Chlorine Compounds in the Stratosphere: HOCl, HOOCl, and ClOO

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Possible reactions leading to the formation and the loss of HOCl and HOOCl in the stratosphere are explored. Since such reactions must be exothermic, the heats of formation of the title compounds are discussed first. Values adopted are $\Delta H_f^0(\mathrm{HOCl}) = -22 \pm 3$, $\Delta H_f^0(\mathrm{ClOO}) = 20.5 \pm 0.4$, $\Delta H_f^0(\mathrm{HOOCl}) = -17$ kcal/mol. Several important reactions are then identified. The most significant reactions apepar to be

$$\begin{array}{llll} \mathrm{HO_2} & + \mathrm{ClO} & \rightarrow \mathrm{HOCl} & + \mathrm{O_2} \\ \mathrm{HOCl} & + h\nu & \rightarrow \mathrm{OH} & + \mathrm{Cl} < 400\ \mathrm{nm} \\ \mathrm{OH} + \mathrm{ClO} & + \mathrm{M} & \rightarrow \mathrm{HOOCl} & + \mathrm{M} \\ \mathrm{HO_2} & + \mathrm{ClOO} & \rightarrow \mathrm{HOOCl} & + \mathrm{O_2} \\ \mathrm{HOOCl} & + h\nu & \rightarrow \mathrm{OH} & + \mathrm{ClO}\,. \end{array}$$

From estimates of the associated rate coefficients and photodissociation factors the steady state concentrations of HOCl and HOOCl are derived. Both are sufficiently low to exclude a significant influence upon the steady state concentrations of ClO and Cl.

Introduction

The list of substances capable of affecting the stratospheric ozone budget has recently been extended to include chlorine and its compounds[1, 2]. Moreover, it appears that man-made chlorofluoromethanes are not readily removed from the troposphere by natural sink mechanisms. These compounds are degraded only by photocomposition at high altitudes, whereby they burden the stratosphere unduly with chlorine[3–5]. This development has raised a considerable current interest in gaseous reactions of chlorine and its compounds.

The principal reactions of chlorine in the stratosphere have been identified by Rowland and Molina[6] as

$$\mathrm{OH} + \mathrm{HCl} \rightarrow \mathrm{H_2O} + \mathrm{Cl} \tag{1}$$

$$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2} \tag{2}$$

$$\mathrm{ClO} + \mathrm{O} \rightarrow \mathrm{Cl} + \mathrm{O_2} \tag{3}$$

$$\mathrm{ClO} + \mathrm{NO} \rightarrow \mathrm{Cl} + \mathrm{NO_2} \tag{4}$$

$$\mathrm{Cl} + \mathrm{CH_4} \rightarrow \mathrm{HCl} + \mathrm{CH_3} \tag{5}$$

$$\mathrm{Cl} + \mathrm{H_2} \rightarrow \mathrm{HCl} + \mathrm{H} \tag{6}$$

The participating chlorine species Cl, ClO and HCl have all been observed by balloon-borne instrumentation[7–12]. HCl serves as pool of chlorine from which the other species are derived by way of reaction 1. The presence of chlorine nitrate in the stratosphere has also been implicated on account of the reaction[13]

$$\mathrm{ClO} + \mathrm{NO_2} + \mathrm{M} \rightarrow \mathrm{ClONO_2} + \mathrm{M} \tag{7}$$

but has not yet been observed. Without doubt, there will exist in the stratosphere a number of additional chlorine compounds whose significance to stratosphere chemistry, however, remains to be assessed.

The present study is concerned with the role of HOCl, HOOCl and its precursor ClOO. It is unfortunate that the literature is particularly devoid of information about the gaseous reactions of these compounds, so that by necessity this study contains many elements of speculation. Nevertheless, certain conclusions can be reached. We discuss first the heats of formation of the compounds of interest because these quantities are required to derive the heats of potential reactions, and in the case of ClOO its equilibrium concentration. Subsequently, we consider conceivable production and removal processes for HOCl and HOOCl. After a selection of the principal reactions involved, calculated steady-state concentration altitude profiles are presented and discussed.

Heats of Formation of HOCl, ClOO and HOOCl

The heat of a reaction, ΔH_R, involving HOCl, ClOO etc. can be calculated from the standard heats of formation of reaction products, $\Delta H_f^0(P_i)$ and of reactants, $\Delta H_f^0(R_i)$, by way of

$$\Delta H_\mathrm{R} = \sum_i n_i\, \Delta H_f^0(P_i) - \sum_i m_i\, \Delta H_f^0(R_i)$$

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where n_i and m_i are the stoichiometry factors associated with the chemical conversion. In the calculations we have employed the commonly adopted reference temperature of 298 K. Standard heats of formation are available for many compounds of interest, but as it turns out, significant uncertainties exist for the species HOCl and ClOO, and for HOOCl no data exist at all. Below, this situation will be reviewed as briefly as possible and estimates for the thermochemical data will be given.

