Kinetics and Mechanism of the IO + ClO Reaction

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The kinetics and mechanism of the reaction between IO and ClO radicals have been studied by the mass spectrometric discharge-flow method at $T = 298$ K and at total pressure around 1 Torr. The value of the overall rate constant $k_1 = (1.1 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} has been determined under pseudo-first-order conditions using an excess of ClO over IO radicals. The quantitative detection of the reaction products OClO, Cl, and ICl allowed for the determination of the branching ratios (0.55 ± 0.03), (0.25 ± 0.02), and (0.20 ± 0.02) for the channels producing I + OClO, I + Cl + O$_2$, and ICl + O$_2$, respectively. In addition, the rate coefficient $(3.2 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} has been measured at room temperature for the reaction I + Cl$_2$O → ICl + ClO. The kinetic data obtained allow for a redetermination of the heat of formation of IO: $\Delta H_f(\mathrm{IO}) = (27.7 \pm 1.2)$ kcal mol^{-1} (based on the current value of $\Delta H_f(\mathrm{OClO}) = (22.6 \pm 1.0)$ kcal mol^{-1}). The data obtained indicate that the reaction IO + ClO, which could be involved in stratospheric ozone depletion if iodine is present in the stratosphere, is much less important than assumed in previous model calculations.

Introduction

The atmospheric chemistry of iodine has been much less studied than that of chlorine and bromine. However, recently the potential impact of iodine on ozone catalytic destruction cycles has been suggested in both the stratosphere and the troposphere. Considering the significant production of CH$_3$I by the oceans, together with a possible very fast transport of this short-lived molecule to the stratosphere via convective clouds in the tropics, a depletion of stratospheric ozone induced by iodine chemistry has been proposed.[1] It was anticipated that, like BrO + ClO, the interhalogen reaction IO + ClO could lead to a catalytic cycle, which depletes ozone:

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

$$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2}$$

$$\mathrm{IO} + \mathrm{ClO} \rightarrow \mathrm{Cl} + \mathrm{I} + \mathrm{O_2}$$

$$\text{net:} \qquad 2\mathrm{O_3} \rightarrow 3\mathrm{O_2}$$

In the IO + ClO reaction, the possible alternative channels forming ClOO and ICl were also considered but would also close the above cycle, since these products rapidly re-form halogen atoms from thermal and photochemical decomposition, respectively. The OClO-forming channel, which leads to a "do nothing" cycle, was not considered to occur. In the absence of laboratory data, the modeling calculation assumed that the IO + ClO reaction led to the net formation of I and Cl with a very high rate constant ($k = 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). The major feature of this iodine chemistry is the lack of stability of the reservoir species (HOI, IONO$_2$) which makes the IO radicals the major atmospheric species and, consequently, drastically enhances the effectiveness of iodine in the catalytic ozone depletion, if iodine is present in the stratosphere.

Besides, it has been speculated[1] that the above catalytic cycle could also participate in the ozone loss events observed in the Arctic troposphere during the spring after sunrise (e.g., refs 2 and 3).

In the present work, the discharge flow−mass spectrometry method was employed to investigate in detail the reaction between IO and ClO. The rate constants and the branching ratios for the following thermochemically feasible channels have been determined at 298 K:

$$\mathrm{IO} + \mathrm{ClO} \rightarrow \mathrm{I} + \mathrm{OClO} \qquad \Delta H = -(4.0 \pm 0.2)\ \mathrm{kcal\ mol^{-1}} \tag{1a}$$

$$\mathrm{IO} + \mathrm{ClO} \rightarrow \mathrm{I} + \mathrm{Cl} + \mathrm{O_2} \qquad \Delta H = (2.3 \pm 1.2)\ \mathrm{kcal\ mol^{-1}} \tag{1b}$$

$$\mathrm{IO} + \mathrm{ClO} \rightarrow \mathrm{ICl} + \mathrm{O_2} \qquad \Delta H = -(47.5 \pm 1.2)\ \mathrm{kcal\ mol^{-1}} \tag{1c}$$

The enthalpy data used are from ref 4, except for IO radicals, for which the value taken for $\Delta H_{f,298}(\mathrm{IO})$ is from the present work. Channel 1b could be written as a two-step reaction, the primary products being either IOO + Cl or I + ClOO. The enthalpy of the primary step forming I + ClOO is 3.3 kcal mol^{-1} exothermic, the alternative step likely having a similar exothermicity.

A study of reaction 1 has been performed simultaneously in another laboratory[5] using the laser photolysis−laser induced fluorescence technique (see Discussion).

Experimental Section

The experimental setup used is schematically shown in Figure 1 and has been described in detail previously.[6] A modulated molecular beam mass spectrometer was used for the detection of the chemical species involved in reaction 1. The reactor consisted of a Pyrex tube (45 cm length and 24 cm i.d.). A movable triple injector was used for the production and introduction of the reactants. The inner surfaces of the reactor

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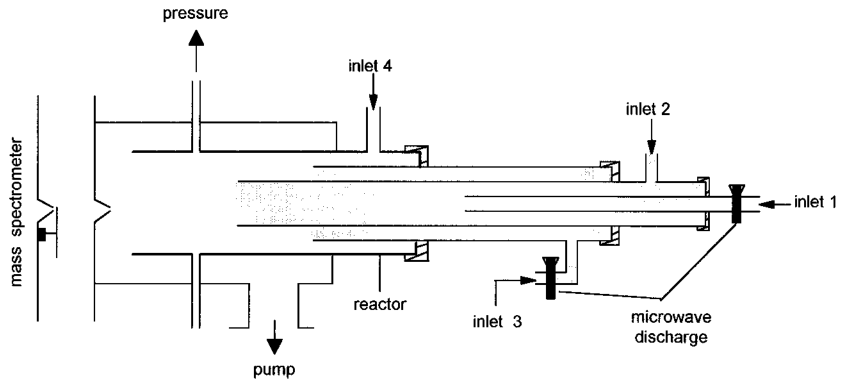

Figure 1. Diagram of the apparatus used.

and of the movable injector were coated with halocarbon wax in order to reduce the heterogeneous loss of active species.

Three different methods were used for the production of IO radicals: the reaction of oxygen atoms (formed in microwave discharge of O_2/He mixtures) with molecular iodine or trifluoromethyl iodide

$$O + I_2 \rightarrow IO + I \qquad k_2 = 1.4 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (\text{ref }4) \quad (2)$$

$$O + CF_3 \rightarrow IO + CF_3 \qquad k_3 = 1.16 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (\text{ref }7) \quad (3)$$

and the reaction of iodine atoms with ozone

$$I + O_3 \rightarrow IO + O_2 \qquad k_4 = 1.0 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (\text{ref }4) \quad (4)$$

(all rate constants are given at 298 K).

