fletcher and Husain's result downward by a factor of 2 gives $k_1 = 3.55 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 300 K still a factor of 1.6 faster than the value obtained in our study. One relative rate measurement of k_1 is also reported in the literature. Jayanty et al. [3] have studied reaction (1a)–(1f) at 298 K using end product analysis in conjunction with continuous 254 nm photolysis of $O_3/O_2/Cl_2CO/N_2O$ mixtures. Using $O(^1D_2) + N_2O$ as the reference reaction,

$$O(^1D_2) + N_2O \rightarrow N_2 + O_2 \qquad \text{(6a)}$$

$$O(^1D_2) + N_2O \rightarrow 2NO \qquad \text{(6b)}$$
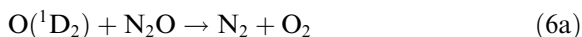
and detection of N_2 (a product of the reference reaction) as the kinetic probe, Jayanty et al. [3] report that k_1 is a factor of 1.57 faster than k_6 (it is currently thought that $k_6 = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [4,7,20,21] and $k_{6b}/k_6 = 0.61$ [22]). Unfortunately, Jayanty et al.'s data analysis required them to assume a value for the rate coefficient ratio k_{3c}/k_{6a} that is now known to be incorrect, and there is insufficient information in their paper to allow a quantitative reanalysis of

their data; it does, however, appear that their results support a slower value for k_1 than the one that is currently recommended [4].

In addition to their competitive kinetics results that are discussed above, Jayanty et al. also report that CO is a major product of reaction (1a)–(1f) with a yield of approximately 0.8 [3]. This result is consistent with our finding that *at least* 76% of the overall deactivation of $O(^1D_2)$ by Cl_2CO is reactive, i.e., results in conversion of O and Cl_2CO to other products. Direct measurement of the yields of atomic chlorine and CO_2 are additional pieces of information that would solidify our mechanistic understanding of reaction (1a)–(1f).

The results reported in this Letter demonstrate that $k_1 - k_{1a}$, the rate coefficient for destruction of Cl_2CO by $O(^1D_2)$, is in the range $(2.0 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. At a mid-stratospheric altitude of 30 km, a typical diurnally averaged $O(^1D_2)$ number density is ∼20 atoms per cm^3 [4] (assuming 15 March, 40°N conditions); hence, under these conditions, the lifetime of Cl_2CO toward destruction by $O(^1D_2)$ is approximately 2.5×10^8 s, i.e., 8 yr. It appears, therefore, that reaction with $O(^1D_2)$ removes phosgene from the stratosphere at a rate that is somewhat slower than, but not negligible compared to, other phosgene removal processes such as photolysis, heterogeneous reaction on stratospheric particles, and transport to the troposphere [1]. Reaction (1a)–(1f) should be included in model calculations of ozone depletion potentials for the phosgene parent compounds, particularly CCl_4, since this compound is destroyed at higher altitudes than the other phosgene parents [1].

Acknowledgements

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