HOCl

The heat of formation of HOCl in aqueous solution is known fairly well [14] to be -31.35 kcal/mol. The heat of solution of HOCl is required to obtain the heat of formation in the gas phase, but appropriate data are lacking. If one estimates the heat of solution of HOCl in water to be similar to that of other weak acids, $\Delta H_{\mathrm{sol}} = -8 \pm 3$ kcal/mol, one obtains $\Delta H_f^0(\mathrm{HOCl}) = -22 \pm 3$ kcal/mol. We accept this estimate. The dissociation energies associated with the two bonds in HOCl are then: $D(\mathrm{HO-Cl}) = 60.3$ kcal/mol; $D(\mathrm{H-OCl}) = 98.2$ kcal/mol.

ClOO

In this asymmetric molecule, chlorine is attached to molecular oxygen by a weak bond. Thermal dissociation occurs even at the low temperatures of the stratosphere and an equilibrium is set up with free chlorine atoms. A reasonable assessment of this equilibrium requires a more accurate value for the heat of formation of ClOO than is currently in use. In reviewing the situation we note that the available experimental data come mainly from two laboratories: Johnston et al.[15] and Clyne and White [16], but they are not entirely independent. Johnston et al. studied the photolysis of Cl_2 in the presence of excess oxygen by the molecular modulation spectroscopy technique, aiming to derive rate coefficients for key reactions. Five of the ten reactions considered by them are

$$\begin{array}{lllll}
\mathrm{b} & \mathrm{Cl} + \mathrm{O_2} + \mathrm{M} & \rightarrow & \mathrm{ClO_2} & + \mathrm{M} \\
\mathrm{c} & \mathrm{ClO_2} + \mathrm{M} & \rightarrow & \mathrm{Cl} & + \mathrm{O_2} + \mathrm{M} \\
\mathrm{d} & \mathrm{ClO_2} + \mathrm{Cl} & \rightarrow & \mathrm{ClO} & + \mathrm{ClO} \\
\mathrm{f} & & \rightarrow & \mathrm{Cl_2} & + \mathrm{O_2} \\
\mathrm{e} & \mathrm{ClO} + \mathrm{ClO} & \xrightarrow{1} & \mathrm{ClO_2} & + \mathrm{Cl} \\
 & & \xrightarrow{2} & \mathrm{Cl_2} & + \mathrm{O_2} \\
 & & \xrightarrow{3} & \mathrm{OClO} & + \mathrm{Cl}
\end{array}$$

where the original notation has been retained. The last two channels of reaction e were not included by Johnston et al., but must be added. The other reactions given in the original paper will not be discussed here. From the analysis of their data, these authors give

$$\frac{K_1(k_d + k_f)}{1 + K_1[\mathrm{O_2}]} = 4.82 \cdot 10^{-31}\ \mathrm{cm^6/particles^2\,sec}\,, \tag{E (1)}$$

$$k_f/k_d = 108\,. \tag{E (2)}$$

The last result is at variance with $k_f/k_d = 15$ obtained by Nicholas and Norrish [17] from flash photolysis experiments. A value $k_f/k_d \approx 15$ has been found also in very recent work of Cox [18], in which techniques similar to that of Johnston et al. were employed.

In order to evaluate the rate coefficients k_d and k_f, Johnston et al. calculated $K_1 = k_b/k_c = [\mathrm{ClO_2}]/[\mathrm{Cl}][\mathrm{O_2}]$ from an estimated $\Delta H_f^0(\mathrm{ClOO}) = 22.8$ kcal/mol, which will be discussed further below, and a recalculated value for the entropy of ClOO using the spectroscopic data of Arkell and Schwager [19]. The equilibrium constant K_1 is determined from the relation

$$-RT \ln K_1 = \Delta H_R(\mathrm{b}) - T\,\Delta S_R(\mathrm{b}) \tag{E (3)}$$

where R is the gas constant and

$$\Delta H_R(\mathrm{b}) = \Delta H_f^0(\mathrm{ClO_2}) - \Delta H_f^0(\mathrm{Cl})\,.$$

The heat of formation of O_2 is zero by definition. The entropy difference is, similarly:

$$\Delta S_R(\mathrm{b}) = S^0(\mathrm{ClO_2}) - S^0(\mathrm{Cl}) - S^0(\mathrm{O_2})\,.$$

Johnston et al. calculated the entropy of ClO_2 as $S^0(\mathrm{ClO_2}) = 63.0$ cal/mol deg and this value will be adopted also here. $\Delta H_f^0(\mathrm{ClO_2})$ was estimated from the equilibrium between reactions d and e, assuming implicitly that the reaction channel e_1 predominates. Johnston et al. estimated the pre-exponential factor of the rate coefficient for reaction d and by comparison with the value derived from their experimental data conclude that reaction d has essentially no activation energy. The activation energy of the reverse reaction e had been measured previously by Clyne and Coxon [20] as 2.5 kcal/mol, so that this value should represent the heat of reaction e. The heat of formation $\Delta H_f^0(\mathrm{ClO_2})$ can then be obtained from the relation

$$\Delta H_R(e) = \Delta H_f(\mathrm{ClO_2}) + \Delta H_f^0(\mathrm{Cl}) - 2\,\Delta H_f^0(\mathrm{ClO})\,, \tag{E (4)}$$

where one takes $\Delta H_{\mathrm{R}}(e) = 2.5$ kcal/mol and the heats of formation for Cl and ClO are known [14]. The assumptions used in the derivation of $\Delta H_{\mathrm{f}}^0(\mathrm{ClO_2})$ in this manner are

1. Reaction d possesses no activation energy;
2. Reaction e goes predominantly to $\mathrm{ClO_2}$ and Cl as products, and the other channels are negligible.

