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Kinetics of Halogen Oxide Radicals in the Stratosphere

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Contents

1. Introduction

Halogen oxide radicals have been the subject of numerous investigations, beginning long before their atmospheric significance was recognized. The existence of the ClO radical was first suggested in the 1920s by Bodenstein and co-workers, following studies of the photosensitized decomposition of gaseous Cl_2O.[1,2] It was one of the first indirect evidences that a transient species, namely ClO, was involved in the chemistry of this decomposition. Later, the identification of ClO was demonstrated in flame studies by Pannetier and Gaydon in 1948,[3] and in photolysis studies by Porter et al. in the 1950s,[4,5] where ClO radicals were clearly detected from their characteristic banded absorption spectra. At the same time, in both laboratories of Porter's and Thrush's groups, the studies on ClO radicals initiated the development of one of the most powerful kinetic methods, the flash-photolysis method.

The atmospheric importance of ClO radicals was first suggested by Stolarski and Cicerone[6] and by Molina and Rowland,[7] as a consequence of the use of the chlorofluorocarbons (CFCs), which provide an efficient source of chlorine atoms in the stratosphere, leading to the well-known problem of ozone destruction. More generally, halogenated source gases containing X atoms (with X = F, Cl, Br, or I) are able to release X atoms in the atmosphere, at a place which depends both on the chemical lifetime of the source gases and on the dynamical atmospheric processes that may affect these source gases. Thus, one may anticipate that the atmospheric impact of these halogenated gases will be highly variable from one X to another (ref 8 and references therein). Following the release of X atoms, XO radicals are formed in the atmosphere from the fast reaction with ozone: $X + O_3 \rightarrow XO + O_2$. XO radicals may then be involved in a number of multistep cycles that lead to ozone depletion.

The main objective of this article is to make clear the need for additional studies on halogen oxides radicals, and particularly on gas-phase reactions involving XO radicals. Section 2 contains a brief review of the current state of knowledge of the role of XO radicals in the atmosphere, mainly in the stratosphere. In section 3, the most recent kinetic data of XO reactions are reviewed and discussed in relation to their potential role in stratospheric chemistry. The present review is based on previous evaluations[9−11] as well as on a well-documented review published by Wayne et al. in 1995.[12] More attention has been given to the studies that appeared after the NASA evaluation of 1997,[9] since in the more recent NASA evaluation[10] the data on XO reactions were not re-evaluated. The most recent evaluation of the XO kinetics was done by IUPAC in 2000.[11] However, considering that stratospheric models generally use the NASA kinetic database, the NASA evaluation of 1997[9] has been taken as a reference in

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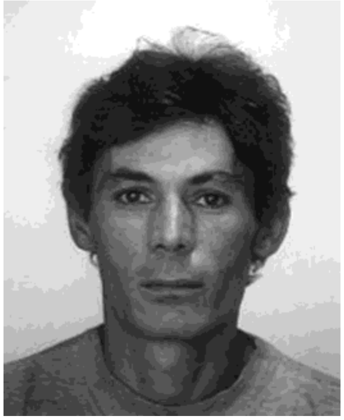
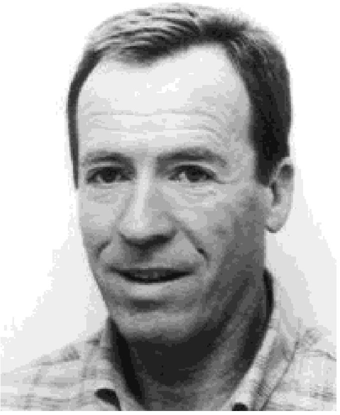


Yuri Bedjanian received his B.S. in physics from the Yerevan State University (Armenia) in 1982. He completed his Ph.D. degree in 1987 at the Institute of Chemical Physics, Russia, Moscow, in the laboratory of Yulii Gershenzon, working on the kinetics of elementary and chain-branched reactions of NF_2 radicals. His introduction to atmospheric chemistry (study of the elementary reactions of FO and FO_2 radicals) came during work as a postdoctoral fellow at the Institute of Chemical Physics in Moscow and as a Senior Research Scientist at the Institute of Chemical Physics in Yerevan. In 1994, Yuri Bedjanian joined CNRS as Associated Scientist (Staff Research Scientist from 1998). His current research focuses on experimental study of gas-phase and heterogeneous reactions of atmospheric importance.



Gilles Poulet received his Ph.D. in physical chemistry in 1979. His research activities are mainly related to stratospheric chemistry. He performed kinetic studies on a number of radical reactions of atmospheric interest at LCSR (Laboratoire de Chimie de la Combustion et des Systèmes Réactifs, CNRS, Orleans). He is currently Professor of Chemistry at Orleans University and research leader at LPCE (Laboratoire de Physique et Chimie de l'Environnement, CNRS, Orleans). His group is using mass spectrometric techniques for laboratory studies related to the reactivity of atmospheric trace gases and to their in situ measurements.

this review for comparison with newly appeared results. While the recent progress and gaps in kinetic databases are outlined, a critical analysis of the existing data and recommendations for use in stratospheric modeling are not in the scope of this review.Additionally, the mechanisms of the halogen reactions are not discussed in detail, considering that theoretical speculations are not necessary in this review dedicated to the atmospheric community.

2. Halogen Oxide Radicals in the Stratosphere

XO radicals (X = F, Cl, Br, I) result from the atmospheric degradation of halogenated source gases in all parts of the atmosphere. In the case of fluorine, catalytic cycles involving F atoms are not efficient in destroying ozone, since F atoms are very efficiently converted (via reactions with CH_4 and H_2O) to HF, which is removed from the stratosphere via deposition/rain-out. Ozone destruction cycles involving fluorine-containing radicals have been suggested:

$$\begin{array}{ll} & RO + O_3 \rightarrow RO_2 + O_2 \\ & \underline{RO_2 + O_3 \rightarrow RO + 2O_2} \\ \text{Net:} & 2O_3 \rightarrow 3O_2 \end{array}$$

where R = F,[13] CF_3,[14,15] and FC(O).[16] The efficiencies of these cycles strongly depend on the rates of the chain propagation reactions of RO and RO_2 with O_3 relative to the rates of the sink reactions of these radicals. Experimental studies of the reactions of RO and RO_2 (R = F, CF_3, FC(O)) with ozone[10,17,18] have shown that these reactions are too slow compared with the sink of the radicals (mainly via RO + NO) and, therefore, these ozone destruction cycles have no significance in the stratosphere.[18,19] In the following, the role of the other XO radicals in the stratosphere is briefly summarized.

2.1. Stratospheric Chemistry and Halogen Oxide Radicals

It is well established that the Chapman mechanism,[20] which is based on oxygen chemistry only, cannot explain the ozone concentration observed in the stratosphere. Various chemical cycles participate to the loss of "odd" oxygen ($O + O_3$), where the active species Y and YO act as catalysts. The Y and YO species are interconverted, leading to the following general scheme:

$$\begin{array}{ll} & Y + O_3 \rightarrow YO + O_2 \\ & \underline{YO + O \rightarrow Y + O_2} \\ \text{Net:} & O + O_3 \rightarrow O_2 + O_2 \end{array}$$

Y and YO can refer to HO_x (OH and HO_2), NO_x (NO and NO_2), or halogen (Cl and ClO, Br and BrO) species. Other ozone destruction cycles exist, with the interplay of Y and YO from different families. The relative importance of each cycle depends on the individual sources and sinks of the active species and is highly variable with altitude. Due to the significant increase of halogen source gases in the atmosphere, mainly due to the CFCs, a downward trend of ozone in the stratosphere has been observed during the past decades.[8]

2.1.1. Chlorine Chemistry (Global Stratosphere)

In the case of the chlorine cycle, the interconversion of Cl and ClO in the mid-latitude stratosphere occurs mainly through the ozone-destroying cycle:

$$\begin{array}{ll} & Cl + O_3 \rightarrow ClO + O_2 \\ & ClO + O \rightarrow Cl + O_2 \\ \hline \text{Net:} & O + O_3 \rightarrow O_2 + O_2 \end{array}$$

However, this interconversion may also occur via other pathways, in which species from other families are involved, such as

$$ClO + NO \rightarrow Cl + NO_2$$

or (in two steps)

$$ClO + HO_2 \rightarrow HOCl + O_2$$

$$HOCl + h\nu \rightarrow OH + Cl$$

Some of the resulting cycles are called “null cycles”, since they may not lead to ozone loss. For example,

$$\begin{array}{ll} & Cl + O_3 \rightarrow ClO + O_2 \\ & ClO + NO \rightarrow Cl + NO_2 \\ & NO_2 + h\nu \rightarrow NO + O \\ & O + O_2 + M \rightarrow O_3 + M \\ \hline \text{Net:} & O_3 \rightarrow O_3 \end{array}$$

ClO is by far the most abundant active halogen species: the ratio [ClO]/[Cl] is typically around 5000 in the mid-latitude lower stratosphere. In the termination steps of catalytic ozone destruction cycles, the active species can be transformed to more stable forms called reservoirs. Thus, Cl and ClO are transformed into the reservoir species HCl and $ClONO_2$, respectively. HCl is produced in various reactions of Cl with hydrogen-containing species, mainly with methane,

$$Cl + CH_4 \rightarrow HCl + CH_3$$

whereas chlorine nitrate, $ClONO_2$, is produced by

$$ClO + NO_2 + M \rightarrow ClONO_2 + M$$

HCl is a relatively stable reservoir, with a lifetime (around 1 month in the lower stratosphere) that is governed by its reaction with OH, which reproduces Cl atoms:

$$HCl + OH \rightarrow Cl + H_2O$$

$ClONO_2$ possesses a much shorter lifetime (on the order of hours), as a consequence of its photolysis:

$$\begin{aligned} ClONO_2 + h\nu &\rightarrow Cl + NO_3 \\ &\rightarrow ClO + NO_2 \end{aligned}$$

Heterogeneous reactions are of major importance in the stratosphere, since they are determining steps in the redistribution of the species within the nitrogen oxides and halogen families. In the global lower stratosphere, such reactions involve hydrolysis occurring on the surfaces of ice (a major component of cirrus clouds) or of the aqueous sulfate aerosols (of volcanic origin):