The fate of CF_3 radicals produced in reaction 3 is not known, but their very low concentrations (similar to those of IO radicals) could not significantly influence the kinetic measurements. In a recent paper also using reaction 3 to produce IO,[8] complications were observed in the presence of O_2, which rapidly reacted with CF_3. In the present experiments, O_2 was not present at concentrations high enough to induce such complications.

In the source of IO using reaction 4, two reactions were used to produce I atoms:

$$Cl + I_2 \rightarrow I + ICl \qquad k_5 = 2.1 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (\text{ref }9) \quad (5)$$

$$H + I_2 \rightarrow I + HI \qquad k_6 = 6.2 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (\text{ref }10) \quad (6)$$

I_2 was used in excess over H or Cl atoms produced by microwave discharge of H_2/He or of Cl_2/He mixtures. The direct dissociation of I_2 as a source of atomic iodine was not used because of its unstability and heterogeneous complications.[9] Molecular iodine was introduced into the reactor by flowing helium through a column containing I_2 crystals. When reaction 4 is used to produce IO, a dark reaction between I_2 and O_3 is sometimes observed, leading to the formation of IO radicals and aerosol.[11] Considering both the time scale of the present experiments and the low concentrations of I_2 and O_3, such complications were not observed here.

The concentration of IO radicals was determined using the titration with NO:

$$IO + NO \rightarrow I + NO_2 \qquad k_7 = 2.2 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (\text{ref }4) \quad (7)$$

with the subsequent mass spectrometric detection of the NO_2 formed and calibration of the mass spectrometer by flowing known concentrations of NO_2 into the reactor. Calibration experiments were carried out under conditions where the possible influence of the self-combination and heterogeneous loss of IO were negligible:

$$IO + IO \rightarrow \text{products} \qquad k_8 = 5.2 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (\text{ref }4) \quad (8)$$

$$IO + \text{wall} \rightarrow \text{products} \qquad k_w \approx 14\ \mathrm{s^{-1}}\ (\text{this work})$$

The absolute concentrations of both atomic and molecular iodine were determined by Cl titration with excess of I_2 through reaction 5: $[I] = \Delta[I_2] = [Cl]$. The mass spectrometric signal of Cl atoms was calibrated either from the measurement of the dissociated fraction of known amount of Cl_2 in the microwave discharge or from the titration of Cl by an excess of vinyl bromide ($[Cl] = \Delta[C_2H_3Br] = [C_2H_3Cl]$):

$$Cl + C_2H_3Br \rightarrow Br + C_2H_3Cl \qquad k_9 = 1.43 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (\text{ref }12) \quad (9)$$

Three different sources of ClO radicals were used:

$$Cl + OClO \rightarrow ClO + ClO \qquad k_{10} = 5.8 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (\text{ref }4) \quad (10)$$

$$Cl + Cl_2O \rightarrow ClO + Cl_2 \qquad k_{11} = 9.6 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (\text{ref }4) \quad (11)$$

$$Cl + O_3 \rightarrow ClO + O_2 \qquad k_{12} = 1.2 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (\text{ref }4) \quad (12)$$

OClO, Cl_2O, and O_3 were synthesized in the laboratory. Chlorine dioxide, OClO, was prepared using the reaction of H_2SO_4 with $KClO_3$,[13] diluted with helium and stored in the dark at around 280 K. Cl_2O was synthesized from the reaction $2Cl_2 + HgO \rightarrow Cl_2O + HgCl_2$.[14] After elimination of the Cl_2 impurity (by trap-to-trap distillation) and dilution with helium, Cl_2O was also stored in the dark at around 280 K. The purity of OClO and Cl_2O was controlled by mass spectrometry by monitoring their main decomposition product Cl_2. Ozone was produced by an ozonizer (Trailigaz) and was collected in a liquid nitrogen trap before dilution with helium and storage at room temperature in a calibrated volume. The titration of Cl via reactions 10−12 as well as the reaction

$$ClO + NO \rightarrow Cl + NO_2 \qquad k_{13} = 1.7 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}\ (ref\ 4) \quad (13)$$

was used for the measurements of the absolute concentrations of ClO radicals.

All the relevant species were detected mass spectrometrically at their parent peaks.

The purities of the gases used were as follows: He > 99.9995% (Alphagaz), passed through two liquid nitrogen traps before use; O_2 > 99.995% (Alphagaz); H_2 > 99.998% (Alphagaz); Cl_2 > 99%(Ucar); I_2, ultrapure (Prolabo); CF_3I > 99% (Fluorochem); NO > 99% (Alphagaz), purified by trap-to-trap distillation in order to remove traces of NO_2; NO_2 > 99% (Alphagaz); C_2H_3Br > 99.5% (Ucar).

Results

All the experiments described below were conducted at room temperature (298 K) and at a total pressure of about 1 Torr of He.

Rate Constant Measurements. Four series of experiments, using different sources for the production of both IO and ClO, were performed to measure the total rate constant of reaction 1:

$$IO + ClO \rightarrow products \quad (1)$$

Pseudo-first-order conditions were always used with an excess of ClO over IO. The rate constant k_1 was derived from the temporal decays of IO according to the expression

$$-d[IO]/dt = (k_1[ClO] + k_w)[IO]$$

where k_w is the rate of the wall loss of IO radicals and includes a contribution from the IO homogeneous recombination. The initial concentrations of IO were in the range (5−10) × 10^{10} molecule cm^{-3}. The loss rate of IO measured in the absence of ClO, $k_w = (20 \pm 5)\ s^{-1}$, was much lower than the rate of the IO consumption by reaction 1. The change of ClO concentration along the reactor was negligible, which was expected from the low value of the rate constant for the ClO self-reaction:

$$ClO + ClO \rightarrow products \qquad k_{14} = 1.6 \times 10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}\ (ref\ 4) \quad (14)$$

and from the low value measured for the ClO heterogeneous loss rate (<3 s^{-1}).

In the first series of experiments, IO and ClO radicals were produced from reactions 3 and 10, respectively. The precursors of radicals were introduced into the reactor as follows (Figure 1): Cl_2, inlet 1; OClO, inlet 2; O_2, inlet 3; and CF_3I, inlet 4. The ranges of concentrations of the molecular precursors in the reactor were [OClO] = (1−3) × 10^{12} and [CF_3I] = (2−4) × 10^{13} molecule cm^{-3}. [ClO] was varied in the range (1.3−24.6) × 10^{12} molecule cm^{-3}. The mean gas flow velocity in the reactor was in the range (1800−1900) cm s^{-1}. The resulting pseudo-first-order plot is shown in Figure 2. The least-squares fit provides the following value for the rate coefficient of reaction 1:

$$k_1 = (1.2 \pm 0.2) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

All the uncertainties given in this section include one standard deviation and 10% for the absolute calibration of ClO concentration.