Both assumptions are approximations giving rise to errors.

Clyne and White [16] have re-examined reaction e and determined its rate coefficient and activation energy with greater precision than previously, using a low pressure flow reactor and optical detection of ClO radicals. The rate coefficient was

$$k_{\mathrm{e}} = 1.3 \cdot 10^{-12} \exp(-2277/R\,T)\ \mathrm{cm^3/molecule\ sec}$$

showing essentially no third body dependence. At 298 K the rate coefficient has the value $k_{\mathrm{e}} = 2.7 \cdot 10^{-14}$ cm³/molecule sec. in good agreement with the more recent determination by Clyne et al.[21] of $k_{\mathrm{e}} = 2.2 \cdot 10^{-14}$ cm³/molecule sec. Clyne and White [1] note that this value is higher than that for k_{e} given by Johnston et al. and attribute the difference to an incorrect value of $\Delta H_{\mathrm{f}}^0(\mathrm{ClO_2})$ used by Johnston et al. to calculate $K_2 = k_{\mathrm{d}}/k_{\mathrm{e}} = [\mathrm{ClO}]^2/[\mathrm{Cl}]\,[\mathrm{ClO_2}]$. Clyne and White therefore adopt the converse procedure and combined their value for k_{e} with the value k_{d} given by Johnston et al. to obtain first $K_2 = 57$ (compared to $K_2 = 227$ as derived by Johnston) and subsequently $\Delta H_{\mathrm{f}}^0(\mathrm{ClO_2}) = 22.2$ kcal/mol using the relations

$$-R\,T \ln K_2 = \Delta H_{\mathrm{R}}(\mathrm{d}) - T\,\Delta S_{\mathrm{R}}(\mathrm{d}), \qquad \mathrm{E}\,(5)$$

where

$$\Delta H_{\mathrm{R}}(\mathrm{d}) = -\Delta H_{\mathrm{R}}(\mathrm{e}) \quad \text{and}$$

$$\Delta S_{\mathrm{R}}(\mathrm{d}) = 2\,S^0(\mathrm{ClO}) - S^0(\mathrm{Cl}) - S^0(\mathrm{ClO_2}).$$

The derivation of $\Delta H_{\mathrm{f}}^0(\mathrm{ClO_2})$ by Clyne and White also involves the assumption that reaction e leads mainly to the products $\mathrm{ClO_2}$ and Cl and that the other channels can be neglected. It has recently been shown by Clyne et al.[21] that reaction channel e 3 contributes very little indeed at 298 K, approximately 4% of the total reaction. The second channel, e 2, will not be negligible, however. Watson [22] estimates a branching ratio of about unity for the channels e 1 and e 2. Accordingly, this feature must be incorporated into the analysis of the data. In addition, one should allow for a small activation energy of reaction d. Such an analysis will be given below. We shall utilyze the most recent thermochemical data for Cl and ClO given by Domalski, Garvin and Wagman [23].

It may be noted that our knowledge of $\Delta H_{\mathrm{f}}^0(\mathrm{ClO_2})$ derives solely from the equilibrium between reactions d and e. The associated equilibrium constant is $K_2 = k_{\mathrm{d}}/\alpha\,k_{\mathrm{e}}$ where $\alpha = k_{\mathrm{e1}}/k_{\mathrm{e}}$ denotes that fraction of reaction e which results in the products Cl and ClOO. K_2 and the equilibrium constant $K_1 = k_{\mathrm{b}}/k_{\mathrm{c}}$ are coupled in that their product does not involve $\Delta H_{\mathrm{f}}^0(\mathrm{ClO_2})$. The value

$$K_1 \cdot K_2 = 546\ (\mathrm{atm^{-1}}) \qquad \mathrm{E}\,(6)$$

may be taken as established. We then write K_2 in the form

$$K_2 = \frac{k_{\mathrm{d}}}{k_{\mathrm{e}}} = \frac{k_{\mathrm{d}}^0}{\alpha\,k_{\mathrm{e}}^0} \exp\{(A_{\mathrm{e}} - A_{\mathrm{d}})/R\,T\}$$

$$= \exp\{S/R - \Delta H_{\mathrm{R}}/R\,T\}$$

$$A_{\mathrm{e}} - A_{\mathrm{d}} = \Delta H_{\mathrm{R}}(\mathrm{d}) = 19.32 - \Delta H_{\mathrm{f}}^0(\mathrm{ClO_2}) \qquad \mathrm{E}\,(7)$$

where the numerical value (in kcal/mol) on the right hand side is computed from the heats of formation for Cl and ClO. $A_{\mathrm{e}} = 2.297$ kcal/mol [16] and A_{d} are the activation energies of reactions e and d. The pre-exponential factor can be calculated from the involved entropies and $k_{\mathrm{e}}^0 = 1.3 \cdot 10^{-12}$ cm³/molecules sec is also known from direct measurement [16]. Combining Eqs. E(1), E(2) and E(6) with E(7) provides a route to calculating the equilibrium constants K_2 and K_1, the values for k_{d} and k_{d}^0, the factor α, and the heats of reaction, $\Delta H_{\mathrm{R}}(\mathrm{d})$, and of formation, $\Delta H_{\mathrm{f}}^0(\mathrm{ClO_2})$, all as a function of the activation energy A_{d}. The results for the most important of these parameters are summarized in Table 1. The employed thermochemical values for ClO and Cl are given in the legend.

