The Atmospheric Chemistry of Iodine Monoxide

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ABSTRACT

Rate constants are reported for the reactions of the iodine monoxide radical, IO, with NO,, **O,,** ClO, BrO, **O,** and itself; for the reaction of BrO with I, **O,** and itself; and the reaction of **O** with I,. **Also,** the absorption spectrum of IO is reported, including a major new region of absorption below **415** nm. These results fill in the data gaps and provide the necessary kinetic and photochemical data to allow a reliable calculation of the ozone depletion potential for CF_3I.

INTRODUCTION

The proposed use of CF_3I as a drop-in replacement for CF_3Br in fire suppression has resulted in a renewed interest in the atmospheric chemistry of iodine. Earlier studies focussed primarily on the possible role of iodine on tropospheric chemistry [1-6]. The principal effect appears to be that of altering the speciation within certain chemical families such as NO,. Largely **as** a result of DoD's interest in the use of halon replacements, attention has also been drawn to the possible **role of** iodine in stratospheric ozone depletion.[7,8]

The major loss mechanism for CF_3I, and the other alkyl iodides, is photolysis[g]

[1] $$CF_3I + hv \rightarrow CF, + I$$

In the atmosphere, the iodine atom can react with ozone to produce the iodine monoxide radical

[2] $$I + O_3 \rightarrow IO + O_2$$

Since I atoms do not readily abstract hydrogen from saturated organic compounds nor readily add to unsaturated compounds, this appears to be their major tropospheric reaction. Because of its long-wavelength absorption (see below), the product IO undergoes rapid photolysis.

[31 $IO + hv \rightarrow I + O$

and the resulting oxygen atoms will react with molecular oxygen to reform ozone. Alternatively, the IO may react with NO to form NO,

[4] $IO + NO \rightarrow I + NO,$

which is then readily photolyzed to return O atoms and thence O,.

A number of non-active reservoir iodine species can also be formed in the troposphere. The most important are HOI, formed in the reaction

[5] $IO + HO, \rightarrow HOI + O,$
and **IONO,,** formed in the reaction

[6] $IO + NO, \rightarrow IONO,$

By analogy with the better-known chlorine and bromine cycles,” iodine is expected to participate in several sets of catalytic reactions leading to the destruction of stratospheric ozone. The simplest cycle involves reaction [2] followed by either

[7a] $IO + O_3 \rightarrow I + 20,$
or
[8] $IO + O \rightarrow I + O,$

IO can also undergo self-reaction“

[9a] $IO + IO \rightarrow 21 + O,, \Delta H = -47$ kJ mol-’
[9b] $\rightarrow I + OIO$
[9c] $\rightarrow I, + O_2, \Delta H = -198$ kJ mol^{-1}

(The thermodynamic values used in these and subsequent calculations are from Stein, *et. al*[12] except for the values used for IO and **OBrO,** which were estimated by Huie and **Laszlo**.[13]**)** The role of this reaction in regenerating atomic iodine in the stratosphere, however, is undeniably quite small due to the relative low concentrations of IO throughout the atmosphere. Just as the reaction between ClO and BrO plays a very important role as a chain carrying step in catalytic ozone loss throughout the polar and mid-latitude stratosphere, however, the possible synergistic role of iodine together with chlorine and bromine must also be considered.[7,8]

[10a] $IO + ClO \rightarrow I + Cl + O_2$, AH = -4 kJ mol-’
[10b] $\rightarrow I + ClOO$, AH = -28 kJ mol-’
[10c] $\rightarrow I + OClO$, AH = -29 kJ mol-’
[10d] $\rightarrow ICl + O_2, \Delta H = -214$ kJ mol^{-1}

[11a] IO + BrO → I + Br + **O,, AH** = -37 kJ mol-'
[11b] → I + BrOO, AH = -40 kJ mol-'
[11c] →I + OBrO, AH = -19 kJ/mol
[11d] → IBr + O_2, ΔH = -215 kJ mol-'

It is important to note that the reaction channels producing two halogen atoms are exothermic, unlike the reactions of ClO with itself and with BrO for which such a channel is endothermic. It is also significant that the channels producing ICl or IBr are the most exothermic and are equivalent to the atom formation channels due to the rapid photolysis of both ICl and IBr in sunlight. The formation of thermally unstable products such as ClOO and BrOO also result in atom regeneration and ozone loss. Only the formation of OClO and OBrO result in a null cycle if their photodissociation leads to **O** + CIO (or BrO). Thus, it is likely that atomic halogen formation reaction channels will be more significant in reactions [10] and [11] than in the reactions ClO + ClO and CIO + BrO. To date, however, there is very little published data on the reaction rates for the various IO reactions that are likely to be important in describing the role of iodine chemistry in stratospheric ozone loss.