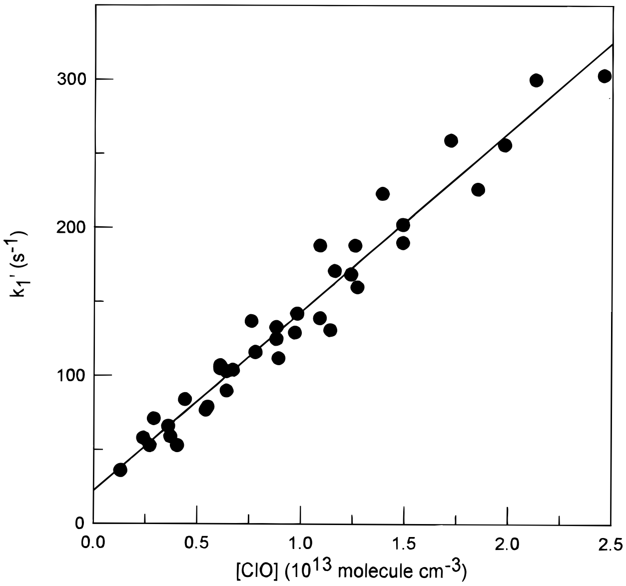

Figure 2. Pseudo-first-order plot of IO consumption in reaction 1: source of IO, reaction O + CF_3I (2); source of ClO, reaction Cl + OClO (10).

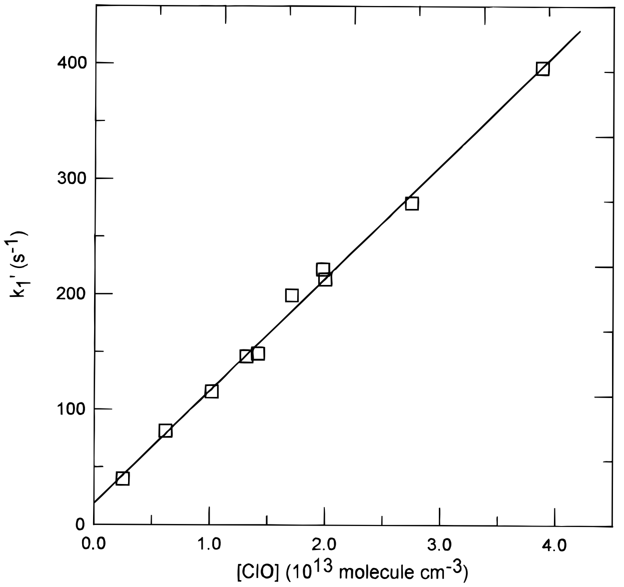

Figure 3. Pseudo-first-order plot of IO consumption in reaction 1: source of IO, reaction O + I_2 (2); source of ClO, reaction Cl + OClO (10).

In the second series of experiments the conditions were the same as in the first series, except that molecular iodine ([I_2] = (3−5) × 10^{12} molecule cm^{-3}) was used instead of CF_3I to generate IO radicals via reaction 2. The ClO concentration range was (2.6−29.3) × 10^{12} molecule cm^{-3}. The pseudo-first-order plot given in Figure 3, leads to

$$k_1 = (1.0 \pm 0.15) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

The intercepts are about the same in both cases, (22.5 ± 5.0) s^{-1} (Figure 2) and (18.7 ± 4.6) s^{-1} (Figure 3), and are similar to the IO loss rate measured in the absence of ClO.

The possible interference of secondary reactions in these two series of measurements of k_1 has been examined. First, the reverse reaction of channel 1a, recently studied in our laboratory,[9] could have reproduced IO radicals:

$$\mathrm{I + OClO \rightarrow IO + ClO}$$
$$k_{-1a} = 1.9 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{(ref 8)} \quad (-1a)$$

However, the combined values of k_{-1a} and of the concentrations of OClO and I ([OClO] = (1−3) × 10^{12} and [I] ≤ 2 × 10^{11} molecule $\mathrm{cm^{-3}}$) make the impact of this reaction negligible.

The other possible secondary reactions

$$\mathrm{IO + Cl \rightarrow I + ClO}$$
$$k_{15} = 4.4 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (15)$$

$$\mathrm{I + ClO \rightarrow products}$$
$$k_{16} \leq 1.7 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (16)$$

have been also studied recently in this laboratory.[9] Despite the high value of k_{15}, reaction 15 could not significantly consume IO because of the low concentration of Cl produced in reaction 1 and rapidly consumed in reaction 5 and also in reaction 10 in the second series of experiments. Reaction 16 is too slow to be a potential source of IO. The upper limit of k_{16} ($k_{16} \leq 1.7 \times 10^{-14}$ $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$) was obtained in our previous work[9] from monitoring the ClO temporal profiles in excess of I atoms. In the present work, the detection of IO as a possible product of reaction 16 has been attempted. For a maximum reaction time of 1.7 × 10^{-2} s and for I and ClO concentrations of 5 × 10^{13} and 1 × 10^{12} molecule $\mathrm{cm^{-3}}$ respectively, no IO could be detected (corresponding to an upper limit of 6 × 10^{9} molecule $\mathrm{cm^{-3}}$ for the IO concentration). The upper limit $k_{16} \leq 7 \times 10^{-15}$ $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$ can be derived for the IO-producing channel of reaction 16.

The reaction IO + OClO → products was also negligible within the time scale of the present experiments, which was checked by the direct monitoring of IO in the presence of an excess of OClO. The possible IO formation in the reaction

$$\mathrm{OClO + I_2 \rightarrow IO + products} \quad (17)$$

was also examined. For a reaction time of 0.035 s, and with [OClO] = 2 × 10^{14} and [I_2] = 6.4 × 10^{13} molecule $\mathrm{cm^{-3}}$, the upper limit $k_{17} \leq 2 \times 10^{-17}$ $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$ was obtained. Finally, from the lack of IO detection in the reaction

$$\mathrm{ClO + I_2 \rightarrow IO + ICl} \quad (18)$$

the upper limit $k_{18} \leq 8 \times 10^{-16}$ $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$ was determined. All these reactions could not interfere in the measurement of k_1.