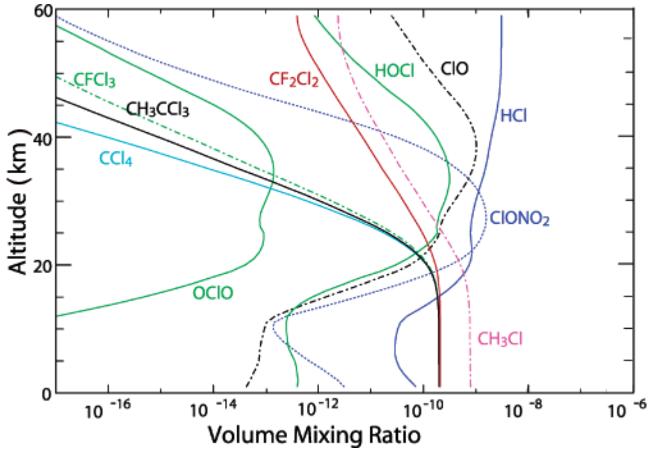


Figure 1. Volume mixing ratio profiles of chlorine species calculated by a 1D model (at noon) (unpublished data provided by Prof. Michel Pirre).

$$N_2O_5 + H_2O(s) \rightarrow 2HNO_3(s)$$

$$ClONO_2 + H_2O(s) \rightarrow HOCl + HNO_3(s)$$

As a consequence of both homogeneous and heterogeneous processes, the abundance of chlorine species in the stratosphere is variable and strongly dependent on the altitude.

In the mid-latitude stratosphere, the HCl reservoir is the most abundant chlorine species, together with the $ClONO_2$ reservoir, which maximizes around 30 km. The mixing ratios for ClO radicals which are important around 40 km at mid-latitudes have been measured by various techniques (see section 2.2). A typical mean distribution of ClO and other chlorine species, including the source gases, is shown in Figure 1.

2.1.2. Bromine Chemistry (Global Stratosphere)

The general scheme for the stratospheric chemistry of bromine is basically similar to that of chlorine. However, there are major differences. The first difference is the very low efficiency of the conversion of Br to HBr (compared to that of Cl to HCl), since HBr is not formed in the Br + CH_4 reaction, which is 17.4 kcal mol^{-1} endothermic. HBr is only produced in reactions of Br with species present at very low concentrations (such as H_2CO or HO_2). Furthermore, HBr is rapidly converted back to Br via its rapid reaction with OH radicals. The alternate bromine reservoir, $BrONO_2$ (formed by the reaction of BrO with NO_2), is also less stable than $ClONO_2$, which is partly due to a more efficient photolysis. The decreased lifetimes of the reservoir species have a large impact on the chain length of the bromine-initiated catalytic ozone destruction cycles.

Another difference between bromine and chlorine resides in the relative importance of the catalytic ozone depletion cycles. For bromine, ozone destruction cycles which couple the chemistry of other families are preponderant. Three examples are the following:

$$\begin{aligned}
\text{Cycle I:}\quad & \mathrm{BrO + HO_2 \rightarrow HOBr + O_2} \\
& \mathrm{HOBr} + h\nu \rightarrow \mathrm{OH + Br} \\
& \mathrm{OH + O_3 \rightarrow HO_2 + O_2} \\
& \underline{\mathrm{Br + O_3 \rightarrow BrO + O_2}} \\
\text{Net:}\quad & \mathrm{2O_3 \rightarrow 3O_2}
\end{aligned}$$

$$\begin{aligned}
\text{Cycle II:}\quad & \mathrm{BrO + NO_2 + M \rightarrow BrONO_2 + M} \\
& \mathrm{BrONO_2} + h\nu \rightarrow \mathrm{Br + NO_3} \\
& \mathrm{NO_3} + h\nu \rightarrow \mathrm{NO + O_2} \\
& \mathrm{NO + O_3 \rightarrow NO_2 + O_2} \\
& \underline{\mathrm{Br + O_3 \rightarrow BrO + O_2}} \\
\text{Net:}\quad & \mathrm{2O_3 \rightarrow 3O_2}
\end{aligned}$$

$$\begin{aligned}
\text{Cycle III:}\quad & \mathrm{BrO + ClO \rightarrow Br + Cl + O_2} \\
& (\text{or } \mathrm{BrCl + O_2} \text{ followed by: } \mathrm{BrCl} + h\nu \rightarrow \mathrm{Br + Cl}) \\
& \mathrm{Cl + O_3 \rightarrow ClO + O_2} \\
& \underline{\mathrm{Br + O_3 \rightarrow BrO + O_2}} \\
\text{Net:}\quad & \mathrm{2O_3 \rightarrow 3O_2}
\end{aligned}$$

The reaction between BrO and ClO leads to another channel producing OClO (often considered as a bromine marker), which leads to a “null cycle” as a consequence of OClO photolysis:

$$\begin{aligned}
& \mathrm{BrO + ClO \rightarrow Br + OClO} \\
& \mathrm{OClO} + h\nu \rightarrow \mathrm{O + ClO} \\
& \mathrm{O + O_2 + M \rightarrow O_3 + M} \\
& \underline{\mathrm{Br + O_3 \rightarrow BrO + O_2}} \\
\text{Net:}\quad & \mathrm{O_3 \rightarrow O_3}
\end{aligned}$$

Like for chlorine, bromine reservoirs participate in heterogeneous reactions on stratospheric aerosols, but again with major differences. Important reactions are

$$\mathrm{BrONO_2 + H_2O \rightarrow HOBr + HNO_3}$$

$$\mathrm{HOBr + HCl \rightarrow BrCl + H_2O}$$

The first reaction is much faster than the hydrolysis reaction of chlorine nitrate and has been shown to be a potential source of OH radicals, produced by HOBr photolysis.

The specificities of bromine chemistry lead to an efficiency of bromine in depleting ozone which is much higher than that of chlorine. The relative efficiency for ozone destruction on a per atom basis (Br/Cl) is currently estimated to lie between 40 and 50. However, bromine is much less abundant than chlorine in the atmosphere: the content of bromine and chlorine in the 2003 atmosphere is ca. 25 ppt and 3.7 ppb, respectively. The measurements of bromine in the stratosphere are more difficult than for chlorine and, except for some scarce values or upper limits for HBr and HOBr, only BrO is measured on a routine basis (see section 2.2). As expected from the specific chemistry of bromine, the active form BrO is the major bromine species measured in the stratosphere. Thus, BrO may represent up to 70% of the total stratospheric bromine during daytime.[21]

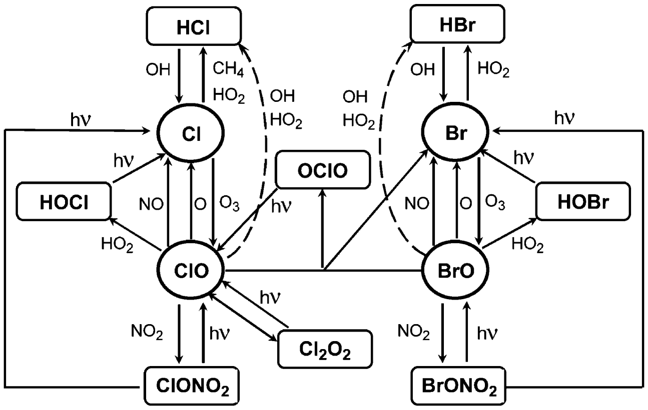


Figure 2. Gas-phase transformation pathways of chlorine and bromine in the stratosphere.

BrO radicals have been also observed recently in the upper troposphere[22] at levels up to 2 ppt, which are higher than expected in this atmospheric region. A possible explanation is the occurrence of an activation mechanism based on heterogeneous processes converting bromine reservoirs into BrO. Another (or simultaneous) cause could be the presence of very short-lived bromine species in the upper troposphere–lower stratosphere (UT–LS). Indeed, recent model calculations have shown that bromine species of short local lifetimes (typically 10–20 days), such as bromoform ($CHBr_3$) or *n*-propyl bromide ($CH_3CH_2CH_2Br$), could contribute to the inorganic bromine budget in the UT–LS, even if their surface concentration is as low as a few ppt.[8] Such a conclusion is based on the existence of very efficient dynamical processes from the boundary layer to the stratosphere, particularly in the tropics, leading to a very rapid vertical transport of these very short-lived species.

To illustrate the central role of both ClO and BrO radicals in the chemistry of the global stratosphere, the major gas-phase transformation pathways of chlorine and bromine are shown in Figure 2. The question of whether this chemistry is truly well established, particularly for bromine, may arise from the recent measurements of relatively high concentrations of OBrO in the night-time stratosphere.[23] The stratospheric halogen chemistry, which is briefly summarized above, cannot explain these observations which need to be confirmed. Similarly, uncertainties still exist at low temperatures on the formation of OClO in the presence of NO_x.[24]

2.1.3. Iodine Chemistry (Global Stratosphere)

Iodine chemistry is not as well understood as that of chlorine and bromine. As a consequence of the very short lifetime (a few days or much less) of volatile alkyl iodides of marine origin (CH_3I, C_2H_5I, CH_2I_2, etc.), iodine may enter the stratosphere only if a sufficiently fast transport exists, which may occur in a similar way as for short-lived bromine species. The formation of IO radicals, followed by its recycling through reactions with HO_2, ClO, and BrO, would lead to the following ozone depletion cycles:

$$\begin{array}{ll} \text{Cycle IV:} & IO + HO_2 \rightarrow HOI + O_2 \\ & HOI + h\nu \rightarrow OH + I \\ & OH + O_3 \rightarrow HO_2 + O_2 \\ & \underline{I + O_3 \rightarrow IO + O_2} \\ & \text{Net: } 2O_3 \rightarrow 3O_2 \end{array}$$

$$\begin{array}{ll} \text{Cycle V:} & IO + XO \rightarrow I + X + O_2 \\ & \qquad (\text{with } X = Br \text{ or } Cl) \\ & (\text{or } IX + O_2 \text{ followed by } IX + h\nu \rightarrow I + X) \\ & I + O_3 \rightarrow IO + O_2 \\ & \underline{X + O_3 \rightarrow XO + O_2} \\ \text{Net:} & 2O_3 \rightarrow 3O_2 \end{array}$$

Similarly to the situations with chlorine and bromine, heterogeneous processes may take place on stratospheric aerosols. Besides, photolysis is a very efficient process for the iodine reservoirs. Finally, inorganic iodine would be partitioned in the stratosphere among I, IO, HI, HOI, and $IONO_2$, with ca. 90% of iodine present as IO radicals.