In the program being summarized here, we have investigated various reactions involving iodine monoxide which are likely to be of atmospheric importance. In this paper, we report on our results on the absorption spectrum of IO, the reaction of **$O(^3P)$** + I,, the kinetics of the self-reaction of IO and the cross-reactions of IO with ClO and BrO, and on the reactions of IO with NO,, O_3, and **$O(^3P)$**. In addition, rate constants for the self-reaction **of** BrO and the reaction of I + BrO were also obtained. Experiments were carried out both at the National Institute of Standards & Technology (NIST), by laser-flash photolysis with kinetic absorption spectrophotometry, and at the Russian Academy of Sciences **(RAS),** by a flow technique with resonance-fluorescence detection of I atoms. More complete discussions of these several investigations are to be published elsewhere and this report is intended to be only a summary of the most important results.

EXPERIMENTAL PROCEDURE

NZST The reactions were initiated by the laser-flash photolysis of N_2O at 193 nm, in the presence of **8** to 80 kPa N,.

[12] N_2O + hv → N, + $\mathbf{O^1D}$
[13] O^1D + N, → O^3P + N,

The resulting oxygen atoms are used to produce the halogen monoxide radicals through their reactions I,, Br,, or IBr

[14] $o + X_{,} \rightarrow \mathbf{XO} + X$

A IO-cm long quartz reaction cell is used. The progress of the reaction is monitored by passing light through the cell two or four times and then into two monochromators which are coupled to a transient digitizer. In this way, the temporal behavior of two wavelengths are monitored simultaneously and are subsequently treated simultaneously through a least-squares fitting routine.

RAS The flow reactor was a thermostatted 1.7-cm i.d. quartz tube, the inner surface of which had been coated with a fluorocarbon wax to reduce heterogeneous atom or radical recombination. Iodine atoms were produced by the photolysis of a dilute mixture of an alkyl iodide, typically CH_3I, in **O,.** They were introduced into the reactor either through a movable inlet, with an internal surface coated with orthophosphoric acid, or through a side-arm. The iodine atoms could be detected downstream of the reaction zone by the use of iodine-atom resonance fluorescence. Typically, iodine atom concentrations of about 2 x $10^{10}cm^{-3}$ were used. The signal was calibrated by titrating atomic oxygen with I,.

Chlorine atoms were produced by a microwave discharge in a dilute mixture of Cl_2 in He and introduced into the reactor through the moveable inlet. They were detected by chlorine-atom resonance fluorescence and the signal calibrated by titration of Cl with C_2H_6.

Iodine monoxide was produced by the fast reaction

[2] $$I + O, \rightarrow IO + O,$$

In the studies of the reactions of IO with NO, and with **O,,** I-atoms were added through the movable inlet and nitric oxide was added at the end of the reaction zone, resulting in the chain propagation reaction

[15] $$IO + NO \rightarrow I + NO,$$

This establishes a steady-state concentration of I and IO, dependent upon the relative concentrations of O_3 and NO. From this information, the change in the I concentration at the end of the reaction zone due to reaction upstream can be calculated.

The study of the reaction of CIO with IO relies on chain propagation provided by the reaction under investigation

[10] $IO + ClO \rightarrow I + \text{products}$

The production of ICl in the reaction of IO with ClO

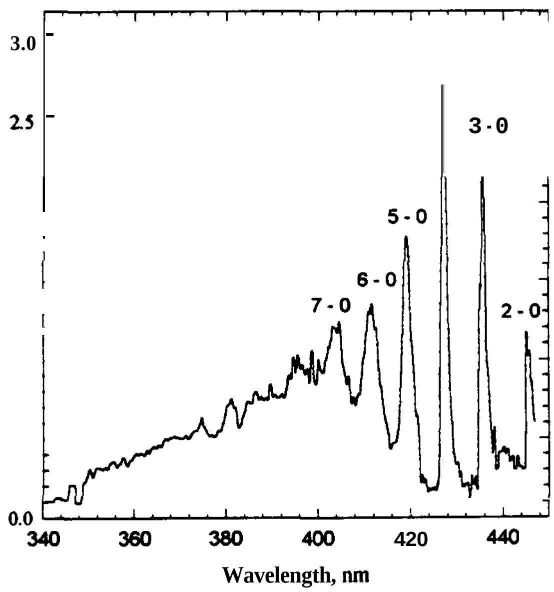
[10d] $IO + ClO \rightarrow ICl + O,$

will result in chain termination.