Table 1. Heat of formation of $\mathrm{ClO_2}$, equilibrium constants K_1 and K_2, rate coefficient k_{d}, pre-exponential faktor k_{d}^0 and $\alpha = k_{\mathrm{e1}}/k_{\mathrm{e}}$, all as a function of the heat of activation A_{d} of reaction d. Exponents indicate powers of ten.

A_{d} (kcal/mol)	ΔH_{f}^0 (kcal/mol)	K_2	K_1 (atm⁻¹)	k_{d} (cm³/molecule sec)	k_{d}^0	α
0.0	21.8	920	0.59	4.6^{-13}	4.6^{-13}	0.018
0.5	21.3	394	1.38	4.4^{-13}	1.0^{-12}	0.041
0.9	20.9	200	2.73	5.5^{-13}	2.5^{-12}	0.10
1.3	20.5	101	5.37	7.5^{-13}	6.7^{-12}	0.27
1.5	20.3	72.4	7.54	1.0^{-12}	1.3^{-11}	0.52
1.7	20.1	51.5	10.6	1.3^{-12}	2.4^{-11}	0.97

Thermochemical values employed: $\Delta H_{\mathrm{f}}^0(\mathrm{ClO}) = 24.3$ and $\Delta H_{\mathrm{f}}^0(\mathrm{Cl}) = 29.08$ kcal/mol; $K_1 \cdot K_2 = 546.3$.

From these data one can determine limits to the range of $\Delta H_f{}^0(\mathrm{ClO_2})$ compatible with the available experimental data. The upper limit is given by setting $A_d = 0$ so that $\Delta H_f{}^0(\mathrm{ClO_2}) = 21.8$ kcal/mol at 298 K. The corresponding fraction of reaction e going into the channel e 1 is $\alpha = 0.018$, indicating that the major products are Cl_2 and O_2 rather than Cl and ClOO. This appears to be inconsistent with the data of Clyne, McKenney and Watson[21]. It is more reasonable to set $\alpha \geqq 0.1$. The upper limit of $\Delta H_f{}^0(\mathrm{ClO_2})$ is then reduced to 20.9 kcal/mol. The lower limit is determined by the fact that α cannot exceed unity. Since the reaction channel e 3 contributes perhaps 4% to the total reaction e, we set $\alpha = 0.96$. The corresponding activation energy is $A_d = 1.7$ kcal/mol and $\Delta H_f{}^0(\mathrm{ClO_2}) = 20.1$ kcal/mol. This value provides a rather definite lower limit. These results suggest that $\Delta H_f{}^0(\mathrm{ClO_2})$ lies in the range 20.1 – 20.9 kcal/mol. The median value of $\Delta H_f{}^0(\mathrm{ClO_2}) = 20.5$ kcal/mol corresponds to $\alpha = 0.27$. This appears to be a reasonable value and we suggest $\Delta H_f{}^0(\mathrm{ClO_2}) = 20.5 \pm 0.4$ kcal/mol. The limits do not yet include the uncertainties inherent in the experimental data so that the true range of uncertainty may be wider. The $Cl - O_2$ bond dissociation energy corresponding to the derived heat of formation of ClO_2 is calculated as $D(\mathrm{Cl - O_2}) = 8.6 \pm 0.4$ kcal/mol. Cox and Derwent[24] have recently obtained $k_f = (2 \pm 1) \times 10^{-11}$ cm^3/molecule sec which they use together with the value $k_f/k_d = 15$ from Nicholas and Norrish[17] to derive $k_d = 1.3 \pm 0.6 \cdot 10^{-12}$ cm^3/molecule sec. This value is in harmony with our conclusions concerning $\Delta H_f{}^0(\mathrm{ClO_2})$ as a comparison with Table 1 shows.

HOOCl

This is a hypothetical molecule, for which a laboratory observation has not yet been reported. HOOCl may nevertheless play a role in stratospheric chemistry provided it is stable. We shall here investigate this possibility. Since the structure of HOOCl will be similar to that of hydrogen peroxide, HOOH, we may assume a bond dissociation energy of the H-atom to oxygen in HOOCl fairly much the same as in hydrogen peroxide which is 89.6 kcal/mol. We can then calculate the heat of formation of HOOCl from the relation

$$D(\mathrm{H - OOCl}) = \Delta H_f{}^0(\mathrm{H}) + \Delta H_f{}^0(\mathrm{ClO_2}) - \Delta H_f{}^0(\mathrm{HOOCl}) \qquad \mathrm{E\,(8)}$$

and find $\Delta H_f{}^0(\mathrm{HOOCl}) = -17.0$ kcal/mol. The negative value indicates a considerable thermal stability. From this estimate for the heat of formation of HOOCl the remaining-bond dissociation energies are obtained as $D(\mathrm{HO - OCl}) = 50.7$ kcal/mol and $D(\mathrm{HOO - Cl}) = 51.0$ kcal/mol. The latter value is particularly interesting when compared with the low bond dissociation energy in ClOO, because it shows that the chlorine-oxygen bond is stabilized by the addition of a hydrogen atom to ClOO.