The first estimate of the ozone removal efficiency by iodine of ca. 1000 compared to chlorine[25] has been re-evaluated on the basis of recent laboratory studies of iodine chemistry. The efficiency factor is currently estimated to range between 150 and 300, higher than that for bromine but still uncertain as a consequence of the lack of knowledge both on the photochemistry of the OIO species and on the heterogeneous reactions of the iodine reservoirs which may reproduce active iodine.

Due to their rapid photolysis, the iodine source gases, mainly the iodoalkanes such as CH_3I of marine origin, have very short local lifetimes (from a few hours to a few days) and very low surface concentrations (lower than 1 ppt). Therefore, even if these compounds could reach the UT−LS, the stratospheric concentration of iodine would be very low. The measurements of iodine species in the stratosphere are very rare, and only column measurements of IO exist, leading to estimated ranges from less than 0.05 ppt to 0.7 ppt.[26−28]

2.1.4. Halogen Chemistry in the Polar Stratosphere

The two major catalytic cycles, also involving halogen oxide radicals ClO and BrO, which are responsible for ozone destruction in the polar stratosphere are

$$\begin{array}{ll} \text{Cycle VI:} & ClO + ClO + M \rightarrow ClOOCl + M \\ & ClOOCl + h\nu \rightarrow 2Cl + O_2 \\ & \underline{2(Cl + O_3 \rightarrow ClO + O_2)} \\ \text{Net:} & 2O_3 \rightarrow 3O_2 \end{array}$$

The second cycle is due to the interaction of chlorine and bromine and has been given above for global bromine chemistry (cycle III). The occurrence of these two cycles results from the elevated level of ClO radicals which prevail in the polar vortex. This is explained by the heterogeneous activation of chlorine in the presence of various types of polar stratospheric clouds (PSCs) that form at the low temperatures of the polar stratosphere during night-time (below ca. 195 K). The main chlorine heterogeneous reactions are

$$ClONO_2 + H_2O(s) \rightarrow HOCl + HNO_3(s)$$

$$ClONO_2 + HCl(s) \rightarrow Cl_2 + HNO_3(s)$$

$$HOCl + HCl(s) \rightarrow Cl_2 + H_2O(s)$$

Due to the simultaneous denitrification of the stratosphere, these reactions lead to the formation of unstable chlorine reservoirs which readily photodissociate during polar springtime. As a consequence, a rapid buildup of ClO radicals and a simultaneous decrease of $ClONO_2$ and HCl are observed. ClO radicals undergo a self-combination which, at the low temperatures of the polar stratosphere, leads to the formation of the ClO dimer, ClOOCl, and to the ozone destruction cycle (cycle VI). This cycle is predominant in the Antarctic stratosphere. Recent observations of BrO in the winter Arctic vortex, together with model calculations,[14] would suggest that the bromine cycle (cycle III) could be as important as cycle VI for ozone loss in the Arctic stratosphere. More generally, as a consequence of the current leveling-off of total atmospheric chlorine, it is expected that the relative contribution of bromine in polar ozone destruction will increase compared to that of chlorine in the next decade.

2.2. Halogen Oxide Measurements

The rate of stratospheric ozone destruction by halogen oxide radicals can be expressed as the product of the rate coefficients for the reactions involved in the catalytic cycles and of the concentrations of the species participating in these reactions. Thus, calculations of ozone loss rates can be based on the measurements of halogen oxide radicals. This approach has often been used, for example, to calculate the rate of destruction of ozone in the polar stratosphere, by constraining the calculations by the amounts of ClO observed both in Antarctica[29−31] and in the Arctic.[33−36] Such calculations also provide a method for the validation of the kinetic parameters of the rate-determining steps in the destruction

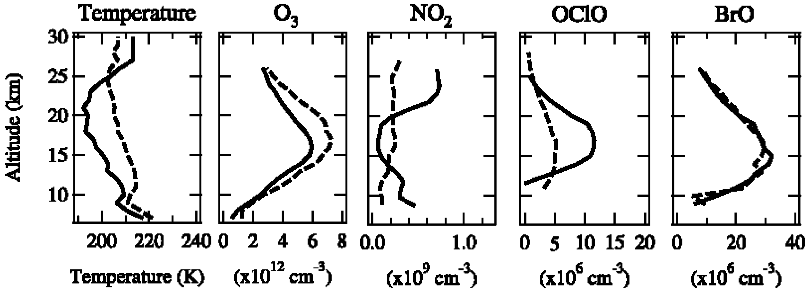


Figure 3. Vertical profiles in the Arctic vortex for temperature and concentration of O_3, NO_2, OClO, and BrO measured by the balloon-borne SAOZ instrument during cold winter (full lines) and warm winter (dotted lines). Reproduced with permission from ref 30. Copyright 2002 American Geophysical Union.

cycles. This has been the case for the reaction ClO + ClO + M → Cl_2O_2 + M, which has been reinvestigated in recent kinetic studies (see section 3.3). This reaction, together with the thermal decomposition of Cl_2O_2, describes the decrease of ClO radicals observed in the polar vortex.[36,37]

Another example of ClO reactions is the measurement of the ClO/HCl ratio in the upper stratosphere, from which a branching ratio of a few percent can be inferred for the HCl formation channel in the OH + ClO reaction (see section 3.5.1). Similar examples can be given for bromine: a very low branching ratio (of 1% or less) for the HBr formation in the BrO + HO_x reactions has a major impact on the calculated stratospheric HBr abundance (see sections 3.5.1 and 3.5.2). The episodes of low levels of ozone in the low tropospheric boundary layer, observed in recent years at different locations, are linked with the enhancements of BrO radicals which have also been measured and which are explained by multiphase chemistry involving sea salt (Barrie and Platt, this review). Such observations also provide a tool for testing the reaction rates involving BrO radicals. In the stratosphere, BrO measurements are sometimes associated with the OClO ones (e.g., ref 38) since these two species are strongly coupled, as shown in the bromine chemistry described above (cycle III). All these measurements of XO radicals may also constrain model calculations under many atmospheric conditions.

Various techniques have been used to measure XO radicals, either in the atmosphere or in the laboratory. Absorption spectroscopy in the UV and visible is a basic tool for the detection of XO radicals. This technique was used in the first laboratory studies that detected XO, as mentioned in the introduction. From ClO to IO, there is a shift in the absorption spectra: For ClO radicals, the absorption spectra are strongly banded between 300 and 270 nm and become continuous at shorter wavelengths. For BrO, the absorption bands peak between 330 and 340 nm, whereas for IO they lie around 430 nm. Absorption spectroscopy has been also widely used to detect XO radicals in the atmosphere. It has been applied to both ClO and BrO in a number of satellite-, balloon-, and aircraft-borne remote sensing instruments developed in the past decade (e.g., ref 39). As an example, Figure 3 shows the BrO profiles, together with profiles of other species (including OClO), which have been observed in the Arctic vortex by the balloon-borne SAOZ instrument,[40] which is based on the UV−visible solar occultation technique.

For IO radicals, similar absorption techniques have provided upper limits for IO concentration from column measurements.[26−28]

Other types of spectroscopy have been employed for the detection of both ClO and BrO, since the spectra of these radicals possess characteristic features in the infrared, far-infrared and microwave regions. These techniques have been applied for in situ and remote sounding of the stratosphere, as shown by recent examples for ClO[41] and BrO.[42]

In situ measurements of ClO and BrO have been also obtained by using an indirect method, based on the chemical conversion of ClO or BrO into Cl or Br, respectively (using the reaction with NO), and on the subsequent measurement of the halogen atom resonance fluorescence. This method, pioneered by Brune and Anderson[43] and since used by other groups (e.g., ref 44), has been very useful for the general understanding of the role of halogen in stratospheric chemistry.

In the laboratory, additional techniques have been used for the detection of XO radicals (electron impact and chemical ionization mass spectrometry, magnetic resonance, REMPI, cavity ring-down spectroscopy). They all have been described in the previous XO review,[12] and some of them will be referred to in section 3 of this article.

3. Kinetics and Mechanism of Halogen Oxide Reactions of Stratospheric Importance

This section is not intended to give an exhaustive review on the kinetics of XO radicals or to make a new data compilation, but rather to report comparative data including the results of most recent studies and existing evaluations. Although the chemistry of FO radicals is known not to be important in the stratosphere, the kinetic data on these species are included for comparison.

The following list gives the abbreviations of the experimental methods and techniques which have been employed in the laboratory studies of XO reactions:

CIMS, chemical ionization mass spectrometry; CRDS, cavity ring-down spectroscopy; CL, chemiluminescence; DF, discharge flow; DTF, discharge turbulent flow; EPR, electron paramagnetic resonance; FP, flash photolysis; FTIR, Fourier transform infrared; LIF, laser-induced fluorescence; LMR, laser magnetic resonance; MM, molecular modulation; MS, electron impact ionization mass spectrometry; LFP,

Table 1. Reactions $X + O_3 \rightarrow XO + O_2$: Summary of the Kinetic Data

			k (10^{-11} cm^3 molecule^{-1} s^{-1})	
reference	technique	T (K)	$k(T)$	k(298 K)
		$F + O_3 \rightarrow FO + O_2$		
DeMore et al., 1997[9]	evaluation	200−300	$2.2 \times \exp(-230 \pm 200/T)$	1.0 ± 0.4
		$Cl + O_3 \rightarrow ClO + O_2$		
DeMore et al., 1997[9]	evaluation	200−300	$2.9 \times \exp(-260 \pm 100/T)$	1.2 ± 0.2
		$Br + O_3 \rightarrow BrO + O_2$		
DeMore et al., 1997[9]	evaluation	200−300	$1.7 \times \exp(-800 \pm 200/T)$	0.12 ± 0.02
		$I + O_3 \rightarrow IO + O_2$		
DeMore et al., 1997[9]	evaluation	200−300	$2.3 \times \exp(-870 \pm 200/T)$	0.12 ± 0.02
Hölscher et al., 1998[45]	LFP/LIF	243−295	$1.6 \times \exp(-750 \pm 194/T)$	0.12 ± 0.01
Atkinson et al., 2000[11]	evaluation	230−370	$1.9 \times \exp(-830 \pm 150/T)$	0.12 ± 0.02

laser flash photolysis; RF, resonance fluorescence; TDLA, tunable diode laser absorption; VisA, visible absorption; UVA, ultraviolet absorption.