RESULTS

The Absorption Spectrum of IO The absorption spectrum of IO over the spectral range **340** to **435** nm was determined by the laser photolysis of a mixture of 2 Pa I, and **130** Pa **N_2O** in 27 kPa N, **(1** Torr = **133** Pa). At each wavelength, the peak IO absorbance **was** read from an average curve of 100-**1SO** laser flashes. This value, along with the

IO SPECTRUM



simultaneously measured drop of I, absorption, provided absolute absorption cross sections for IO. Due to the absorption from molecular iodine, at 435 nm and longer wavelengths absolute cross section measurements on IO could not be performed. Relative absorbances were determined using CF_3I as IO radical source in the wavelength region of 430-447 nm, however, and were scaled to the absolute measurements over the region of overlap. With the high-resolution grating in the Kratos monochromator, we could not carry out studies above 447 nm. Overlapping 20 nm wide sections were scanned with 0.6 nm steps below and with 0.3 nm steps above 400 nm. Any 1 nm part of the spectrum contains 2-7 points measured in two or more different runs. A total of 485 points were taken which were then smoothed assuming a 0.3-nm Gaussian slit function. At the absorption maximum, the (4-0) band, we find $\sigma_{427.2nm} = (2.7\pm0.5)\times10^{-17}$ cm^2, in good agreement with previous determinations.

Over the spectral region 415 to 445nm, our spectrum agrees well with that presented by Stickel, *et al.*,[14] but the agreement with the spectrum presented by Cox and Coker[15] is somewhat poorer. The various measurements of the cross section at the absorption maximum (427.2 nm) are all in good agreement with that reported here.[15,14,16,11]

Rate Constants for O + I, and O + IO In the laser photolysis of I_2/N_2O mixtures, the reaction of atomic oxygen with iodine is in competition with its reaction with the product IO. By simultaneously monitoring the formation of IO and the loss of I„ at relatively low I, concentrations, we have been able to obtain kinetic information on these reactions. The system was modeled with the set of reactions:

[16] $O + I_2 \rightarrow IO + I$
[8] $IO + O \rightarrow I + O,$
[9] $IO + IO \rightarrow$ products
[17] $I + I \rightarrow I_2$

In the fitting procedure, the rate constants for reactions [16] and [8] were allowed to vary, the rate constant for reaction [9] was taken from the analysis described below, and the rate constant for reaction [17] taken as 1.2×10^{-12} cm^3 s^{-1}, from a fit to the tail of the I_2 formation curve. A typical fit is given in Figure 2. From 8 experiments, we obtained. *k,,* = $(1.4\pm0.2)\times10^{-10}$ cm^3 s^{-1}, in excellent agreement with the previous measurement,[17] and k_8 = $(1.2\pm0.6)\times10^{-10}$ cm^3 s^{-1}. The quoted uncertainty is twice the standard deviation and probably reflects mostly the uncertainty in the I, concentration. The rate constant for the reaction of atomic oxygen with iodine monoxide is about four times greater that the previously recommended value, which was based on the rate constants for the comparable reactions of atomic oxygen with chlorine monoxide and with bromine monoxide.”

Rate Constant for IO + NO, The reaction of iodine monoxide with nitrogen dioxide was investigated by an atomic resonance fluorescence-flow technique in the presence of 130 to 800 Pa O, over the temperature interval 295 - 343 K. Iodine atoms at a concentration of $\approx2\times10^{10}$ cm^{-3} were allowed to react with ozone, which was at a concentration of $\approx1\times10^{15}$ cm^{-3} to produce iodine monoxide. Nitrogen dioxide at various concentrations were added upstream of the I-atom injector. At the very low IO concentrations employed, homogeneous self-reaction of IO was not important and the only loss processes for this radical were due to the reaction under investigation