In two other series of experiments, the kinetics of reaction 1 was studied using reaction 11 between Cl and Cl_2O as the source of ClO radicals. Reaction 11 took place in the movable injector, Cl_2 being introduced through inlet 1 and Cl_2O through inlet 2. IO radicals were produced from reactions 2 or 3 (the reactants being introduced into the reactor as described above). The concentrations used were [ClO] = (2.6−29.3) × 10^{12}, [CF_3I] ≈ 4 × 10^{13}, [I_2] ≈ 5 × 10^{12}, and [Cl_2O] ≤ 1 × 10^{13} molecule $\mathrm{cm^{-3}}$. The gas flow velocity in the reactor was around 2000 cm $\mathrm{s^{-1}}$. The IO consumption rates measured in these experiments are shown on the pseudo-first-order plot of Figure 4, leading to

$$k_1 = (1.0 \pm 0.15) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

The zero intercept, (22.0 ± 3.2) $\mathrm{s^{-1}}$, is in agreement with the values obtained in the two first series of experiments.

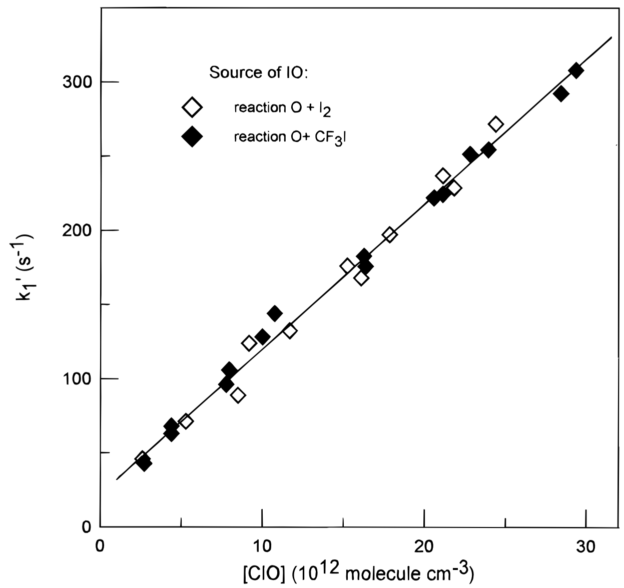

Figure 4. Pseudo-first-order plot of IO consumption in reaction 1: source of ClO, reaction Cl + Cl_2O (11); source of IO, reaction O + CF_3I (2) and reaction O + I_2 (3).

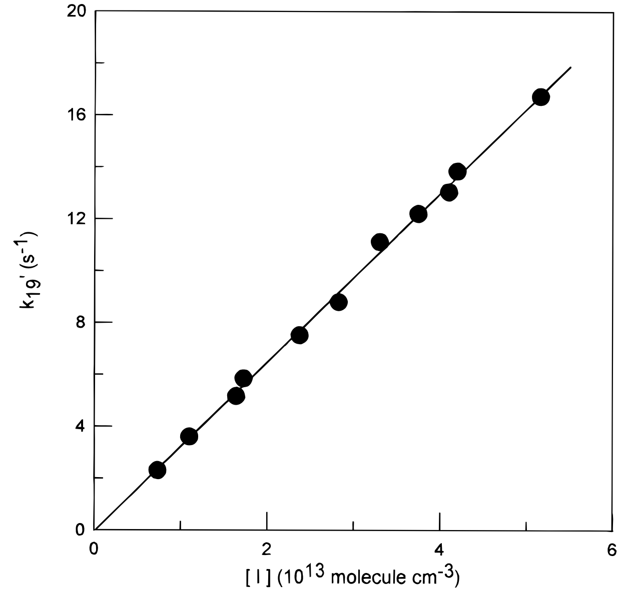

Figure 5. Reaction I + Cl_2O (19): pseudo-first-order plot of Cl_2O consumption.

Possible secondary and side reactions are reactions 15, 16, and 18, discussed above, and also reaction 19 which could generate IO radicals in channel 19a:

$$\mathrm{I + Cl_2O \rightarrow Cl_2 + IO}$$
$$\Delta H_{19a} = -(17.3 \pm 1.2)\ \mathrm{kcal\ mol^{-1}} \quad (19a)$$

This reaction was studied in independent experiments. The rate constant k_{19} was first derived from the temporal profiles of the Cl_2O concentration observed in the presence of an excess of I atoms. Iodine atoms were produced in the movable injector via reaction 6 (H_2 and I_2 being introduced through inlets 1 and 2, respectively), and Cl_2O molecule were introduced through the side-arm tube of the reactor (inlet 4). Under the following experimental conditions, [Cl_2O]$_0$ = (1−2) × 10^{12} molecule $\mathrm{cm^{-3}}$, [I]$_0$ = (0.7−5.2) × 10^{13} molecule $\mathrm{cm^{-3}}$, and flow velocity = 750 cm $\mathrm{s^{-1}}$, the obtained pseudo-first-order plot, given in Figure 5, provides the value for k_{19}:

$$k_{19} = (3.25 \pm 0.40) \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

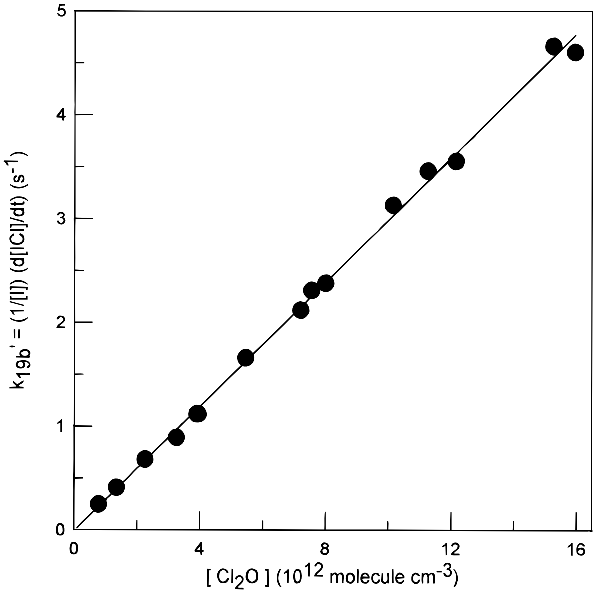

Figure 6. Reaction I + Cl_2O (19): pseudo-first-order plot of ICl formation.