3.1. Reactions of Halogen Atoms with Ozone

Reactions of halogen atoms with O_3,

$$F + O_3 \rightarrow FO + O_2 \qquad \Delta H = -27\ \text{kcal mol}^{-1}$$

$$Cl + O_3 \rightarrow ClO + O_2 \qquad \Delta H = -38.8\ \text{kcal mol}^{-1}$$

$$Br + O_3 \rightarrow BrO + O_2 \qquad \Delta H = -32.3\ \text{kcal mol}^{-1}$$

$$I + O_3 \rightarrow IO + O_2 \qquad \Delta H = -31.2\ \text{kcal mol}^{-1}$$

are the sources of XO radicals in the atmosphere (enthalpy data used are from ref 11). They have been the subject of numerous laboratory investigations. The available kinetic data have been evaluated by DeMore et al.[9] (Table 1). A recent study of the $I + O_3$ reaction by Hölscher et al.[45] agrees with the recommended value.[9,11]

It appears that all the Arrhenius expressions for the $X + O_3$ reactions have similar pre-exponential factors and activation energies for F and Cl reactions and for Br and I reactions. The kinetics of these reactions are not determined by their exothermicities but are rather driven by the variation of the electronic energies during the approach of the reactants.[45]

3.2. Reactions of XO Radicals with O

The reactions of XO radicals with O atoms regenerate the active halogen atoms:

$$O + XO \rightarrow O_2 + X$$

The termolecular association channels (which would form XO_2 or OXO) are negligible. The O + XO reaction plays an important role (at least in the case of ClO) in determining the stratospheric ozone budget and its trend during the two past decades. The kinetic data for O + XO reactions are shown in Table 2. Reactions of O with FO and BrO radicals have been investigated only once each, respectively by Bedzhanyan et al.[46] and Thorn et al.[47] A recent study of the O + ClO reaction by Goldfarb et al.[48] supports the recommendation of DeMore et al.[9] Three relatively recent studies of the O + IO reaction at room temperature[49−51] have found a high value for the rate constant and are in satisfactory agreement with each other. High reactivity is observed for all O + XO reactions, indicating that the activation barriers are very low or even nonexistent. The data of Table 2 indicate a slight trend in reactivity, the rate constant increasing along the series X = F, Cl, Br and I.

3.3. Self-Reactions of Halogen Oxide Radicals

Among the self-reactions of XO radicals, the reaction of ClO with ClO is the most important for atmospheric implications, as it is central to the ozone depleting cycle (cycle VI) in the polar stratosphere (see section 2.1.4). The BrO + BrO and IO + IO reactions (as well as the ClO + ClO reaction out of the polar vortex) are slow compared to the reactions of these radicals with other atmospheric species, which is due to the low concentrations found for the radicals in the atmosphere. The available kinetic data for XO + XO reactions have been evaluated by De More et al.[9] and Sander et al.[10] (where only the ClO + ClO + M reaction was re-evaluated). Theses reactions possess various channels:

$$XO + XO \rightarrow X + X + O_2 \qquad \text{(a)}$$

$$\rightarrow X + OXO \qquad \text{(b)}$$

$$\rightarrow X_2 + O_2 \qquad \text{(c)}$$

$$\xrightarrow{(+M)} X_2O_2 \qquad \text{(d)}$$

Channel (a) could be written as a two-step reaction, the primary products being X and XOO.

Table 3 shows the rate constant data for the possible bimolecular channels of the self-reactions of XO (X = F, Cl, Br) radicals. It should be noted that somewhat different results have been obtained for channels (a) and (c) of the BrO + BrO reaction at low temperatures ($T \approx 220$ K) in a recent study of this reaction.[53] The IO + IO reaction has been intensively studied during the past few years (Table 4). The room-temperature value of the total rate constant seems to be well established: $k = (8-10) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Recent results obtained by Bloss et al.[60] support the temperature-independent value of the rate constant measured by Harwood et al.[57] rather than the earlier data of Sander.[54] It should be noted that all the temperature-dependent

Table 2. Reactions $O + XO \rightarrow X + O_2$: Summary of the Measurements of the Rate Constant

			k (10^{-11} cm^{3}molecule^{-1}s^{-1})	
reference	technique	T (K)	$k(T)$	k(298 K)
$O + FO \rightarrow F + O_2$				
Bedzhanyan et al., 1993[46]	DF/LMR	298		2.7 ± 0.2
$O + ClO \rightarrow Cl + O_2$				
DeMore et al., 1997[9]	evaluation	200–300	$3.0 \times \exp(70 \pm 70/T)$	3.8 ± 0.8
Goldfarb et al., 2001[48]	DF/LFP/RF	227–362	$3.0 \times \exp(75 \pm 40/T)$	3.9 ± 0.6
$O + BrO \rightarrow Br + O_2$				
Thorn et al., 1995[47]	LFP/RF	231–328	$1.9 \times \exp(230 \pm 150/T)$	4.1 ± 0.6
$O + IO \rightarrow I + O_2$				
Laszlo et al., 1995[49]	LFP/UVA	295		12 ± 5
Payne et al., 1998[50]	DF/MS	298		15 ± 7
Canosa-Mas et al., 1999[51]	DF/RF/CL	296		13.5 ± 1.5

Table 3. Reactions $XO + XO \rightarrow$ Products: Kinetic Data for Bimolecular Channels[a]

$XO + XO$	(a) $X + XOO$ (or $2X + O_2$)	(b) $OXO + X$	(c) $X_2 + O_2$	reference
$FO + FO$	$1.0 \times 10^{-11}(T/300)^{0.85}$		$<3 \times 10^{-14}$	Bedzhanyan et al., 1993[52]
$ClO + ClO$	$3.0 \times 10^{-11} \exp(-2450/T)$	$3.5 \times 10^{-13} \exp(-1370/T)$	$1.0 \times 10^{-12} \exp(-1590/T)$	DeMore et al., 1997[9]
$BrO + BrO$	$2.4 \times 10^{-12} \exp(40/T)$		$2.8 \times 10^{-14} \exp(860/T)$	DeMore et al., 1997[9]

[a] Rate constants are in cm^3 molecule^{-1} s^{-1} units.

Table 4. Reaction $IO + IO \rightarrow$ Products: Summary of the Measurements of the Rate Constant

				k (10^{-11} cm^3 molecule^{-1} s^{-1})	
reference	technique	pressure (Torr)	T (K)	$k(T)$	k(298 K)
Sander, 1986[54]	FP/UVA	20–700	250–373	$0.17 \times \exp(1020 \pm 200/T)$	5.6 ± 1.2
Martin et al., 1987[55]	DF/MS	1	298		3.0 ± 0.5
Barnes et al., 1991[56]	DF/MS	1–5	298		5.5 ± 0.8
Laszlo et al., 1995[49]	LFP/UVA	60–610	295		8.0 ± 1.8
Harwood et al., 1997[57]	LFP/UVA	610	250–320	9.9 ± 1.5	9.9 ± 1.5
Atkinson et al., 1999[58]	LFP/CRDS	9.4–30.1	295		10 ± 3
Ingham et al., 2000[59]	LFP/UVA/RF	60	295		9.0 ± 1.7
Bloss et al., 2001[60]	LFP/UVA	100–760	222–325	$4.1 \times \exp(220 \pm 230/T)$	8.2 ± 1.0
Vipond et al., 2002[61]	DF/RF	1.9–2.2	296		9.3 ± 1.0

Table 5. Reactions $XO + XO \rightarrow$ Products: Branching Ratio for Bimolecular Channels (Low Pressure, $T = 298$ K)

$XO + XO$	(a) $X + XOO$ (or $2X + O_2$)	(b) $X + OXO$	(c) $X_2 + O_2$	reference
$FO + FO$	~1.0	negligible	negligible	Bedzhanyan et al.,1993[52]
$ClO + ClO$	0.21	0.5	0.29	DeMore et al., 1997[9]
$BrO + BrO$	0.85	negligible	0.15	DeMore et al., 1997[9]
$IO + IO$	0.56	0.44	negligible	Vipond et al., 2002[61]

studies of the IO + IO reaction were carried out using the UV absorption technique, where the reaction rate constant is directly related to the temperature-dependent cross sections of IO radicals, σ(IO). The results from the three studies are in a reasonable agreement when the different temperature trends in σ(IO) are considered.[60] The measurement of the temperature dependence of the rate constant of the IO + IO reaction employing another IO detection method, independent of absorption cross sections, is desirable.