[18] IO + NO, + O, → IONO, + O,

and by the heterogeneous decay of IO

[19] IO + wall → products

Heterogeneous interaction of IO with NO, is also possible,

[20] IO + NO, + wall → IONO, + wall

The first-order rate constant for the loss of IO is then given by:

$$k^{1st} = k_{19} + k_{18}[NO_2][O_2] + k_{20}[NO_2]$$

Experimental values of k^{1st} are plotted against [NO,] to obtain k,, as the intercept and $k_{II} = k_{18}[O_2] + k_{20}$ as the slope. Values of k„ when plotted against $[O_2]$, give k„ as the intercept and k_{18}, the desired rate constant, as the slope. Rate constants were determined at 295, 303, 323, and 343 K and the expression

$$k_{,,} = (1.80\pm0.07)\mathrm{x}10^{-31}(T/300)^{-(2.6\pm0.5)}\mathrm{cm}^6\mathrm{s}^{-1}$$

was derived (for $M=O_2$), where the error limits correspond to the 95% confidence limits. Taking into account the relative efficiencies of O,, N„ and He as third bodies in association reactions, we find that these results are in good agreement with the earlier results of Jenkin and Cox[16], but are about a factor of three slower than those of Daykin and Wine[19] and of Maguin, *et. al.*[20]

Rate Constant and Mechanism for IO + O, There are two possible reactions of IO with O,:

[7a] IO + O, → I + 20,
[7b] IO + O_3 → IO_2 + O,

These reactions were studied in the flow system by adding ≈$2\mathrm{x}10^{10}$ cm^{-3} I through a moveable inlet to a stream of oxygen containing 0.16 - $7.2\mathrm{x}10^{15}$ cm^{-3} O,. The reduction in the concentration of IO at the end of the reactor is due to reaction 7b and the heterogeneous loss of IO, reaction 17, so the first-order rate constant for IO loss is given by

$$k^{1st} = k_{11} + k_{7b}[O_3]$$

For a 40-fold change in the ozone concentration at 323 K, there was an almost imperceptible change in the decay rate for IO. From these results, we estimate $k_{7b} < 2.3\mathrm{x}10^{-16}\ \mathrm{cm}^3\mathrm{s}^{-1}$.

The rate constant for the reaction channel leading to chain propagation, reaction 7a, by determining the steady-state concentration of I atoms and IO radicals established by the pair of reactions

[2] $I + O_3 \rightarrow IO + O,$
[7a] $IO + O_3 \rightarrow I + 20,$

The ratio of these rate constants is

$$k_2/k_{7a} = [I]_o/[I]_{st} - 1$$

where [I], = [I],, + [IO],,. This ratio was found to be >1000, so that $k_{7a} < 1.2 \times 10^{-15}$ $cm^3 s^{-1}$.

Although there have been no previous reports of rate constants for the reaction of IO with **O,,** the observation that the reaction is, at best, very slow is in keeping with the pattern established by the radicals ClO and BrO, for which also only upper limits have been reported.

*Rate **Constant for** IO + IO* Rate constants for the self-reaction of IO were determined by simultaneously monitoring the absorption due to IO at 427.2 nm and that due to I, at 530 nm. In these experiments, the I, concentrations was kept above 1×10^{14} cm^{-3} so that reaction (8) could be ignored and the temporal behavior of IO described by the two reactions.

[16] $O + I, \rightarrow IO + I$
[9] $IO + IO \rightarrow$ products

Rate constants were measured at total pressures ranging from 8 to 80 kPa, I, concentrations between 1.4×10^{14} to 1.5×10^{15} cm^{-3}, and N_2O concentrations ranging from 2×10^{15} to 6.8×10^{16} cm^{-3}. The rate constant was found to be independent of these various parameters and an average value of $k,$ $= (8.0 \pm 1.7) \times 10^{-11}$ cm^3 s^{-1} was derived (the uncertainty being twice the standard deviation from 27 experiments).