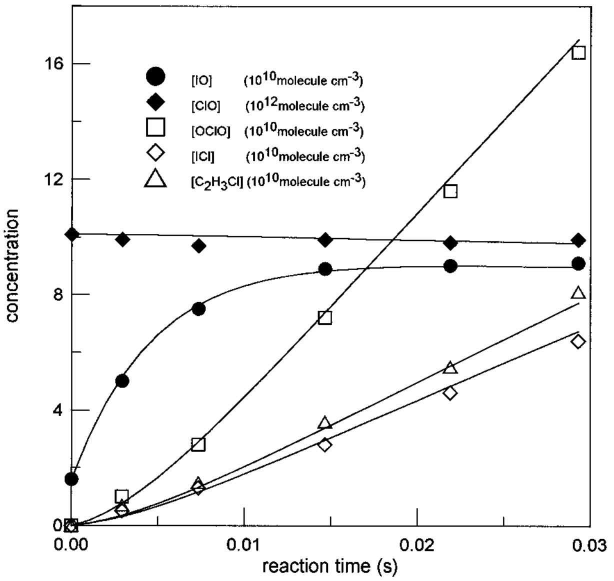

Figure 7. Reaction IO + ClO (1): example of experimental (points) and simulated (solid lines) kinetics for reactants ClO and IO and products OClO, Cl (detected as C_2H_3Cl), and ICl. Initial concentrations of reactants: $[O_3] = 4 \times 10^{13}$, $[I_2] = 5 \times 10^{12}$, $[I] = 3.9 \times 10^{11}$, and $[C_2H_3Br] = 3 \times 10^{14}$ molecule cm^{-3}. Best fit was obtained with $k_{1a} = 7.3 \times 10^{-12}$, $k_{1b} = 3.45 \times 10^{-12}$, and $k_{1c} = 2.75 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Reaction 19 possesses another thermochemically feasible channel producing ICl molecules:

$$I + Cl_2O \rightarrow ICl + ClO \qquad \Delta H_{19b} = -16 \text{ kcal mol}^{-1} \qquad (19b)$$

ICl was detected and the rate constant for the ICl formation channel was derived from the temporal profiles of ICl concentration. Using the following concentrations, $[Cl_2O]_0 = (0.8-16) \times 10^{12}$ and $[I]_0 = (0.7-1.8) \times 10^{13}$ molecule cm^{-3}, the consumption of the reactants was low (<20%) and a linear dependence of [ICl] with reaction time could be observed (according to $[ICl] = k_{19}[I][Cl_2O]t$). The results obtained from the kinetics of ICl formation for different Cl_2O concentrations are given in Figure 6, yielding the value for the rate constant of channel 19b:

$$k_{19b} = (3.0 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Comparing this value with that obtained for k_{19}, it can be concluded that reaction 19b is the major, unless unique, channel of reaction 19. These data also indicate that reaction 19 has no influence on the present measurements of k_1.

Branching Ratio Experiments. In a first approach, it appeared very difficult to determine the branching ratios of the various channels of reaction 1 by using the same experimental conditions as those described above (with ClO in excess over IO). One of the major reasons was that the sensitivity of the mass spectrometer was lower for the possible products of reaction 1 than for IO. It was not possible to obtain relatively high concentrations of IO radicals because of their fast homogeneous combination and of the heterogeneous complications (revealed by a brown deposition in the zone of IO generation when higher concentrations were attempted to be produced). Besides, important interferences could exist between the mass spectrometric signals of the precursors of ClO and IO and the signals of the expected products of reaction 1, such as OClO. Therefore, in the branching ratio experiments, the reactions of O_3 with Cl atoms (12) and I atoms (4) were used for the production of ClO and IO radicals, respectively. Cl atoms, introduced through the outer tube of the movable injector (inlet 3), were titrated with an excess of O_3 (inlet 4), forming ClO radicals. I atoms, produced in reaction 6 with H_2 and I_2 introduced through inlets 1 and 2, respectively, were introduced in the main reactor where they reacted with an excess of O_3 to form IO radicals. An example of the temporal behavior of IO radicals thus observed is shown in Figure 7. After an increase of [IO] in the first milliseconds, due to its production in reaction 4, a steady state was observed. This steady state resulted from the simultaneous IO production and consumption in reactions 4 and 1, respectively. Thus, considering the reaction zone where constant concentrations were observed for both reactants, a constant rate of formation of the products (Pr) could be expected:

$$d[Pr]/dt = k_{pr}[IO]\,[ClO] \qquad (20)$$

where k_{pr} is the partial rate constant. The absolute measurement of the individual k_{pr} implied that the calibration of each product could be made. The monitored products formed in channels 1a, 1b, and 1c were OClO, Cl, and ICl, respectively. OClO and ICl were calibrated as for the kinetics experiments. Cl atoms were rapidly converted to C_2H_3Cl after scavenging with an excess of vinyl bromide (C_2H_3Br) via reaction 9, with a typical time constant of conversion of 0.2 ms. C_2H_3Br was introduced into the reactor through inlet 2 of the movable injector (together with I_2). The concentrations of C_2H_3Br and I_2 were chosen in order (i) to make reaction 9 predominant over reactions 5 and 12 ($k_9[C_2H_3Br] \gg k_5[I_2] + k_{12}[O_3]$) and (ii) to avoid the reaction of hydrogen atoms with C_2H_3Br in the source of I atoms ($k_{21}[C_2H_3Br] \ll k_6[I_2]$):

$$H + C_2H_3Br \rightarrow \text{products}$$
$$k_{21} = 2.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 15)} \qquad (21)$$

First, it should be noted that the addition of vinyl bromide had no impact on the ionization efficiency of the mass spectrometer. Secondly, the ClO, IO, and OClO kinetics were not affected by this addition of vinyl bromide.

For the OClO-forming channel 1a, it was verified that the OClO formation from the ClO + ClO reaction was negligible under the present conditions. No OClO could be observed in the absence of IO, as one could expect from the low rate constant for this ClO + ClO reaction.[4]

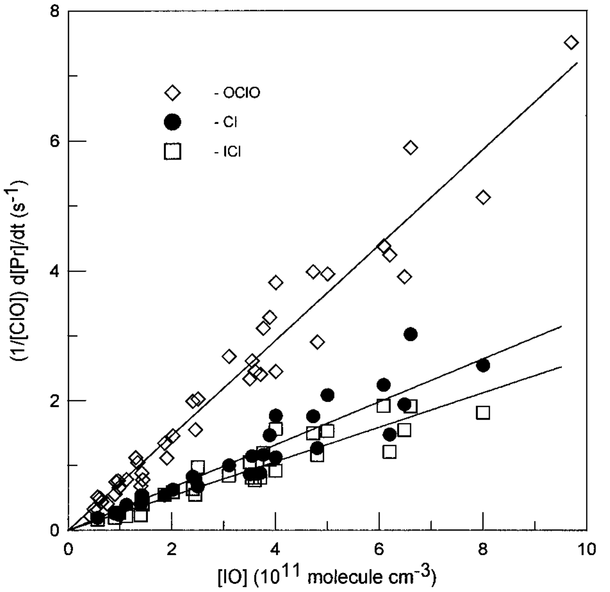

Figure 8. Reaction IO + ClO (1): pseudo-first-order rate constant of product formation as a function of IO concentration.