Laboratory studies have demonstrated that ClO, BrO, and IO self-reactions also exhibit a termolecular association channel. The Cl_2O_2 dimer formation channel is predominant at pressures ≥10 Torr.[9] Recently, Bloss et al.[62] have carried out a detailed kinetic study of the dimerization of ClO radicals and have measured the reaction rate constant at low temperatures (183–245 K). For temperatures lower than 200 K, the rate coefficient was found to be up to 40% faster than the value extrapolated from previous results. Evidence for a similar behavior has been found by Harwood et al.[53] for the BrO self-reaction. However, it has been shown that the BrOOBr dimer is much less stable than ClOOCl and that the bimolecular channels of the BrO self-reaction dominate, even at low temperatures. Bloss et al.[60] have identified I_2O_2 as a major product of the IO self-reaction under ambient conditions (branching ratio of 0.42–0.55 at $T = 295$ K and $P = 600$ Torr). Earlier, the invariance of the total rate constant of the IO + IO reaction, measured in the presence and in the absence of ozone in the reactive system, was considered as evidence that the I_2O_2-forming channel is a dominant reaction pathway.[54,57]

Table 6. Reactions IO + XO → Products (X = Br, Cl): Summary of the Measurements of the Rate Constants

reference	technique	pressure (Torr)	T (K)	k (10^{-11} cm^3 molecule^{-1} s^{-1})	
				$k(T)$	k(298 K)
		IO + ClO → Products			
Turnipseed et al., 1997[63]	DF/LFP/UVA/LIF	5−16	200−362	$0.51 \times \exp(280 \pm 80/T)$	1.3 ± 0.3
Bedjanian et al., 1997[64]	DF/MS	1	298		1.1 ± 0.2
		IO + BrO → Products			
Laszlo et al., 1997[67]	LFP/UVA	200	295		6.9 ± 2.7
Gilles et al., 1997[68]	DF/LFP/UVA/LIF	6−15	204−368	$2.5 \times \exp(260 \pm 100/T)^a$	6.05 ± 0.57^a
Bedjanian et al., 1998[65]	DF/MS	1	298		8.5 ± 1.5
Rowley et al., 2001[66]	LFP/UVA	100−760	210−333	$0.67 \times \exp(760 \pm 30/T)$	8.5 ± 1.4

[a] Non-I-forming channel (see text).

The branching ratios for the bimolecular channels (at low pressure and room temperature) of the XO + XO reactions are presented in Table 5. Channel (a) appears to be the dominant one and decreases along the series X = F, Br, and I. That is not the case for the ClO + ClO reaction, for which reaction pathway (a) is endothermic by 3.7 kcal mol^{-1}.

3.4. Inter-Halogen Oxide Reactions

BrO + ClO Reaction. This reaction is the most intensively studied among the cross reactions of XO radicals. This is due to its importance in stratospheric ozone chemistry (see section 2.1). The kinetic and mechanistic data seem to be well established, and the rate constants recommended for the three reaction pathways are[10] (in cm^3 molecule^{-1} s^{-1})

$$\mathrm{BrO + ClO \rightarrow Br + OClO} \qquad 9.5 \times 10^{-13} \exp(550 \pm 150/T)$$

$$\rightarrow \mathrm{Br + ClOO} \qquad 2.3 \times 10^{-12} \exp(260 \pm 150/T)$$

$$\rightarrow \mathrm{BrCl + O_2} \qquad 4.1 \times 10^{-13} \exp(290 \pm 150/T)$$

However, mechanistic data at low temperatures are still required for this important reaction, which is considered so far as the unique source of OClO in the stratosphere.

IO + ClO Reaction. This reaction has been investigated in two complementary studies.[63,64] Turnipseed et al.[63] have measured the temperature dependence of the rate constant (see Table 6), whereas Bedjanian et al.[64] have performed a detailed mechanistic study of the reaction at room temperature. The quantitative detection of the reaction products OClO, Cl, and ICl allowed for the determination of the branching ratios for the channels producing I + OClO, I + Cl + O$_2$, and ICl + O$_2$:[64]

$$\mathrm{IO + ClO \rightarrow I + OClO} \qquad k_a/k = 0.55 \pm 0.03 \qquad \text{(a)}$$

$$\rightarrow \mathrm{I + Cl + O_2} \qquad k_b/k = 0.25 \pm 0.02 \qquad \text{(b)}$$

$$\rightarrow \mathrm{ICl + O_2} \qquad k_c/k = 0.20 \pm 0.02 \qquad \text{(c)}$$

$$\rightarrow \mathrm{Cl + OIO} \qquad \text{(d)}$$

Although no evidence has been found for the OIO-forming channel (d), its existence cannot be completely excluded. These mechanistic data are in good agreement with the findings of Turnipseed et al.,[63] who measured branching ratios of 0.8 ± 0.2 and 0.14 ± 0.04 for the sum of iodine atom-forming channels (a + b) and nonforming channels (c + d), respectively. Despite this apparent good agreement, additional experiments are needed, especially to determine the branching ratios for the different reaction pathways at the low temperatures of the stratosphere.

IO + BrO Reaction. Bedjanian et al.[65] have performed a detailed mechanistic study of this reaction, leading to the following branching ratios at room temperature:

$$\mathrm{IO + BrO \rightarrow Br + OIO} \qquad k_a/k = 0.65{-}1.0 \qquad \text{(a)}$$

$$\rightarrow \mathrm{I + Br + O_2} \qquad k_b/k < 0.3 \qquad \text{(b)}$$

$$\rightarrow \mathrm{I + OBrO} \qquad k_c/k < 0.2 \qquad \text{(c)}$$

$$\rightarrow \mathrm{IBr + O_2} \qquad k_d/k < 0.05 \qquad \text{(d)}$$

$$\xrightarrow{(+M)} \text{adduct (IOOBr)} \qquad \text{(e)}$$

Using a different approach, an upper limit of 0.3 was also determined for the total branching ratio of the iodine atom-forming channels (b + c). These results have been confirmed by the study by Rowley et al.,[66] where OIO was detected as a product, whereas no evidence was found for the formation of either OBrO ($k_c/k < 0.15$) or IBr ($k_d/k < 0.2$). In addition, no evidence has been observed for the addition channel (e).[66]

The kinetic data for this reaction are summarized in Table 6. The Arrhenius expression obtained by Gilles et al.[68] corresponds to the rate constant of the non-iodine atom-producing channels of the reaction. Gilles et al.[68] have also given an upper limit of 0.35 for the I atom-producing channels, leading to an upper limit of 1.0×10^{-10} cm^3 molecule^{-1} s^{-1} for the total rate constant at 298 K. The room-temperature values of the rate coefficients from all studies are in good agreement. However, at low temperature the values measured by Gilles et al.[68] (for the non-I-forming channels) and Rowley et al.[66] (for the total rate constant) differ significantly, by up to a factor of 3 near 210 K. Rowley et al.[66] have considered this as an indication of a decrease of the branching ratio for the non-I atom-forming channels with decreasing temperature and invoked the possibility that the I + Br + O$_2$ channel (b) could dominate at low temperature. Clearly, this possibility should be verified by additional studies, including the measurements of the temperature dependence of the total rate

Table 7. Reaction ClO + OH → Products: Summary of the Measurements of the Rate Constant

				k (10^{-11} cm^3 molecule^{-1} s^{-1})	
reference	technique	pressure (Torr)	T (K)	$k(T)$	k(298 K)
Leu and Lin, 1979[73]	DF/RF	2−3	298		0.91 ± 0.26
Ravishankara et al., 1983[74]	DF/RF	1	248−335	1.17 ± 0.33	1.17 ± 0.33
Burrows et al., 1984[75]	DF/RF	1−5	243−298	1.19 ± 0.09	1.19 ± 0.09
Hills and Howard, 1984[76]	DF/LMR	1	219−373	$0.8 \times \exp(235 \pm 46/T)$	1.75 ± 0.31
Poulet et al., 1986[77]	DF/LIF/MS	0.5−0.9	298		1.94 ± 0.38
Lipson et al., 1997[78]	DTF/CIMS	100	205−298	$0.55 \times \exp(292 \pm 72/T)$	1.46 ± 0.23
Kegley-Owen et al., 1999[79]	DF/UVA&LFP/LIF	4.2−15.4	234−356	$0.89 \times \exp(295 \pm 95/T)$	2.40 ± 0.63
Bedjanian et al., 2001[80]	DF/MS	1	230−360	$0.67 \times \exp(360 \pm 70/T)$	2.2 ± 0.4
Wang and Keyser, 2001[81]	DF/UVA/RF	1	218−298	$0.72 \times \exp(333 \pm 70/T)$	2.22 ± 0.33

Table 8. Reaction ClO + OH → HCl + O_2 (b): Rate Constant and Branching Ratio Data

				k_b (10^{-13} cm^3 molecule^{-1} s^{-1})		
reference	technique	pressure (Torr)	T (K)	$k_b(T)$	k_b(298 K)	k_b/k(298 K)
Lipson et al., 1999[82]	DTF/CIMS	100−200	207−298	$3.2 \times \exp(325 \pm 60/T)$	9.5 ± 1.6	0.043 ± 0.010[a]
Wang and Keyser, 2001[83]	DF/RF/IR/UVA	1	218−298			0.090 ± 0.048
Bedjanian et al., 2001[80]	DF/MS	1	230−320	$0.97 \times \exp(600 \pm 120/T)$	7.3 ± 2.2	0.033 ± 0.011[a]
Tyndall et al., 2002[84]	LFP/TDLA	30−40	297		12.5 ± 4.5	0.057 ± 0.022[a]

[a] Calculated with $k_{total}(298\ K) = (2.2 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

constant as well as the direct determination of the reaction products at low temperature.

3.5. Reactions of XO with HO$_x$ Radicals

3.5.1. OH Reactions

ClO + OH Reaction. The reaction of OH with ClO,

$$\mathrm{OH} + \mathrm{ClO} \rightarrow \mathrm{Cl} + \mathrm{HO_2} \qquad \Delta H = -1.8 \pm 0.4 \text{ kcal mol}^{-1} \quad \text{(a)}$$

$$\rightarrow \mathrm{HCl} + \mathrm{O_2} \qquad \Delta H = -55.8 \pm 0.4 \text{ kcal mol}^{-1} \quad \text{(b)}$$

plays an important role in the partitioning of chlorine between its active forms and reservoir species in the upper stratosphere. Until recently, one of the unresolved questions in stratospheric chlorine chemistry was that of why models failed to reproduce the measured HCl concentration profiles in the upper stratosphere. The underestimated calculated concentration could be explained by a missing HCl source in the models. In this respect, the minor channel (b) of reaction between OH and ClO radicals has been proposed as an additional source of HCl in the stratosphere.[69] It has been shown that a branching ratio of a few percent for the HCl-forming channel (b) would reconcile model calculations and HCl measurements.[70−72]

All data for the overall reaction rate constant are presented in Table 7. One can note the excellent agreement between the results of the latest three temperature-dependent studies,[79−81] even though they were obtained with different experimental techniques and various sources for the reactants. An unweighted fit to the rate constant data from these studies gives the following Arrhenius expression:

$$k = 7.3 \times 10^{-12} \exp(340 \pm 40/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