Although the measured rate constant for IO decay did not depend on total pressure, the extent of reformation of I, did. The temporal behavior of I, lagged the decay of IO, indicating that the I, was not a primary product of the self-reaction of IO (reaction 9c). Rather, this behavior could be explained by a secondary reaction between iodine atoms and a product of the IO + IO reaction, or from enhanced recombination of I atoms in this photochemical system. This conclusion is supported by the results of several experiments carried out with ICl **as** a radical source, where IO is generated without appreciable concentrations of I. Subsequent to the laser photolysis of a mixture of N_2O and ICl, no ClO absorption was detected at 265 nm, indicating that at least 90% of the reaction between O atoms and ICl occurs via

[21] $O + ICl \rightarrow IO + Cl$

In this system, no I, formation was detected at 8, 27, or 80 kPa total pressure, supporting the conclusion that the self-reaction of IO is not a major direct source **of I,.**

Finally, the extent of regeneration of iodine atoms in the self-reaction of IO was briefly investigated in the flow system at relatively high (>2×10^{11} cm^{-3}) IO concentrations.

[9a] $IO + IO \rightarrow 21 + O,$

From the slope of a plot of the dependence of $[I]_{st}/[I]_o$ on $[I]_o/[O_3]$, the ratio of k_{9a}/k_2 is obtained. From this, we obtain $k_{9a} = (2.8\pm1.2)\mathrm{x}10^{-11}$ cm^3s^{-1}. The absolute accuracy of this value, however, depends on the absolute calibration of the iodine atom sensitivity and is probably even less certain than the quoted error limits, which are derived from the scatter in the data.

There have been several previous determinations of the rate constant for the self-reaction of IO: three by discharge-flow techniques and four by photolytic methods. The more recent work using a discharge-flow system with mass spectrometric detection have resulted in rate constants of 3.0 x 10^{-11} and 5.5 x 10^{-11} cm^3 s^{-1}.[21,22] In the earliest photolytic study, I was produced by the modulated photolysis of CH_3I and allowed to react with O_3.[15] A considerable amount of aerosol was observed, and a very high rate constant was reported, k = $4.0\mathrm{x}10^{-10}$ cm^3 s^{-1}. In subsequent work from the same laboratory, in which IO was produced by the photolysis of I, in the presence of O,, a lower rate constant was measured, but the reaction was observed to have both first- and second-order components, with the second-order component having pressure independent and pressure dependent parts.[16] The most thorough study of the self-reaction of IO involved the use of both the flash photolysis of I, in the presence of O_3 and the flash photolysis of O, in the presence of I_2.[11] The apparent rate constant obtained from the I + O, system exhibited a pressure dependence, increasing from 3.1 to $4.6\mathrm{x}10^{-11}$ cm^3 s^{-1} as the pressure was raised from 2.8 to 87 kPa, while the rate constant from the O + I, system exhibited no pressure dependence. The room temperature rate constant obtained in that work, k = $5.6\mathrm{x}10^{-11}$ cm^3 s^{-1}, is somewhat lower than that obtained here when N_2O was used as the oxygen atom source, but similar to the value we obtained when we used O, as the source. In a study involving the laser photolysis of I, in the presence of O_3 and laser absorption spectroscopy for the detection of IO, a rate constant of $6.6\mathrm{x}10^{-11}$ cm^3 s^{-1} was obtained at a total pressure of one atmosphere, slightly lower than that measured in the present work.[14]

Rate Constantsfor O + Br_2 and O + BrO In the laser photolysis of Br_2/N_2O mixtures, the reaction of atomic oxygen with bromine is in competition with its reaction with the product BrO. By simultaneously monitoring the formation of BrO and the loss of Br,, at relatively low Br, concentrations, we have been able to obtain kinetic information on these reactions. The system was modeled with the set of reactions:

[22] O + Br, → BrO + Br
[23] BrO + O → Br + O,
[24] BrO + BrO → products
[25] Br + Br → Br,

In the fitting procedure, the rate constants for reactions [22] and [23] were allowed to vary, the rate constant for reaction [24] was taken from the analysis described below, and the rate constant for reaction [25] taken as $5.8\mathrm{x}10^{-13}$ cm^3 s^{-1}, from a fit to the tail of the Br, formation curve. From 9 experiments, we obtained *k,* = $(1.5\pm0.3)\mathrm{x}10^{-11}$ cm^3s^{-1} and *k,* = $(3.2\pm1.3)\mathrm{x}10^{-11}$ cm^3s^{-1}. These values are in agreement with most recent studies.[23]

Rate Constantfor BrO + BrO The rate constant for the self-reaction of BrO was measured by simultaneously monitoring the absorption due to BrO at 338.3 nm and that due to Br, at 430 nm after the flash photolysis of a mixture of $Br_2/N_2O/N_2$. Under the conditions employed, the temporal behavior of the absorptions was due to the pair of reactions