Together with the IO concentration−time profile, the profiles measured for ClO, OClO, Cl and ICl are shown in the example of Figure 7. In all experiments, only the parts of the plots [Pr] = *f*(*t*) corresponding to the steady state concentrations of IO ($t > 0.01$ s in Figure 7) were used for the determination of k_{pr}. This allowed for a simple analytical treatment of the experimental data according to expression 20.

The concentrations of the reactants used in these experiments were $[I_2] = (2-5) \times 10^{12}$, $[C_2H_3Br] = (3-5) \times 10^{14}$ and $[O_3] = (2-5) \times 10^{13}$ molecule cm^{-3}. The concentration of ClO radicals was varied in the range $3 \times 10^{12}-2 \times 10^{13}$ molecule cm^{-3}. The observed steady state concentration of IO (strongly depending on [O$_3$] and [I]) was in the range $3 \times 10^{10}-1.0 \times 10^{12}$ molecule cm^{-3}. The rate of formation of each product, d[Pr]/d*t*, was measured as a function of steady state ClO and IO concentrations. From the determination of the absolute concentrations of the reactants and products, the rate constant for each channel of reaction 1 could be calculated. Figure 8 shows the pseudo-first-order plots for the OClO, Cl (as C_2H_3Cl), and ICl-forming channels as a function of IO concentration. The linear least squares fits are well correlated and their slopes yield the values of the partial rate constants:

$$k_{1a} = (7.3 \pm 1.8) \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_{1b} = (3.3 \pm 0.9) \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_{1c} = (2.7 \pm 0.8) \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

(uncertainties include one standard deviation and 15% for systematic errors, mainly on the absolute concentrations of reactants and products).

Another procedure was also used for the calculation of k_{pr} consisting in a complete simulation of the chemical system (summarized in Table 1). The plotted curves shown in Figure 7 result from such modeling calculations. The best fits to experimental data provided the same values for the rate constants as those given above. The simulation calculations also confirmed the observed steady state concentration of IO, in spite of the significant radical loss arising from channel 1c producing ICl and O$_2$. This was due to the fact that IO formation in reaction 4 mainly resulted from the relatively high initial concentration of I atom (produced in the H + I$_2$ source) and not from I formed in channels 1a and 1b.

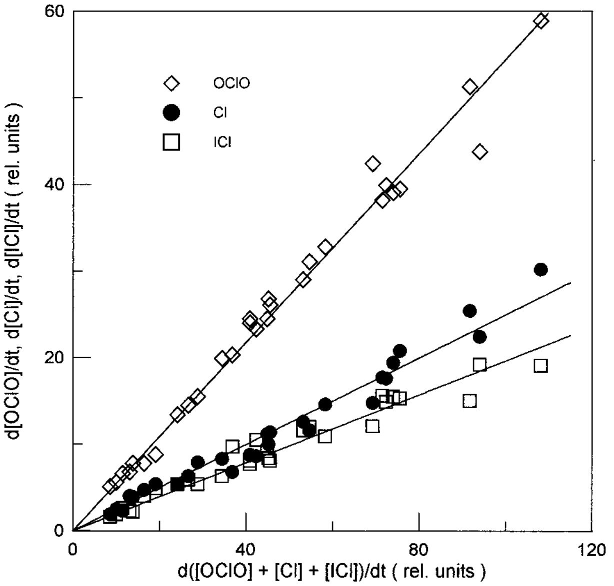

Figure 9. Reaction IO + ClO (1): formation rates of OClO, Cl, and ICl as a function of total formation rate of products (see text).

TABLE 1: Reactions Used in Modeling Calculations

no.	reaction	rate constant (cm^3 molecule^{-1} s^{-1})	reference
1a	$IO + ClO \rightarrow I + OClO$	k_{1a}, variable	
1b	$IO + ClO \rightarrow I + Cl + O_2$	k_{1b}, variable	
1c	$IO + ClO \rightarrow ICl + O_2$	k_{1c}, variable	
8	$IO + IO \rightarrow$ products	5.2×10^{-11}	4
21	$IO +$ wall $\rightarrow$ loss	14 s^{-1}	this work
4	$I + O_3 \rightarrow IO + O_2$	1.0×10^{-12}	4
−1a	$I + OClO \rightarrow IO + ClO$	1.9×10^{-13}	9
5	$Cl + I_2 \rightarrow ICl + I$	2.1×10^{-10}	9
9	$Cl + C_2H_3Br \rightarrow Br + C_2H_3Cl$	1.4×10^{-10}	12
12	$Cl + O_3 \rightarrow ClO + O_2$	1.2×10^{-11}	4
22	$Br + I_2 \rightarrow I + IBr$	1.2×10^{-10}	16

In order to reduce the experimental uncertainties arising from the measurements of the absolute concentrations, a "relative" procedure with internal calibration was adopted. Using the titration of initial concentration of Cl which was kept constant, with the successive reactants (in excess) OClO, C$_2$H$_3$Br, and I$_2$ (via reactions 10, 9, and 5, respectively), it was possible to calibrate the mass spectrometer for each product (OClO, C$_2$H$_3$Cl, ICl) as well as for the initial reactant ClO. This procedure allowed for a simplified treatment of the data, since only the relative intensities of the signal of each product (I_{pr}) were needed to be known. Thus, under fixed experimental conditions (for chosen IO and ClO concentrations and for reaction times corresponding to the stationary state of IO), the formation rates of each product dI_{pr}/d*t* was plotted as a function of the sum of the partial rates (d[OClO]/d*t* + d[Cl]/d*t* + d[ICl]/d*t*), as shown in Figure 9. The advantage of such a procedure was that the knowledge of the absolute concentrations of all reactants and products of reaction 1 was not required. It should be noted again that only the three channels 1a−c were considered to occur. The following branching ratios were obtained for these channels (errors are two standard deviations):