In earlier studies, channel (a), forming HO_2 and Cl, has been shown to be the major pathway of the reaction.[73−77] In these studies, the branching ratio k_a/k was reported to be in the range 0.65−1.0. However, the branching ratio for the HCl-forming channel was not measured, and this channel could not be ruled out. In the most recent studies,[80,82−84] the formation of HCl in the reaction between OH and ClO was directly observed. Table 8 reports the data available for reaction (b). Lipson et al.,[82] Bedjanian et al.,[80] and Tyndall et al.[84] have measured the rate constant for the channel (b), whereas Wang and Keyser[83] have reported the branching ratio k_b/k. Given the difficulty of the measurements of the very low HCl yield in the OH + ClO reaction, the agreement between the room-temperature values of k_b can be considered reasonable. Although quite different Arrhenius expressions were found for k_b in two temperature-dependent studies of reaction (b),[80,82] the absolute values of k_b determined in both studies agree well within combined uncertainty and in the temperature ranges used. The Arrhenius expression $k_b(T) = 6.0 \times 10^{-13} \exp(230 \pm 150/T)$, with $k_b(298\ K) = 1.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (uncertainty factor of 3), recommended by Sander et al.[10] is based on the data of Lipson et al.[82] and those of Wang and Keyser.[83]

BrO + OH Reaction. This reaction is of potential importance for the stratospheric chemistry of bromine for a similar reason as for the ClO + OH reaction. Two channels exist:

$$\mathrm{OH} + \mathrm{BrO} \rightarrow \mathrm{Br} + \mathrm{HO_2} \qquad \Delta H = -8.2 \pm 1.8 \text{ kcal mol}^{-1} \quad \text{(a)}$$

$$\rightarrow \mathrm{HBr} + \mathrm{O_2} \qquad \Delta H = -46.6 \pm 1.4 \text{ kcal mol}^{-1} \quad \text{(b)}$$

One of the issues in stratospheric bromine chemistry is that models underestimate the measured HBr concentrations. The existence of even a minor HBr-forming pathway in the OH + BrO reaction could

Table 9. Reaction BrO + OH → Products: Summary of the Measurements of the Rate Constant

reference	technique	pressure (Torr)	T (K)	k (10^{-11} cm^3 molecule^{-1} s^{-1}) $k(T)$	k(298 K)
Bogan et al., 1996[98]	DF/MS	1	300		7.5 ± 4.2
Gilles et al., 2001[89]	DF/UV-LFP/VisA/LIF	3.6−4.8	298		4.5 ± 1.8
Bedjanian et al., 2001[90]	DF/MS	1	230−355	$1.65 \times \exp(250 \pm 50/T)$	3.8 ± 0.9

Table 10. Reaction ClO + HO_2 → Products: Summary of the Measurements of the Rate Constant

reference	technique	pressure (Torr)	T (K)	k (10^{-12} cm^3 molecule^{-1} s^{-1}) $k(T)$	k(298 K)
Reimann and Kaufman, 1978[92]	DF/RF	2−3	298		3.8 ± 0.5
Stimpfle et al., 1979[93]	DF/MS	0.8−3.4	235−393	$0.33 \times \exp(-850/T) + 4.5(T/300)^{-3.7}$	6.4 ± 1.1
Leck et al., 1980[94]	DF/MS	2−6	298		4.5 ± 0.9
Burrows and Cox, 1981[95]	FP/CL	760	300		5.4 ± 4.0
Cattell and Cox, 1986[96]	MM/UVA	50−760	308		6.2 ± 1.5
DeMore et al., 1997[9]	evaluation		200−300	$0.48 \times \exp(700 \pm^{250}_{700}/T)$	5.0 ± 2.0
Nickolaisen et al., 2000[97]	FP/UVA	50−700	203−364	$2.8 \times \exp(312 \pm 60/T)$	8.0 ± 1.3
Knight et al., 2000[98]	DF/MS	1.1−1.7	215−298	$7.1 \times \exp(-16 \pm 17/T)$	7.1 ± 1.8
Sander et al., 2003[10]	evaluation		200−300	$2.7 \times \exp(220 \pm 200/T)$	5.6 ± 1.7

significantly influence the overall partitioning of bromine in the stratosphere, as well as the bromine-mediated ozone loss. It has been shown that a value of the branching ratio as low as 0.01−0.02 for HBr formation could reconcile model calculations[85,86] and stratospheric HBr measurements.[87]

There are only three experimental studies of this reaction[88−90] (Table 9), the first one by Bogan et al.[88] published in 1996. This is in contrast with the analogous ClO + OH reaction (see above) and can be explained by “unavoidable experimental difficulties”.[89] Nevertheless, the room-temperature values of the reaction rate constant measured in the two recent studies[89,90] are in good agreement.

The major reaction product, the HO_2 radical, has been observed by Bogan et al.[88] and Bedjanian et al.[90] In the study by Bedjanian et al.,[90] the measurement of the branching ratio for the minor HBr-forming channel has been attempted. Due to the difficulties in measuring very low HBr concentrations, only an upper limit for k_b could be derived:[90]

$$k_b < 1.0 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \qquad (k_b/k < 0.03)$$

The attempt to measure the small yield of DBr from the analogous OD + BrO reaction was more successful, and Bedjanian et al.[90] have determined the value of

$$k_b = (3.7 \pm 1.8) \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

which corresponds to a branching ratio of 1.0 ± 0.5% for the DBr-forming channel in the OD + BrO reaction. The branching ratio for HBr formation in the OH + BrO reaction is likely similar to that for the DBr-forming channel of the reaction OD + BrO, since this assumption has been verified for the analogous reactions of ClO radicals with OH and OD.[78,82] The observed formation of HBr in the OH + BrO reaction at room temperature is in contradiction with the theoretical work of Sumathi and Peyerimhoff,[91] where the HBr formation in the reaction OH + BrO was predicted to be of importance only at temperatures above 2000 K. Therefore, additional studies are necessary in order to confirm the results of the only mechanistic study[90] of the OH + BrO reaction.

3.5.2. HO_2 Reactions

The reactions of ClO and BrO with HO_2 radicals are important steps in the ozone depletion mechanisms, especially in the lower stratosphere at midlatitudes (see sections 2.1.1 and 2.1.2). The IO + HO_2 reaction is a rate-limiting step of one of the potentially important iodine-mediated catalytic processes of ozone destruction (see section 2.1.3).

ClO + HO_2 Reaction. The kinetic data available for this reaction are shown in Table 10. The possible channels are

$$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2 \qquad \text{(a)}$$

$$\rightarrow \text{HCl} + \text{O}_3 \qquad \text{(b)}$$

$$\xrightarrow{(+\text{M})} \text{adduct (HOOOCl)} \qquad \text{(c)}$$

The results obtained in all studies of the reaction were recently discussed and updated by Sander et al.[10] The room-temperature values of the rate constant measured in two recent studies[97,98] agree well with each other and are somewhat higher than the recommended value,[10] which represents the mean of all studies. The temperature dependencies of the rate constant measured in three studies[93,97,98] are quite different. Stimpfle et al.[93] have observed a nonlinear Arrhenius behavior of the reaction, whereas Knight et al.,[98] in a low-pressure study, have found that the reaction is almost temperature independent between 215 and 298 K ($E/R = -16 \pm 17$ K). Nickolaisen et al.[97] have reported a linear Arrhenius behavior of the rate constant between 203 and 364 K and in the pressure range 50−700 Torr, with a small negative activation factor $E/R = 312 \pm 60$ K.[97] In contrast, at low pressures (near 1 Torr) they observed a some-

Table 11. Reaction $BrO + HO_2 \rightarrow HOBr + O_2$: Summary of the Measurements of the Rate Constant

reference	technique	pressure (Torr)	T (K)	k (10^{-11} cm^3 molecule^{-1} s^{-1}) $k(T)$	k(298 K)
Cox and Sheppard, 1982[100]	MM/UVA	760	303		$0.5 \pm^{0.5}_{0.3}$
Poulet et al., 1992[101]	DF/MS	1	298		3.3 ± 0.5
Bridier et al., 1993[102]	FP/UV	760	298		3.4 ± 1.0
Larichev et al., 1995[103]	DF/MS	1	233−344	$0.48 \times \exp(580 \pm 100/T)$	3.3 ± 0.5
Elrod et al., 1996[104]	DF/MS	100	210−298	$0.25 \times \exp(520 \pm 80/T)$	1.4 ± 0.3
Li et al., 1997[105]	DF/MS	1	233−348	$0.31 \times \exp(540 \pm 210/T)$	1.9 ± 0.6
DeMore et al., 1997[9]	evaluation		200−300	$0.34 \times \exp(540 \pm 200/T)$	$2.1 \pm^{1.0}_{0.7}$
Cronkhite et al., 1998[106]	LFP/UV/TDLA	12−25	296		2.0 ± 0.6
Bedjanian et al., 2001[107]	DF/MS	1	230−360	$0.94 \times \exp(345 \pm 40/T)$	3.1 ± 0.8
Bloss et al., 2002[108]	FP/UV	760	298		2.35 ± 0.82

Table 12. Reaction $IO + HO_2 \rightarrow$ Products: Summary of the Measurements of the Rate Constant

reference	technique	pressure (Torr)	T (K)	k (10^{-11} cm^3 molecule^{-1} s^{-1}) $k(T)$	k(298 K)
Jenkin et al., 1991[112]	MM/UVA	760	298		6.4 ± 0.7
Maguin et al., 1992[113]	DF/MS	0.6	298		10.3 ± 1.3
DeMore et al., 1997[9]	evaluation		298		$8.4 \pm^{4.2}_{2.8}$
Canosa-Mas et al., 1999[51]	DF/RF/CL	1.7−2.0	296		7.1 ± 1.6
Cronkhite et al., 1999[114]	LFP/TDLA/VisA	12−25	274−373	$0.93 \times \exp(680 \pm 110/T)$	9.7 ± 2.9
Knight et al., 2001[115]	DF/MS	1.0−2.0	273−353	$2.2 \times \exp(400 \pm 80/T)$	8.4 ± 0.3

what lower temperature dependence but a significantly lower value of the rate constant at room temperature.[97] The origin of the discrepancy in the results from these studies is not clear. Although ab initio calculations show that the possible HOOOCl adduct formation cannot be excluded,[97] the rate constant of the $ClO + HO_2$ reaction seems to be independent of pressure. Nickolaisen et al.[97] did not observe any pressure dependence between 50 and 700 Torr (at room temperature) and obtained a value for the rate constant at 298 K in good agreement with that measured by Knight et al.[98] at 1 Torr total pressure.