Individual Reactions Producing and Removing HOCl and HOOCl

Table 2 presents a list of reactions of Cl, ClO, ClOO and $ClONO_2$ with hydrogeneous substances which are known to occur in the stratosphere and from which HOCl or HOOCl may be formed. The list is probably not exhaustive. Many of the reactions are hypothetical in the sense that their laboratory observation has not been reported. The heats of reaction were calculated from the standard heats of formation tabulated by Domalski et al.[23] supplemented by the data given in the previous section and $\Delta H_f{}^0(\mathrm{ClONO_2}) = 6.28$ kcal/mol provided by Knauth et al.[25].

Only exothermic reactions need to be considered further, since the endothermic reactions will not contribute significantly at the temperatures prevailing in the stratosphere. Room temperature rate coefficients are given in the fourth column of Table 2. For some reactions rate coefficients are available from measurements, but uncertainties still exist in several cases with respect to the product channel yields. The other reactions require an estimate of the associated rate coefficient. Estimates were made in the following way: Termolecular recombination reactions were assumed to have rate coefficients of $1 \cdot 10^{-32}$ cm^6/molecule^2 sec. All bimolecular reactions between two radicals will be rapid and rate coefficients of the order of $5 \cdot 10^{-11}$ cm^3/molecule sec were assigned. The only exception is the reaction $\mathrm{ClOO + HO_2 \rightarrow HOOCl + O_2}$ whose rate was taken to be similar to that of $\mathrm{HO_2 + HO_2 \rightarrow H_2O_2 + O_2}$ (Hamson and Garvin[27]). The reaction of ClO with H_2O_2 probably is not faster than that of OH with H_2O_2 and it is expected to require a modest activation energy. We adopt a rate coefficient of $2 \cdot 10^{-13}$ cm^3/molecule sec as an upper limit. Among the reactions of ClOO with stable trace gases only ClOO

Table 2. Pathways, enthalpies and rate coefficients associated with gaseous reactions leading to the formation of HOCl and HOOCl. Exponents indicate powers to ten.

No.	Reaction		ΔH_R (kcal/mol)	k_{298} (cm^3/molec. sec)	References and remarks
8	$Cl + OH$	$\rightarrow HCl + O$ $ClO + H$	− .09 +38.0	5.0^{-11}	estimate
9	$Cl + OH + M$	$\rightarrow HOCl + M$	−60.3	1.0^{-32}	estimate
10	$Cl + HO_2$	$\rightarrow HCl + O_2$ $\rightarrow ClO + OH$ $\rightarrow HOCl + O$	−56.1 − 0.5 + 3.4	3.0^{-11}	Leu and deMore[26] Cox and Derwent[24]
11	$Cl + H_2O_2$	$\rightarrow HCl + HO_2$ $\rightarrow HOCl + OH$	−13.5 − 9.2	6.0^{-13}	Leu and deMore[26]
12	$Cl + HNO_3$	$\rightarrow HCl + NO_3$ $\rightarrow HOCl + NO_2$ $\rightarrow ClO + HNO_2$	− 1.9 −10.9 + 8.4	 6.8^{-15}	 Leu and deMore[26]
13	$ClO + OH$	$\rightarrow HOCl + O$	+ 3.5	slow	endothermic
*14	$ClO + OH + M$	$\rightarrow HOOCl + M$	−50.7	1.0^{-32}	estimate
*15	$ClO + HO_2$	$\rightarrow HOCl + O_2$ $\rightarrow OClO + OH$ $\rightarrow ClOO + OH$	−51.0 + 4.6 + 2.1	 5.0^{-11}	 estimate
*16	$ClO + H_2O_2$	$\rightarrow HOCl + HO_2$ $\rightarrow HOOCl + OH$	− 8.6 + 2.7	2.0^{-13}	estimate
17	$ClO + HNO_3$	$\rightarrow HOCl + NO_3$ $HOOCl + NO_2$	+ 3.0 +32.9	slow	endothermic
18	$ClO + H_2$	$\rightarrow HOCl + H$ $\rightarrow HCl + OH$	+ 5.8 − 3.7	$<5.0^{-16}$	Clyne and Coxon[20]
19	$ClO + CH_4$	$\rightarrow HOCl + CH_3$ $\rightarrow HCl + CH_3O$	− 6.4 −24.6	$<4.0^{-15}$	Watson[22]
20	$ClOO + OH$	$\rightarrow HOCl + O_2$	−51.8	5.0^{-11}	estimate
*21	$ClOO + HO_2$	$\rightarrow HOOCl + O_2$	−42.5	5.0^{-12}	estimate
22	$ClOO + H_2O_2$	$\rightarrow HOOCl + HO_2$ $\rightarrow HOCl + OH + O_2$ $\rightarrow HCl + HO_2 + O_2$	~ 0 − 0.6 − 4.9	 5.0^{-13}	 estimate
23	$ClOO + HNO_3$	$\rightarrow ClOOH + NO_3$	+11.8	slow	endothermic
24	$ClOO + H_2$	$\rightarrow ClOOH + H$ $\rightarrow HCl + HO_2$	+14.6 −37.5	1.0^{-14}	estimate
25	$ClOO + CH_4$	$\rightarrow ClOOH + CH_3$	+14.6	slow	endothermic
26	$ClONO_2 + OH$	$\rightarrow HOCl + NO_3$	−20.6	2.0^{-13}	estimate
27	$ClONO_2 + H_2O$	$\rightarrow HOCl + HNO_3$	− 2.8	1.0^{-19}	estimate
28	$ClONO_2 + HO_2$	$\rightarrow HOOCl + NO_3$	−11.3	slow	estimate
29	$OH + CH_3Cl$	$\rightarrow HOCl + CH_3$	+23.1	slow	endothermic