$$k_{1a}/k_1 = (54.5 \pm 2.6) \times 10^{-2}$$

$$k_{1b}/k_1 = (25.0 \pm 1.8) \times 10^{-2}$$

$$k_{1c}/k_1 = (19.5 \pm 1.6) \times 10^{-2}$$

Finally, it was also possible to measure independently the

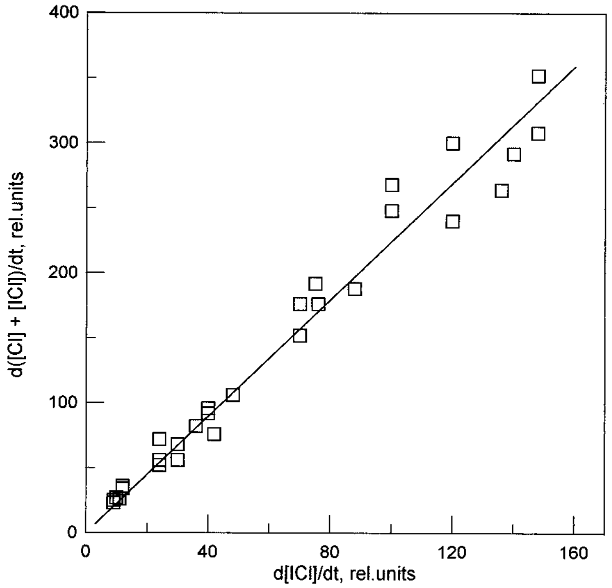

Figure 10. Reaction IO + ClO (1): sum of the rates of reactions 1b and 1c as a function of the rate of reaction 1c. The relative units are the same and correspond to ICl^+ signal intensity in the absence and in the presence of C_2H_3Br, respectively.

ratio k_{1b}/k_{1c} by monitoring the kinetics of ICl production successively in the absence and in the presence of C_2H_3Br. Since C_2H_3Br scavenged efficiently Cl atoms formed in channel 1b, provided $k_9[C_2H_3Br] \gg k_5[I_2]$, the ICl formation rate, in the presence of C_2H_3Br, was only due to channel 1c. In the absence of C_2H_3Br and with high concentration of I_2 (so that $k_5[I_2] \gg k_{12}[O_3]$), Cl atoms were converted into ICl via reaction 5:

$$Cl + I_2 \rightarrow ICl + I \tag{5}$$

In this case, the production rate of ICl was due to both channels 1b and 1c. Thus, the relative measurements of the ICl^+ ion intensity as a function of reaction time, in the absence and in the presence of C_2H_3Br allowed for the determination of the ratio $(k_{1b} + k_{1c})/k_{1c}$. With concentrations of ClO = $(1-3) \times 10^{12}$ and IO = $(0.5-6) \times 10^{11}$ molecule cm^{-3}, the data obtained are plotted in Figure 10. The slope of the straight line gives

$$(k_{1b} + k_{1c})/k_{1c} = 2.20 \pm 0.15$$

Again, no absolute calibration of any species was required. The derived value for $k_{1b}/k_{1c} = (1.20 \pm 0.15)$ is in excellent agreement with the value obtained in the previous series of experiments (1.3 ± 0.2).

Discussion

The present direct determination of the rate constant for reaction 1 at 298 K, using various precursors for IO and ClO radicals, gave values ranging from $k_1 = (1.0 \pm 0.15) \times 10^{-11}$ to $(1.2 \pm 0.2) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. In the subsequent branching ratio experiments, the rate constants were measured for the individual channels considered for reaction 1:

$$IO + ClO \rightarrow I + OClO \tag{1a}$$

$$IO + ClO \rightarrow I + Cl + O_2 \tag{1b}$$

$$IO + ClO \rightarrow ICl + O_2 \tag{1c}$$

The sum of the individual rate constants gives $k_1 = (1.33 \pm 0.35) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. The uncertainty range is larger, as expected, and makes this value in acceptable agreement with the two other determinations. However, the apparent difference can be briefly discussed. First, as described in the Experimental Section, possible secondary and side reactions have been taken into account, with the kinetic data obtained in this work and in a previous study from this laboratory.[9] It can be considered that the apparently higher value of k_1 given above could be due to the occurrence of a fourth channel:

$$IO + ClO \rightarrow Cl + OIO \tag{1d}$$

Channel 1d would have produced Cl atoms, as channel 1b, thus leading to an overestimation of k_{1b} since the measured k_{1b} would have included the k_{1d} in that case. Similarly, the value (1.20 ± 0.15) measured for k_{1b}/k_{1c} (with and without C_2H_3Br) would have corresponded to $(k_{1b} + k_{1d})/k_{1c}$. The OIO molecule formed in channel 1d could not be identified by mass spectrometry. OIO is likely very unstable and has never been observed in the laboratory, except in a recent flash photolysis study of I_2/O_3 mixture.[17] Furthermore, if OIO has been produced, it could have reacted with ClO in the present chemical system:

$$OIO + ClO \rightarrow IO + OClO \tag{22}$$

Reaction 22 would have produced OClO, in parallel to channel 1a, also leading to an overestimation of k_{1a}. In addition, reaction 22 producing IO would have led to underestimation of k_1 measured from the IO decay in the presence of excess ClO. Finally, considering the above speculative discussion and the small difference between the values of k_1 derived either from the decay rate of IO or from the formation rates of the observed products, only channels 1a−c are likely to occur and not channel 1d. Also, combining all the data obtained in this work, the recommended values for k_1 and the branching ratios of channels 1a−c are, at 298 K,

$$k_1 = (1.1 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{1a}/k_1 = (0.55 \pm 0.03)$$

$$k_{1b}/k_1 = (0.25 \pm 0.02)$$

$$k_{1c}/k_1 = (0.20 \pm 0.02)$$

These results can be compared with those obtained simultaneously in a study[5] using the pulsed laser photolysis−laser induced fluorescence technique, associated with a continuous discharge flow source for ClO radicals. The value of k_1, measured in the temperature range 200−362 K, was $k_1 = (5.1 \pm 1.7) \times 10^{-12} \exp[(280 \pm 20)/T]$ cm^3 $molecule^{-1}$ s^{-1}. The value at 298 K, $k_1 = 1.3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, is in excellent agreement with the present determination. In ref 5, the only identified products were iodine atoms, which were found to be the major product of reaction 1. The product yield for the channel forming I atoms was measured: $\Phi(I) = (0.8 \pm 0.2)$. This result is consistent with the present data, yielding for the branching ratio of two channels producing I atoms $(k_{1a} + k_{1b})/k_1 = (0.80 \pm 0.05)$, which also confirms that the OIO-forming channel 1d, if it exists, is of very minor importance.