Channel (a) is the dominant reaction pathway.[11] The room-temperature studies place an upper limit for channel (b) of between 0.003 and 0.02. In contrast, Finkbeiner et al.[99] measured a branching ratio k_b/k of 0.05 ± 0.02 at $T = 210$ K and a total pressure of 700 Torr. However, in the low-pressure (near 1 Torr) study by Knight et al.,[98] an upper limit of only 0.01 was obtained for channel (b) in the temperature range 298−215 K.

As outlined by Nickolaisen et al.,[97] at the temperatures of the lower stratosphere (200−220 K), an uncertainty factor of 3−4 currently exists for the rate constant of this important atmospheric reaction. Clearly, additional kinetic studies of this reaction are needed in order to better determine the temperature dependence of its rate constant and the product distribution as a function of temperature and pressure.

$BrO + HO_2$ Reaction. This reaction has been studied in a number of laboratories using different experimental approaches (see Table 11). Although the negative temperature dependence of the rate constant was confirmed in all studies,[103−105,107] a discrepancy in the room-temperature data for the rate constant of around a factor of 1.5 exists and remains unexplained.

HOBr is the major and only reaction product which has been observed:[103−105,107]

$$BrO + HO_2 \rightarrow HOBr + O_2 \qquad \Delta H = -46.4 \pm 2.5 \text{ kcal mol}^{-1} \quad \text{(a)}$$

$$\rightarrow HBr + O_3 \qquad \Delta H = -6.7 \pm 2.7 \text{ kcal mol}^{-1} \quad \text{(b)}$$

However, the HBr-forming channel, which is also exothermic, may occur. It has been proposed that the HBr reaction pathway is potentially an important source of HBr in the stratosphere. Model calculations[86] have shown that a branching ratio even as low as 0.01 could lead to a reasonable agreement between observed and calculated stratospheric HBr profiles.

Data on the branching ratio for the HBr-forming channel (b) have been reported in three studies.[103,107,109] From the investigation of the reverse reaction $HBr + O_3 \rightarrow HO_2 + BrO$, and using the known thermochemical data, Mellouki et al.[109] have calculated an upper limit for the branching ratio of the channel (b): $k_b/k < 0.0001$ at $T = 300$ K. In a direct experimental determination of this branching ratio by Larichev et al.,[103] an upper limit of 0.015 was derived at $T = 233$−300 K from the absence of detection of O_3 in the reaction products. Finally, using a similar experimental approach, Bedjanian et al.[107] have derived an upper limit of 0.004 for the branching ratio of channel (b) at $T = 298$ K. These experimental data have been supported by theoretical calculations indicating the existence of a significant barrier (106 kJ mol^{-1})[110] for HBr elimination from the HOOOBr intermediate complex,[110,111] implying a negligible branching ratio for this channel.

$IO + HO_2$ Reaction. Kinetic data available for this reaction are summarized in Table 12. In all studies, the reaction has been found to be very fast. The

Table 13. Reaction $ClO + CH_3O_2 \rightarrow$ Products: Summary of the Measurements of the Rate Constant

				k (10^{-12} cm^3 molecule^{-1} s^{-1})	
reference	technique	pressure (Torr)	T (K)	$k(T)$	k(298 K)
Simon et al., 1989[117]	FP/FTIR	240	300		3.1 ± 1.7
Kenner et al., 1993[118]	DF/MS	1.9	293		1.9 ± 0.4
Helleis et al., 1993[119]	DF/MS	3	225−355	$3.25 \times \exp(-114 \pm 38/T)$	2.2 ± 0.4
Kukui et al., 1994[120]	DF/MS	3.8−4.5	233−300	$2.0 \times \exp(80 \pm 50/T)$	2.5 ± 0.3

values of the reaction rate constant at room temperature measured in the three most recent studies are in good agreement. Although the Arrhenius expressions obtained by Cronkhite et al.[114] and Knight et al.[115] are quite different, the absolute values of the rate constant from these two temperature-dependent studies agree well within the temperature ranges explored. An unweighted fit to the data of the three direct studies of the reaction[105−107] provides the following Arrhenius expression:[115]

$$k = (1.4 \pm 0.5) \times 10^{-11} \exp(554 \pm 100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The possible reaction pathways are[115]

$$\begin{aligned} HO_2 + IO &\rightarrow HOI + O_2 & \Delta H &= -47.3 \text{ kcal mol}^{-1} \\ &\rightarrow OH + OIO & \Delta H &= -2.9 \text{ kcal mol}^{-1} \\ &\rightarrow HI + O_3 & \Delta H &= +9.8 \text{ kcal mol}^{-1} \\ &\rightarrow IO_2 + OH & \Delta H &= +1.9 \text{ kcal mol}^{-1} \\ &\xrightarrow{(+M)} HOIO_2 & \Delta H &= -83.7 \text{ kcal mol}^{-1} \end{aligned}$$

HOI is the only species that has been observed in the reaction products.[113,115] The $HOIO_2$ adduct formation channel is likely negligible, since no pressure dependence of the total rate constant has been observed (see Table 12). No O_3 was observed in the reaction products,[113,115] and an upper limit of 0.1 has been placed for the branching ratio of the $HI + O_3$-forming channel.[115] In conclusion, HOI is the major product of the $IO + HO_2$ reaction. However, the occurrence of other reaction pathways cannot be excluded, and further studies are needed to determine the branching ratios for the minor channels of this reaction. The measurement of the overall rate constant in an extended temperature range is also very desirable.

3.6. Halogen Oxide Reactions with CH_3O_2

$ClO + CH_3O_2$ Reaction. The reaction between ClO and CH_3O_2 radicals is of potential importance in the chemistry of the ozone destruction in polar regions. Crutzen et al.[116] have shown that this reaction, in association with the heterogeneous reaction $HOCl + HCl \rightarrow Cl_2 + H_2O$, may participate in the reactivation of chlorine.

The results from four measurements[117−120] of the overall rate constant at room temperature are in acceptable agreement (Table 13). A slight temperature dependence of the rate constant has been observed,[119,120] a negative one by Kukui et al.[120] and a positive one by Helleis et al.[119] Extrapolation of these data to temperatures around 200 K gives values which differ by a factor of 1.5.

Mechanistic studies[117,119−122] of the reaction have identified two reaction pathways:

$$\begin{aligned} ClO + CH_3O_2 &\rightarrow ClOO + CH_3O & \text{(a)} \\ &\rightarrow CH_3OCl + O_2 & \text{(b)} \end{aligned}$$

However, a serious disagreement exists on the relative importance of these channels, since the values reported for the branching ratio of channel (a) at room temperature range between 0.2 and 0.85. Low-temperature mechanistic studies[118,121] (down to 215 K) have shown that both channels occur at polar stratospheric temperatures. Crowley et al.[124] have shown that CH_3OCl should photolyze in the stratosphere (a lifetime of ~4 h with respect to photodissociation has been calculated), with CH_3O and Cl as the most likely products. This would lead to the formation of the same final products from either channel (b) or channel (a), and to the conclusion that the branching ratio for the $ClO + CH_3O_2$ reaction would not influence the atmospheric impact of this reaction. However, other processes may occur, such as the heterogeneous reaction of CH_3OCl with HCl, forming Cl_2 (by analogy with HOCl), which would also lead to the reactivation of chlorine.

$BrO + CH_3O_2$ Reaction. This reaction may proceed following several channels:

$$\begin{aligned} BrO + CH_3O_2 &\rightarrow Br + O_2 + CH_3O & \text{(a)} \\ &\rightarrow OBrO + CH_3O & \text{(b)} \\ &\rightarrow HOBr + CH_2O_2 & \text{(c)} \\ &\rightarrow HBr + CH_2O + O_2 & \text{(d)} \\ &\rightarrow CH_3OBr + O_2 & \text{(e)} \\ &\rightarrow CH_3Br + O_3 & \text{(f)} \end{aligned}$$

Although this reaction is likely negligible in the stratosphere, it is potentially significant in the remote boundary layer and may contribute to the ozone loss events observed in the Arctic troposphere in spring. The reaction has been investigated only in the study by Aranda et al.[125] The value of $(5.7 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} has been measured for the reaction rate constant at room temperature. HOBr has been identified as the major reaction product, with a branching ratio of 0.8 ± 0.2 for channel (c). A branching ratio of 0.3 ± 0.1 has been found for the sum of the CH_3O-forming channels (a)

Table 14. Reactions $XO + NO \rightarrow X + NO_2$: Summary of the Measurements of the Rate Constants

reference	technique	T (K)	k (10^{-11} cm^3 molecule^{-1} s^{-1}) $k(T)$	 k(298 K)
$FO + NO \rightarrow F + NO_2$				
DeMore et al., 1997[9]	evaluation	200–300	$0.82 \times \exp(300 \pm 200/T)$	2.2 ± 0.8
$ClO + NO \rightarrow Cl + NO_2$				
DeMore et al., 1997[9]	evaluation	200–300	$0.64 \times \exp(290 \pm 100/T)$	1.7 ± 0.25
$BrO + NO \rightarrow Br + NO_2$				
DeMore et al., 1997[9]	evaluation	200–300	$0.88 \times \exp(260 \pm 130/T)$	2.1 ± 0.3
$IO + NO \rightarrow I + NO_2$				
DeMore et al., 1997[9]	evaluation	200–300	$0.91 \times \exp(240 \pm 150/T)$	2.0 ± 0.4
Atkinson et al., 1999[58]	LFP/CRDS	295		1.9 ± 0.5
Knight and Crowley, 2001[115]	DF/MS	273–353	$0.83 \times \exp(269 \pm 85/T)$	2.0 ± 0.3
Hôlscher and Zellner, 2002[126]	LFP/LIF	233–346	$0.43 \times \exp(397 \pm 65/T)$	1.7 ± 0.3