[22] $O + Br_2 \rightarrow BrO + Br$
[24] $BrO + BrO \rightarrow$ products

Rate constants were derived by simultaneous fitting of these curves over the range of conditions: $[Br_2] = 1\text{-}10\times10^{15}$ cm^{-3} and $[N_2O] = 2\text{-}15\times10^{16}$ cm^{-3}, all at a total pressure of 27 kPa in N_2. The rate constant and cross section were found to be independent of these parameters and average values of $k_{24} = (2.8\pm0.1)\times10^{-12}$ cm^3s^{-1} and $\sigma_{338.3nm} = (1.4\pm0.2)\times10^{-17}$ cm^2 were derived, both of which are in very good agreement with the most recent recommendations.[18]

Rate Constants for IO + BrO and I + BrO The cross reaction between IO and BrO was investigated by the laser photolysis of a mixture of $Br_2/I_2/N_2O$ in N_2 followed by simultaneously monitoring the temporal behavior of the IO and BrO absorptions. The BrO signal decayed in a normal manner; the behavior of the IO signal, however, was more complex. After an initial decay, the signal increased and then decreased. We have concluded that this is due to the rapid reaction of I atoms, produced both in the flash and in the reaction of O with I_2, with BrO. We have simultaneously modelled the temporal behavior of these signals with the set of reactions:

[24] $BrO + BrO \rightarrow$ products
[9] $IO + IO \rightarrow$ products
[11] $IO + BrO \rightarrow$ products
[26] $I + BrO \rightarrow IO + Br$

The solid line through the data points represents the least-squares fit. Rate constants were measured at a total pressure of 27 kPa, I_2 concentrations between $3 - 50\times10^{13}$ cm^{-3}, Br_2 concentrations between $1\text{-}3\times10^{15}$ cm^{-3}, and N_2O concentrations of $2\text{-}10\times10^{16}$ cm^{-3}. The rate constant was found to be independent of the halogen concentrations over this range and an average value of $k_{11} = (6.9\pm2.7) \times 10^{-11}$ cm^3 s^{-1} and $k_{26} = (1.2\pm0.6)\times10^{-11}$ cm^3s^{-1} were derived (the uncertainty being twice the standard deviation from 18 experiments).

Some experiments were also carried out with IBr as a source of the halogen monoxides.

[27a] $O + IBr \rightarrow IO + Br$ (74%)
[27b] $O + IBr \rightarrow I + BrO$ (26%)

The fits to the experimental data generated in these experiments were generally not as good as those obtained in the I_2/Br_2 system and the derived rate constants were significantly different. A detailed analysis led to the conclusion that this system was not mathematically well behaved. The mathematical surface sampled by the least-squares minimization does not have a well defined minimum, but, rather, has a trough so that a range of rate constants would satisfy the minimization criteria. A similar investigation of the I_2/Br_2 system showed a well defined minimum. It appears that the problem in the IBr system arises from the much higher relative IO concentration which results from the branching ratio for the generation reaction.

The Rate Constant and Mechanism for IO + *ClO* The cross reaction between IO and ClO was investigated in a flow reactor with a fixed source of I atoms and a movable source of Cl atoms. In the initial work, the I atoms were produced by the photolysis of CH_3I and Cl atoms were produced by a microwave discharge in a dilute mixture of Cl_2 in He. The reaction

[28] $$Cl + CH_3I \rightarrow I + CH_3Cl$$

made CH_3I an unsatisfactory source at low O, concentrations, however, and it was replaced by C_3F_7I. (In some experiments, reaction [28] was used to probe subsequent Cl production.) CIO and IO were produced by reaction of the halogen atoms with O,. In the presence of excess ClO, steady-state concentrations of IO and I are established by the pair of reactions:

[2] $$I + O_3 \rightarrow IO + O,$$
[1Oa-c] $$IO + ClO \rightarrow I + \text{products}$$

If we assume that there are no chain termination steps, then the ratio of the initial concentration of I atoms, [I],, to the steady-state concentration, [I],,, is given by:

$$[I]_o/[I]_{st} = k_2[O_3]/k_{10a-c}[ClO] + 1$$

Experiments were carried out with [O,] > $4x10^{14}$ cm^{-3}, [I], ≈ $3x10^{10}$ cm^{-3}, and [Cl] = [ClO] = $1\text{-}10x10^{12}$ cm^{-3}. The results indicated that either there was a significant contribution from the chain-termination reaction [1Od]