An application of the present study is the determination of the heat of formation of IO radicals. Considering the rate constant measured in this work for channel 1a together with the rate constant of the reverse reaction (−1a) measured in our previous work[9] ($k_{-1a} = (1.90 \pm 0.25) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}), the equilibrium constant, $\ln K = (3.45 \pm 0.35)$, can be calculated for

$$IO + ClO \leftrightarrow I + OClO (1a, -1a)$$

Using the recommended values at 298 K[4] for the enthalpy of formation, for ClO (24.4), for I (25.52), and for OClO (22.6 ± 1.0) kcal mol^{-1}, and the following entropy data $S°_{298}$, for ClO (54.17), for I (43.21), for OClO (61.48), and for IO (57.12) cal K^{-1} mol^{-1} (values from ref 18 except for IO[19]), the heat of reaction 1a is $\Delta H = -(4.01 \pm 0.21)$ kcal mol^{-1}. This gives for the enthalpy of formation of IO

$$\Delta H_f(IO) = (27.7 \pm 1.2) \text{ kcal mol}^{-1}$$

In our previous paper,[9] the range for ΔH_f(IO) was found to be (25.8−27.5) kcal mol^{-1} and was compared to the most recent literature data. The value given in ref 4 ($\Delta H_f(IO) \leq 28$ kcal mol^{-1}), which agreed with this range, disagrees with a more recent determination based on the measurement of the ionization energy of IO:[20] $\Delta H_f[IO] = (31 \pm 1)$ kcal mol^{-1}. The upper limit ($\Delta H_f[IO] \leq 27.5$ kcal mol^{-1}) given in our previous study was calculated using the highest value for ΔH_f(OClO) (23.6 kcal mol^{-1}), for which a significant uncertainty exists (1 kcal mol^{-1} [4]), and the central value was about 1 kcal mol^{-1} lower than the present determination. Finally, considering all the uncertainties in these thermochemical calculations and specially on ΔH_f(OClO), the value $\Delta H_f(IO) = (27.7 \pm 1.2)$ kcal mol^{-1} from this work is preferred.

The atmospheric implications of the present kinetic data can be briefly discussed. Model calculations of stratospheric ozone depletion[1] have considered the possible contribution of iodine through cycles initiated by interhalogen reactions, especially reaction 1 between ClO and IO. Since no kinetic data were available for this reaction, the model calculations assumed that the value of k_1 was as high as 1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} and that the only formed products were I, Cl, and O_2 (channel 1b). The experimental data obtained in this study and in the simultaneous work of ref 5 differ significantly from these assumptions. First, reaction 1 has a rate constant lower by 1 order of magnitude, and our measured branching ratio for channel 1b at $T = 298$ K is $k_{1b}/k_1 = 0.25$, instead of 1 as assumed in the model calculation. Consequently, the potential impact of reaction 1 on ozone destruction should be modified.

Considering the three observed channels, the major one which produces I + OClO leads to a null cycle for ozone depletion. On the contrary, the ICl-forming channel (channel 1c) should have the same effect as channel 1b, since the ICl molecule should be readily photolyzed under sunrise conditions:

$$ICl + h\nu \rightarrow I + Cl$$

Therefore, a rate constant for the process leading to the net formation of I + Cl via reactions 1b and 1c of 5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} can be estimated, which is 20 times lower than the value assumed in ref 1. The present estimate considers that our branching ratio data obtained at $T = 298$ K are the same at the temperature of the lower stratosphere, which is a reasonable hypothesis regarding the rather low temperature dependence of k_1 measured in ref 5. Thus, the efficiency of iodine in depleting ozone, which was estimated to be more than 1000 times higher than that of chlorine in the lower stratosphere,[1] should be reevaluated as well as the relative importance of the other ozone-depleting cycles involving iodine. The other cycles are rate controlled by the IO + BrO and IO + HO_2 reactions:

$$IO + BrO \rightarrow \text{products} \quad (23)$$

$$IO + HO_2 \rightarrow \text{products} \quad (24)$$

The IO + BrO reaction has been recently investigated[5,21] and has a rate constant much higher than that of reaction 1, approaching the collision frequency: $k_{23} = 2.32 \times 10^{-11} \exp(-269/T)$ cm^3 $molecule^{-1}$ s^{-1}.[5] Although the branching ratios for the possible channels of this reaction are still uncertain, it can be assumed that the reaction will lead to the net formation of I, Br, and O_2. Concerning the IO + HO_2 reaction, two earlier kinetic studies[22,23] have also provided a high rate constant value ($k_{24} \approx 1 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} at $T = 298$ K), and the major, if not unique, reaction product HOI rapidly photodissociates to yield I and OH. Then, a rough estimate of the relative importance of the ozone depletion cycles involving iodine can be made by calculating the relative rates of reactions 1b + 1c, 23, and 24: $(k_{1b} + k_{1c})[ClO]/k_{23}[BrO]/k_{24}[HO_2]$. Using $(k_{1b} + k_{1c}) = 5 \times 10^{-12}$, $k_{23} = 1 \times 10^{-10}$, and $k_{24} = 1 \times 10^{-10}$ (cm^3 $molecule^{-1}$ s^{-1}) and the mean mixing ratios typical of the contemporary lower stratosphere, 30 pptv (ClO), 10 pptv (BrO), and 3 pptv (HO_2), the relative rates are

$$(k_{1b} + k_{1c})[ClO]/k_{23}[BrO]/k_{24}[HO_2] = 1/7/2$$

These relative rates are very different from those assumed in the model calculation of ref 1 (1/0.33/0.1), and the cycle involving the IO + ClO reaction would no more be the dominant one. Considering now the total depletion rate of O_3 by iodine cycles,

$$-d[O_3]/dt = 2[IO]((k_{1b} + k_{1c})[ClO] + k_{23}[BrO] + k_{24}[HO_2])$$

the present calculation gives a value which is about 3 times lower than that obtained in ref 1. Consequently, iodine would not be ca. 1000 times more efficient than Cl (per atom basis) to deplete ozone, but only ca. 300 times higher. This relative efficiency could even be lower if the IO + BrO reaction does not lead to a 100% net production of I + Br + O_2.

The impact of iodine on the stratospheric chemical budget remains speculative since no iodine has been observed so far in the stratosphere. An upper limit of 0.1 pptv of IO in the stratosphere has been reported recently from balloon-borne UV−visible absorption measurements.[24] Even if IO has not been firmly observed so far in the stratosphere, the possible impact of iode on stratospheric zone is still an open question since at mixing ratios as low as a few tenths of pptv iodine could still significantly deplete ozone.[1] Besides, iodine is present in the lower troposphere and the IO radical may contribute to cycles, especially those including reactions 1 and 23, which deplete ozone during the ozone loss events observed in Arctic regions (e.g., refs 2 and 3). This is supported by recent tentative in situ identification of IO by DOAS analysis.[25]

Finally, regarding the potential role that iodine can play in ozone chemistry in both the stratosphere and the troposphere, further kinetic and mechanistic data are needed for iodine reactions (especially IO + BrO) together with field data (especially IO measurements).

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