The important reactions are indicated by an asteric.

$+ H_2O_2$ need to be considered. The H abstraction channel is approximately thermoneutral and may be rapid despite a small activation energy. The associated rate coefficient probably does not exceed 10^{-12} cm^3/molecule sec, however. The other two channels which are also exothermic require a rearrangement and thus will be slower. The last three reactions involve chlorine nitrate. The reaction with OH is assumed to proceed via abstraction of chlorine. The homogeneous reaction with water vapor can proceed only via an extension, rearrangement and will certainly be slow. Its rate coefficient will be similar to that of the reaction $H_2O + N_2O_5$ (Morris and Niki[28]). The rate of the reaction between HO_2 and $ClONO_2$ is difficult to estimate and we shall assume it to be slow.

Loss reactions for HOCl and HOOCl are given in Table 3. We take into account only photo-decomposition processes and reactions with atomic oxygen. Owing to the stability of HOCl and HOOCl their reactions with many trace constituents in the atmosphere are endothermic. Reactions with OH are feasible. The concentrations of OH are lower than those of O-atoms by at least an order of magnitude. Reactions of OH with HOCl and HOOCl would be important only if the associated rate coefficients greatly exceed those for the O-atom reactions. The rate coefficients adopted for the latter reactions are considered to be upper limits. The absorption spectrum of HOOCl is unknown. We presume it to be similar to that of H_2O_2 and use a photodissociation rate of $J \approx 10^{-4}$ sec^{-1} outside the atmosphere. The value decreases somewhat when going from the upper to the lower stratosphere due to radiation shielding by ozone. The absorption spectrum of HOCl is known through the work of Fergusson et al[29]. Absorption begins at about 390 nm and extends throughout the ultraviolet spectral range. A first maximum of the continuum occurs at 320 nm. We associate this first absorption band with the dissociation into the products OH and Cl. Fergusson et al. determined the absorption strength by plate densitometry. This method does not give reliable absorption cross sections. Fortunately, these authors recorded the spectrum of H_2O_2 in the same study, so that one can determine absorption intensities relative to those of H_2O_2. Absolute absorption cross sections for HOCl are then obtained using the known cross section values[30, 31] for H_2O_2. Cross sections estimated in this way are shown in Table 4. From the integral over the product of the cross sections and the solar photon flux[32] an estimate of the photodissociation rate for HOCl outside the earth's atmosphere can be obtained with the additional assumption that the quantum yield is unity. In this manner we find J HOCl $\approx 9 \cdot 10^{-3}$ sec^{-1}. This value is similar to that for the photo-dissociation of NO_2 and will vary little with altitude. Fergusson et al. obtained their HOCl by distillation from hypochlorous acid. It must be recognized that HOCl is in equilibrium with its anhydride Cl_2O

$$2\,HOCl \rightleftharpoons Cl_2O + H_2O$$

so that one can not exclude the presence of Cl_2O in amounts sufficient to contaminate the spectrum. Fergusson et al. examined this possibility and argued that there must be little contamination, since the observed absorption resembles in no way that of Cl_2O. Recent ab initio calculations of HOCl potential surfaces by Hirsch et al.[33] indicate that a strong transition exists at about 220 nm in agreement with the data of Fergusson et al., but the transition in the 320 nm region should be weak suggesting that the 320 nm absorption feature could be caused by contamination. Thus, the photodissociation coefficient given here must be considered an upper limit.

Model Calculations

We must now decide which of the reactions listed in Tables 2 and 3 are important and which may be neglected. For this purpose the product of the rate coefficient and the concentrations of the reactants involved was calculated for each reaction and the leading terms were singled out. The concentrations employed for a variety of atmospheric constituents are assembled in Table 5. As far as possible, the data were taken from measurements. For many constituents such as NO the data points scatter widely and some procedure for averaging was required. In these cases, the comparison of one-dimensional theoretical models by Shimazaki and Whitten[35] was employed as a guide. For H_2O_2 and HO_2 only model profiles are available, and considerable variations exist between the various models. The concentrations of $ClONO_2$ were taken from recent calculations by Sze[34]. Steady state concentrations of ClO and Cl were computed on the basis of reactions

Table 3. Destruction reactions for HOCl and HOOCl in the stratosphere. Exponents indicate powers of ten.