[10d] $$IO + ClO \rightarrow ICl + O,$$

or the overall reaction was primarily heterogeneous, taking place on the walls of the reactor. We were able to exclude the heterogeneous reaction and establish the magnitude of the chain-termination step by investigating the magnitude of the iodine-atom signal as a function of the contact time. From the combination of the dependence of the steady-state concentration of I on [ClO] and [O,] and the dependence of I on contact time, we obtained $k_{,,}$ = $(1.2\pm0.35)x10^{-11}$ cm^3s^{-1} and $k_{10a-c} = (4.9\pm0.2)x10^{-11}$ cm^3s^{-1}, for a total rate constant of k_{10} = $(6.1\pm0.6)x10^{-11}$ cm^3s^{-1}.

In addition to the studies on the reaction of IO with ClO carried out on the flow system, we also briefly investigated this reaction by laser photolysis-absorption spectrophotometry. Experiments were carried out in which IO and CIO were generated by reaction of O with a mixture of I, and Cl_2 or by reaction of O with a mixture of ICl and ClO_2. In both cases, a significant amount of aerosol formation was observed, rendering any kinetic analysis difficult. From these experiments, all we are able do is confirm the flow system observation that the reaction is very fast.

DISCUSSION

In Table I, we present a summary of all the kinetic results obtained in this project. These results confirm the assumption that was made in the initial modelling study:' that the key reactions of IO with the other halogen oxides are very fast; the reaction of IO with O is even faster than previously thought. All of these reactions are important in the possible role of iodine in ozone depletion. On the other hand, the reaction of IO with O_3 is very slow, as expected, so that this reaction will not play a role in ozone depletion. Apparently, the reaction of I with BrO was not included in the model.

Also of importance in understanding the role of iodine in the atmosphere is our extended absorption spectrum for IO. The inclusion of the previously undetected absorption below **415** nm increases the rate of photodissociation from **0.18** s^{-1} to **0.28** s^{-1}. This photolysis rate means an atmospheric photolytic lifetime of **3.7** s at 40° solar zenith angle, considerably shorter than published values and suggests that photolysis is the dominant loss process for IO during daytime in the troposphere.

The actual impact of the tropospheric release of iodinated compounds such as CF_3I on stratospheric ozone is mitigated by their short tropospheric lifetime, due to photodissociation.[9] The kinetic data presented here should allow more complete modelling studies to establish clearly any possible effect of these compounds.

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Table I. Summary of results.

Reaction	Rate Constant
$O + I_2 \rightarrow IO + I$	$k_{298K} = (1.4 \pm 0.2) \times 10^{-10}$ cm^3 s^{-1}
a) $O + IO \rightarrow I + O_2$	$k_{298K} = (1.2 \pm 0.6) \times 10^{-10}$ cm^3 s^{-1}
$IO + NO_2 + O_2 \rightarrow IONO_2 + O_2$	$k = (1.80 \pm 0.07) \times 10^{-31} (T/300)^{-(2.6 \pm 0.5)}$ cm^6 s^{-1}
a) $IO + O_3 \rightarrow I + 2O_2$	$k_{292K} < 1.2 \times 10^{-15}$ cm^3 s^{-1}
a) $IO + O_3 \rightarrow IO_2 + O_2$	$k_{323K} < 2.3 \times 10^{-16}$ cm^3 s^{-1}
$IO + IO \rightarrow$ products	$k_{298K} = (8.0 \pm 1.7) \times 10^{-11}$ cm^3 s^{-1}
$IO + IO \rightarrow 2I + O_2$	$k_{298K} = (2.8 \pm 1.2) \times 10^{-11}$ cm^3 s^{-1}
$O + Br_2 \rightarrow BrO + Br$	$k_{298K} = (1.5 \pm 0.3) \times 10^{-11}$ cm^3 s^{-1}
$O + BrO \rightarrow Br + O_2$	$k_{298K} = (3.2 \pm 1.3) \times 10^{-11}$ cm^3 s^{-1}
$BrO + BrO \rightarrow$ products	$k_{298K} = (2.8 \pm 0.1) \times 10^{-12}$ cm^3 s^{-1}
b) $I + BrO \rightarrow IO + Br$	$k_{298K} = (1.2 \pm 0.6) \times 10^{-11}$ cm^3 s^{-1}
a) $IO + BrO \rightarrow$ products	$k_{298K} = (6.9 \pm 2.7) \times 10^{-11}$ cm^3 s^{-1}
a) $IO + ClO \rightarrow I +$ products	$k_{298K} = (4.9 \pm 0.2) \times 10^{-11}$ cm^3 s^{-1}
a) $IO + ClO \rightarrow ICl + O_2$	$k_{298K} = (1.2 \pm 0.35) \times 10^{-11}$ cm^{3}s^{-1}