Table 15. Reactions $XO + NO_2 \rightarrow XONO_2$: Summary of the Measurements of the Rate Constants

reference	technique	T (K)	$k(T)$ low-pressure limit (cm^6 molecule^{-2} s^{-1})	 high-pressure limit (cm^3 molecule^{-1} s^{-1})
$FO + NO_2\ (+M) \rightarrow FONO_2\ (+M)$				
Bedjanian et al., 1993[127]	DF/EPR-LMR	300	$(5.3 \pm 0.6) \times 10^{-32}$[He]	
$ClO + NO_2\ (+M) \rightarrow ClONO_2\ (+M)$				
Sander et al., 2003[10]	evaluation	200–300	$(1.8 \pm 0.3) \times 10^{-31}(T/300)^{-3.4\pm0.2}$[air]	$(1.5 \pm 0.4) \times 10^{-11}(T/300)^{-1.9\pm0.5}$
$BrO + NO_2\ (+M) \rightarrow BrONO_2\ (+M)$				
Sander et al., 2003[10]	evaluation	200–300	$(5.2 \pm 0.4) \times 10^{-31}(T/300)^{-3.2\pm0.8}$[air]	$(6.9 \pm 1.0) \times 10^{-12}(T/300)^{-2.9\pm0.1}$
$IO + NO_2\ (+M) \rightarrow IONO_2\ (+M)$				
Jenkin and Cox, 1985[128]	MM/UVA	277	$(4.3 \pm 2.0) \times 10^{-31}[N_2]$	$(1.6 \pm 0.8) \times 10^{-11}$
Daykin and Wine, 1990[129]	PLP/UVA	254–354	$7.7 \times 10^{-31}(T/300)^{-5}[N_2]$	1.55×10^{-11}
Maguin et al., 1992[113]	DF/MS	298	$(7.9 \pm 2.2) \times 10^{-31}[N_2]$	$(1.0 \pm 0.1) \times 10^{-11}$
DeMore et al., 1997[9]	evaluation	200–300	$(5.9 \pm 2.0) \times 10^{-31}(T/300)^{-3.5\pm1.0}$[air]	$(9.0 \pm 1.0) \times 10^{-12}(\mathrm{T}/300)^{-1.5\pm1.0}$
Hölscher and Zellner, 2002[126]	LFP/LIF	238–298	$(4.1\pm0.6) \times 10^{-31}(T/300)^{-6.3}$[air]	$(1.0 \pm 0.1) \times 10^{-11}$

and (b). The results of this only study need to be confirmed.

3.7. Halogen Oxide Reactions with NO and NO_2

Reactions of XO with NO. The reactions of halogen oxide radicals with NO are important atmospheric processes which interconvert the active forms of halogen and oxidize NO to NO_2:

$$XO + NO \rightarrow X + NO_2$$

During the past few years, new kinetic data have been published only for the IO + NO reaction[58,115,126] (Table 14), which agree well with the value recommended by DeMore et al.[9] for the rate constant at 298 K. Although Hölscher and Zellner[126] have found a somewhat higher negative temperature dependence than that recommended by DeMore et al.[9] or that measured by Knight et al.,[115] the values of the rate constant extrapolated to stratospheric temperatures are very close (within 10% at $T = 220$ K). Very similar Arrhenius expressions are derived for all the XO + NO reactions along the series X = F, Cl, Br, I.

Reactions of XO with NO_2. The association reactions of XO with NO_2 are important processes in stratospheric chemistry, since they affect the halogen atom-catalyzed destruction of ozone through the formation of the reservoir species $XONO_2$:

$$XO + NO_2 + M \rightarrow XONO_2 + M$$

There is only one study (at $T = 300$ K) of the reaction of FO radicals with NO_2 [127] (Table 15). The kinetic data for the other XO reactions with NO_2 have been evaluated by Sander et al.[10] For the IO + NO_2 reaction, the results of the only recent study, by Hölscher and Zellner,[126] differ significantly (by a factor of 1.7 at $T = 220$ K) from the recommendation[10] (which is based on the data of Daykin and Wine[129]), indicating that the reaction rate constant at low temperatures remains uncertain and needs to be better determined.

3.8. Thermochemistry of Halogen Oxide Radicals

Thermochemical data can be determined from kinetic parameters using the well-known second and third law methods (e.g., refs 130 and 131). Some recent kinetic studies of XO reactions have improved the database for the enthalpies of XO formation. These data are listed in Table 16, together with those from recent evaluations.[10,11]

3.8.1. Enthalpy of Formation for IO Radical

$Cl + IO \leftrightarrow I + ClO$. From the measurements of the rate constant of the forward reaction and of the upper limit for the reverse one, Bedjanian et al.[138] have calculated a lower limit for the enthalpy of IO formation at room temperature: $\Delta H_f(IO) \geq 25.8$ kcal mol^{-1}.

$O + CH_3I \leftrightarrow IO + CH_3$. Considering a slight negative temperature dependence of the forward reaction, Gilles et al.[139] have found the upper limit $\Delta H_f(IO) \leq 28.8$ kcal mol^{-1}.

Table 16. Enthalpy of Formation for XO Radicals (at $T = 298$ K, in kcal mol^{-1})

radical	evaluation from NASA[10]	evaluation from IUPAC[11]	data from NIST−JANAF	data from recent kinetic studies
FO	26 ± 3	26.1 ± 2.4	26.1 ± 2.4[132]	
ClO	24.3 ± 0.03	24.3 ± 0.03	24.3 ± 0.03[133]	
BrO	30.2 ± 0.4	28.6 ± 1.4	30.0 ± 0.6[134]	28.6 ± 1.4[136,137]
IO	27.7 ± 1.2	27.7 ± 1.2	30.1 ± 4.3[135]	27.7 ± 1.2[65]

IO + ClO ↔ OClO + I. Using the rate constant data for the forward[65] and reverse[138] reactions, Bedjanian et al.[65] have found ΔH_f(IO) = 27.7 ± 1.2 kcal mol^{-1}, where the error includes 1 kcal mol^{-1} uncertainty on ΔH_f(OClO). This value is consistent with the upper and lower limits of ΔH_f(IO) given above, which were derived from the kinetic data for different reactions. The above value is exactly the same as that currently given in the thermochemical data evaluations (Table 16).

3.8.2. Enthalpy of Formation for BrO Radical

Br + IO ↔ I + BrO. Both forward and reverse reactions have been studied at $T = 298$ K by two groups.[136,137] Application of the third law procedure leads to ΔH_f(BrO) = 28.6 ± 1.4 kcal mol^{-1} [136] (with uncertainty arising mainly from the uncertainty on ΔH_f(IO)).

BrO + ClO ↔ Br + OClO. Applying the same procedure and using the recommended rate constant data,[9] Gilles et al.[137] have calculated ΔH_f(BrO) = 28.5 ± 1.0 kcal mol^{-1} (uncertainty is only uncertainty on ΔH_f(OClO)). The two reported values of ΔH_f(BrO), derived from the kinetic data for different chemical systems,[136,137] are in excellent agreement.

4. Conclusions

There has been a significant improvement in the knowledge of the gas-phase kinetic data for XO radical reactions over the past few years. In particular, the kinetic database has increased for a number of radical−radical reactions, not only for the overall rate constant but also for the individual rate constant of the various reaction channels. This has been the case for the reactions of IO radicals with other XO radicals, and also for the reactions of ClO and BrO with HO_x radicals.

For iodine, the lower overall rate constant measured for the IO + ClO reaction (compared to previous estimates) has significantly reduced the effectiveness of ozone destruction by iodine compared to chlorine (from 1000 on a per atom basis to 150−300). The impact of even very small injections of iodine in the stratosphere (mainly through CH_3I) strongly depends on the products formed in the IO reactions with ClO and BrO, since the reaction channels may or may not lead to ozone loss cycles. The OClO- and OIO-forming channels have been found to be the major ones for the reactions of IO with ClO and BrO, respectively. If the OClO photolysis leads to a null cycle for ozone, the OIO may lead to an ozone loss cycle, if the photoproducts are I + O_2, as recently suggested.[140] Furthermore, the efficiency of iodine is also dependent on the heterogeneous reactions of its reservoirs such as HOI and $IONO_2$. More laboratory studies on the stability of the iodine reservoirs are required to firmly establish the role of iodine in stratospheric chemistry.

For the ClO and BrO reactions with HO_x radicals, the major recent findings and remaining questions are as follows. For the OH + ClO reaction, the value of the overall rate constant is now reliable, and the branching ratio of a few percent for the HCl-forming channel at stratospheric temperatures has been confirmed, allowing for an acceptable agreement between model calculations and field measurements of HCl in the upper stratosphere. For the OH + BrO reaction, the temperature dependence of the rate constant has been measured and the formation of HBr in a minor channel has been definitively established. The impact of this channel on the total HBr budget in the stratosphere appears to be less important than predicted, as a consequence of the lower value measured for both the overall rate constant and the branching ratio for the HBr formation channel (0.01, which is the lower limit of the range considered by modeling calculations: 0.01−0.03).

However, despite the important new kinetic data obtained in recent years, it remains that additional studies are required for the reactions of XO radicals (X = Cl, Br, and I). These include crossed reactions of XO, as well as the reactions of XO with other free radicals such as the peroxy radicals, HO_2 and CH_3O_2. There is a general need for the measurements of the kinetic parameters at the low temperatures of the upper troposphere−lower stratosphere, and for a better quantification of the reaction products at these temperatures. For a better understanding of the reaction mechanisms, which may change with temperature, experimental identification of possible intermediate adduct should be attempted with the support of theoretical calculations.

This section has focused on the reactions of XO radicals that play a key role in the halogen−ozone interactions in various atmospheric regions, from the upper stratosphere to the marine boundary layer. For a long time, it has been thought that these interactions mainly take place in the atmospheric gas phase. Many examples of much more complex interactions have been demonstrated in recent years, such as the unexpectedly high concentration of the active form of the halogens (XO), which has been attributed to the regeneration of XO by heterogeneous processes undergone by the halogen reservoirs. Detailed laboratory studies of such multiphase processes are required to better describe all the various halogen−ozone interactions encountered in our atmosphere.

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