No.	Reaction	ΔH_R (kcal/mol)	k_{298} (cm^3/molec. sec)	References and remarks
30	$HOCl + h\nu \rightarrow Cl + OH$	+60.3	$J = 9.0^{-3}$	from Fergusson et al.[29]
31	$HOCl + O \rightarrow ClO + OH$	− 3.5	2.0^{-13}	estimate
32	$HOOCl + h\nu \rightarrow ClO + OH$	+50.7	$J = 5.0^{-5}$	estimate
33	$HOOCl + O \rightarrow ClO + HO_2$	−13.2	2.0^{-13}	estimate
	$\rightarrow ClOO + OH$	−12.7		

$1-7$ set down in the introduction and were found to agree favorably with the values given by Sze[34]; the ClO concentrations are lower than the measurements by Anderson[12] indicate.

The concentration of ClO_2 can be obtained from that of Cl and the equilibrium constant K_1 discussed previously, provided the equilibrium is not disturbed by other reactions. A number of sample calculations were performed to ensure that this condition is met. The forward rate constant of the equilibrium

$$Cl + O_2 + M \underset{k_c}{\overset{k_b}{\rightleftharpoons}} ClOO + M$$

has been measured to have a value of approximately $1 \cdot 10^{-33}$ cm^6/molecule sec[17, 20] 19 so that estimates for the reverse reaction rates can be made for various altitudes. The reverse reaction turns out to be faster than many conceivable reactions of ClO_2 with atmospheric constituents. We have also calculated the approach to equilibrium as a function of time and found it rapid. Time constants for the approach to equilibrium range from $1.4 \cdot 10^{-3}$ sec at 20 km altitude to $7 \cdot 10^{-2}$ sec at 40 km. The rate of ClO_2 formation at 20 km altitude is about twenty times faster than the reaction of Cl atoms with ozone, at 40 km it is still about twice as fast. It is thus evident that the equilibrium is not perturbed. The equilibrium number densities of ClOO computed for the local temperatures and oxygen partical pressures are also entered in Table 5.

Wave length (nm)	Cross section (cm^2)
220	$1.6 \cdot 10^{-18}$
260	$6.7 \cdot 10^{-19}$
280	$4.5 \cdot 10^{-19}$
300	$8.0 \cdot 10^{-19}$
320	$1.1 \cdot 10^{-18}$
340	$8.0 \cdot 10^{-19}$
360	$3.3 \cdot 10^{-19}$
380	$4.5 \cdot 10^{-20}$
400	$4.5 \cdot 10^{-22}$

Table 4. Estimated absorption cross sections for HOCl.

On the basis of these data and the rate-coefficients given in Tables 2 and 3 one finds that the principal reactions involved in the formation and loss of HOCl are reactions 15, 16 and 30. Reaction 16 contributes about 10% to the total rate of HOCl formation, i. e. it is much less important than reaction 15. The formation of HOOCl involves mainly reactions 14 and 21, and both reactions are about equally significant. The loss of HOOCl occurs via reactions 32 and 33. Again, both turn out to be important. In calculating number densities of HOCl and HOOCl, we have invoked the usual steady state assumption. This assumption is reasonable for HOCl in view of its short life time due to photodestruction, about 10^2 sec. The steady state assumption is probably not rigorous in the case of HOOCl because its life time in the lower stratosphere is $2 \cdot 10^4$ sec and HOOCl may therefore be subject to accumulation and transport. This aspect has been neglected here. The steady state expressions for the concentrations of these constituents are

$$n(\mathrm{HOCl}) = [k_{15}\, n(\mathrm{HO_2}) + k_{16}\, n(\mathrm{H_2O_2})]\, n(\mathrm{ClO})/J_{\mathrm{HOCl}}\,, \quad \mathrm{E}\ (9)$$

$$n(\mathrm{HOOCl}) = [k_{14}\, n(\mathrm{OH})\, n(\mathrm{Cl})\, n(M) + k_{21}\, n(\mathrm{HO_2})\, n(\mathrm{ClOO})]/[k_{33}\, n(\mathrm{O}) + J_{\mathrm{HOOCl}}]\,. \quad \mathrm{E}\ (10)$$

The computed number densities of HOCl, ClO_2 and HOOCl are shown in Fig. 1 as a function of altitude. The corresponding mixing ratios are presented in Fig. 2 in a similar way. Also shown in these figures for comparison are the altitude profiles for Cl, ClO and HCl.

In discussing these results it should first be noted that in the altitude regime considered here the concentration of ClOO differs from that of Cl by not much more than an order of magnitude, so that it does not tie up any appreciable amounts of chlorine. This fact was noted earlier by Rowland and Molina[6]. Since ClOO is lost predominantly by thermal dissociation, it does not affect the Cl concentration profile. ClOO acts as a precursor to HOOCl, but the concentrations of the latter are also not sufficient to influence the balance between Cl, ClO and HCl set up by reactions $1-7$ given in the introduction. The

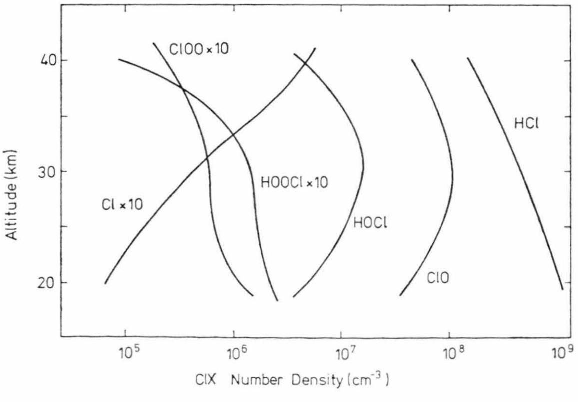

Fig. 1.