a) - Included in ozone depletion mechanism -- rate constant not previously determined.

b) - Suggested for consideration for inclusion in ozone depletion mechanism.

REFERENCES

(1) Zafiriou, O. C. *J. Geophys. Res.* **1974,** *79,* 2730.
(2) Chameides, W. L.; Davis, D. D. *J. Geophys. Res.* **1980,** *85,* 7383.
(3) Chatfield, R. B.; Crutzen, P. J. *J. Geophys. Res.* **1990,** *95,* 22319.
(4) Jenkin, M. E.; Cox, R. A.; Candeland, D. E. *J. Atmos. Chem.* **1985,** *2,* 359.
(5) Barnes, I.; Bonsang, B.; Brauers, T.; Carlier, P.; Cox, R. A.; Dorn, H. P.; Jenkin, M. E.; Le Bras, G.; Platt, U. "Air Pollution research Report," OCENO-NOX-CEC Project, 1991.
(6) Jenkin, M. E. A ***comparative assesment of the role of iodine photochemistry in tropospheric ozone depletion;*** Jenkin, M. E., Ed.; Springer-Verlag: Berlin, 1993; Vol. NATO-AS1 series no. 17.
(7) Solomon, S.; Burkholder, J. B.; Ravishankara, A. R.; Garcia, R. R. *J. Geophys. Res.* **1994,** *99,* 20929.
(8) Solomon, S.; Garcia, R. R.; Ravishankara, A. R. *J. Geophys. Res.* **1994,** *99,* 20491.
(9) **Fahr,** A.; Nayak, A. K.; Huie, R. E. ***Ultraviolet absorption spectrum of CF_3I***; Halon Options Technical Conference: Albuquerque, NM, 1994, pp 465.
(10) Wayne, R. P. ***The chemistry of atmospheres;*** Clarendon Press: Oxford, 1991.
(11) Sander, S. P. *J. Phys. Chem.* **1986,** *90,* 2194.
(12) Stein, S. E.; Rukkers, J. M.; Brown, R. M. ***NIST Structures & Properties Database;*** ver. 1.2; Stein, S. E.; Rukkers, J. M.; Brown, R. M.; NIST, 1991.
(13) Huie, R. E.; Laszlo, B. ***Advances in Chemistry Series*** **1994,** ***in press.***
(14) Stickel, R. E.; Hynes, A. J.; Bradshaw, J. D.; Chameides, W. L.; Davis, D. D. *J. Phys. Chem.* **1988,** *92,* 1862.
(15) Cox, R. A.; Coker, G. B. *J. Phys. Chem.* **1983,** *87,* 4478.
(16) Jenkin, M. E.; **Cox,** R. **A.** *J. Phys. Chem.* **1985,** *89,* 192.
(17) Ray, G. W.; Watson, R. T. *J. Phys. Chem.* **1981,** *85,* 2955.
(18) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. ***JPL Publication 94-26*** **1994,** ***Evaluation 11.***
(19) Daykin, E. P.; Wine, P. H. *J. Phys. Chem.* **1990,** *94,* 4528.
(20) Maguin, F.; Laverdet, G.; Le Bras, G.; Poulet, G. *J. Phys. Chem.* **1992,** *96,* 1775.
(21) Martin, D.; Jourdain, J. L.; Laverdet, G.; Le Bras, G. *Znt. J. Chem. Kinet.* **1987,** *19,* 503.
(22) Barnes, I.; Bastian, **V.**; Becker, K. H.; Overath, R. D. *Int. J. Chem. Kinet.* **1991,** *23,* 579.
(23) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref: Data* **1992,** *21,* 1125.