Table 5. Number densities of key stratospheric constituents. Exponents indicate powers of ten.

Constituent	Altitude (km) 20	25	30	35	40	Source
$M=N_2+O_2$	1.9^{18}	8.4^{17}	3.8^{17}	1.8^{17}	8.5^{16}	Cole et al. [37]
O_3	4.5^{12}	5.0^{12}	2.5^{12}	1.5^{12}	5.9^{11}	Shimazaki and Whitten [35]
O	1.2^{6}	8.0^{6}	5.0^{7}	2.5^{8}	1.0^{9}	Shimazaki and Whitten [35]
H_2	1.0^{12}	5.0^{11}	2.0^{11}	8.0^{10}	3.1^{10}	Shimazaki and Whitten [35]
CH_4	2.5^{12}	1.0^{12}	3.1^{11}	1.2^{11}	4.0^{10}	Shimazaki and Whitten [35]
H_2O	6.3^{12}	3.1^{12}	1.6^{12}	6.3^{11}	4.0^{11}	Shimazaki and Whitten [35]
H_2O_2	3.1^{8}	3.1^{8}	2.5^{8}	1.5^{8}	3.0^{7}	Shimazaki and Whitten [35]
HO_2	2.0^{7}	2.5^{7}	2.5^{7}	2.5^{7}	1.6^{7}	Shimazaki and Whitten [35]
OH	6.0^{5}	8.0^{5}	3.0^{6}	8.0^{6}	1.0^{7}	Shimazaki and Whitten [35], Anderson [36]
HNO_3	8.0^{9}	5.0^{9}	8.0^{8}	1.0^{8}	1.0^{7}	Shimazaki and Whitten [35]
NO	8.0^{8}	1.2^{9}	1.1^{9}	9.0^{8}	7.0^{8}	Shimazaki and Whitten [35]
NO_2	2.0^{9}	3.1^{9}	3.1^{9}	1.0^{9}	3.1^{8}	Shimazaki and Whitten [35]
HCl	9.5^{8}	7.5^{8}	4.5^{8}	2.8^{8}	1.6^{8}	Ackerman et al. [9]
$ClONO_3$	3.9^{8}	5.5^{8}	2.7^{8}	4.7^{7}	1.8^{7}	Sze [34]
Cl	6.8^{3}	1.5^{4}	4.6^{4}	1.6^{5}	4.6^{5}	Anderson [12], Sze [34]
ClO	4.2^{7}	7.3^{7}	1.1^{8}	8.0^{7}	4.6^{7}	Anderson [12], Sze [34]
ClO_2	1.1^{5}	6.4^{4}	6.0^{4}	4.5^{4}	2.3^{4}	This paper

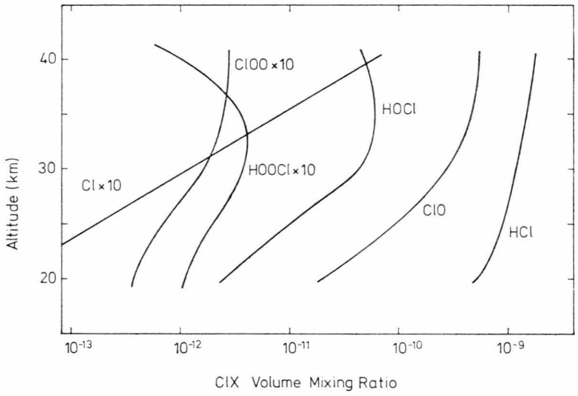

Fig. 2.

concentration of HOOCl is perhaps even too small to make its detection possible with present day optical techniques. Thus, HOOCl probably will remain a hypothetical molecule. The concentration of HOOCl would be much higher, however, if reaction 28: $HO_2+ClONO_2 \rightarrow HOOCl+NO_3$ which was assumed to be slow, were as rapid as reaction 15. The concentrations of HOCl are about a factor of ten lower than those of ClO at all altitudes. The ratio is just small enough to leave the ClO concentration profile unaffected. The HOCl concentration would increase, however, and the ClO concentration would decrease somewhat, if either the HOCl photodissociation coefficient were lower by a factor of at least three or the HO_2 concentration were similarly higher compared with the values used in our estimates. Such possibilities exist, but we will not consider them in detail due to the uncertainties associated with the present estimates of the HOCl concentrations. The rate coefficient for the important reaction 15 is not expected to exceed the value assumed ($5 \cdot 10^{-11}$ cm^3/molecule sec), although it may be lower. Hence, it appears unlikely that the concentrations of HOCl will be much greater than those shown in Figure 1. This conclusion, of course, is based upon the list of reactions in Table 2 and the neglect of additional ones which were not considered.

In summary, it has been shown that at least one reaction each exists for the formation of HOCl and HOOCl in the stratosphere. Also, we believe that an improved value for the heat of formation of ClOO has been derived; and the hypothetical molecule HOOCl has been found to have a considerable thermal stability.

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