HCFC-31: the $CHClFO_2$ + NO $\rightarrow$ CHClFO + NO_2 reaction and Cl atom elimination from CHClFO

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Abstract

The kinetics and mechanism of the reaction of $CHClFO_2$ radicals with NO were studied by time-resolved mass spectrometric monitoring of the molecular ions of NO_2 and NO. The rate constant was determined to be $(1.31 \pm 0.20) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at $(26 \pm 1)°C$, and was found to be independent of pressure over the range 6–25 Torr. The CHClFO radicals formed in this reaction were found to dissociate by unimolecular C–Cl bond scission. The unimolecular rate coefficient for Cl atom loss was estimated to be greater than 3×10^3 s^{-1} at $(26 \pm 1)°C$.

1. Introduction

Partially halogenated methanes and ethanes have been proposed and are being used as replacements for the chlorofluorocarbons (CFCs) in many industrial and technological applications. These alternatives, also known as hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs), are insoluble in water and volatile in nature and will eventually escape into the atmosphere. It is imperative to understand the atmospheric chemistry of these compounds in order to determine the environmental acceptability of their industrial use on a global scale.

All the proposed replacements (RH) have at least one C–H bond, which makes them reactive towards the OH radical in the troposphere. This reaction results in the formation of a haloalkyl radical (R·)

due to H atom abstraction by the hydroxyl radical. These haloalkyl radicals then rapidly combine with O_2 and are completely converted to peroxy radicals ($RO_2·$).

Chlorofluoromethane (HCFC-31, CH_2ClF) belongs to the class of HCFCs that have been proposed as replacements to CFCs in many industrial applications. In the case of HCFC-31, the reaction with OH radicals will produce CHClF radicals which will be quantitatively converted to $CHClFO_2$ radicals in the atmosphere. Information about the subsequent reactions of these peroxy radicals with the other components of the atmosphere is highly desired to ascertain the fate of HCFC-31. Though peroxy radicals can react with HO_2, RO_2, $R'O_2$ (other peroxy radicals), and NO_2 [1], their reaction with NO is usually dominant in the atmosphere [2,3].

This is the first report on the kinetics of the reaction of $CHClFO_2$ radicals with NO. The fate of the CHClFO radicals formed by the $CHClFO_2$ + NO

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reaction was also determined in this study. A previous product study by Tuazon and Atkinson [4] gave evidence that CHClFO radicals eliminate Cl atoms at 298 K and 740 Torr. In the present investigation CHClFO$_2$ radicals were generated from Cl atom initiated oxidation of mixtures of HCFC-31–O$_2$–N$_2$. Mass spectrometry was used to monitor the rate of formation of NO$_2$ and the decay of NO to determine the kinetics and mechanism of the title reaction and the fate of the oxy radical. All the experiments were done at (26 ± 1)°C and in the pressure range 6–25 Torr.

2. Experimental

2.1. Apparatus

All the experiments were carried out in the existing experimental apparatus which is briefly described here. For a more detailed description, see the papers listed in Ref. [5]. The reactions were initiated in a jacketed, purged flow reactor by focussing a broadband flash of UV–VIS light into the reactor. The flash lamp was pulsed at 6 kV with a frequency of 5 Hz. A fraction of the reacting mixture from the reactor leaked into the ionization chamber where it was bombarded with 30 eV electrons to create ions which were then extracted to the quadrupole of the mass spectrometer. The mass-selected ions then exited to the Daly detector to produce a pulse of current which was amplified, averaged and recorded.

2.2. Procedure

Chlorine atoms were used as substitutes for OH radicals as they are much easier to generate in the laboratory, and are generally more reactive toward HFCs and HCFCs. Flash photolysis of Cl$_2$ produced Cl atoms which initiated oxidation in mixtures of HCFC-31, O$_2$ and N$_2$ (diluent). The initial concentration of Cl atoms, [Cl]$_0$, was determined by NOCl actinometry, which has been described in detail before [6]. The formation of Cl atoms from photodissociation of HCFC-31 was negligible. Flash irradiation of HCFC-31–NOCl mixtures showed that all of the Cl$_2$ formed could be accounted for by NOCl photolysis. The formation of Cl$_2$ from C–Cl bond scission

Table 1
Reaction scheme and initial concentrations

Reaction	k [a]	Reference
(1) Cl$_2$ + $h\nu$ → 2 Cl		
(2) Cl + CH$_2$ClF → CHClF + HCl	1.1×10^{-13}	[11]
(3) CHClF + O$_2$ → CHClFO$_2$	2.0×10^{-12}	[1]
(4) 2 CHClFO$_2$ → 2 CHClFO + O$_2$	2.6×10^{-12}	[1]
(5) CHClFO$_2$ + NO → CHClFO + NO$_2$		this work
(6) CHClFO → HC(O)F + Cl	1.0×10^5	[1]

initial concentration	
[HCFC-31]	1.21–5.44 Torr
[O$_2$]	0.51–2.29 Torr
[Cl]	0.17–1.18 mTorr
[NO]	0.48–1.46 mTorr

[a] Units are cm^3 molecule^{-1} s^{-1}, except for k_6: s^{-1}.

followed by Cl + NOCl = Cl$_2$ + NO was undetectable. The upper limit to Cl from HCFC-31 photolysis was estimated to be 1% of the Cl from Cl$_2$ photolysis. This is in accord with the weak absorption of HCFC-31 in the far UV [7]. The Cl atoms abstract H atoms from HCFC-31 to produce CHClF radicals, which in the presence of excess O$_2$ are completely converted to peroxy radicals, CHClFO$_2$. Oxygen is present in a sufficient amount that other reactions competing for CHClF radicals are unimportant. To study the kinetics of the reaction of CHClFO$_2$ with NO, several different concentrations of NO in N$_2$ were used. All the experiments were carried out in the pressure range 6–25 Torr at (26 ± 1)°C. The initial concentrations are given in Table 1.

2.3. Materials

HCFC-31 of > 97% stated purity was procured from PCR and degassed before use. The mass spectrum of degassed samples indicated no hydrocarbon impurities. Cl$_2$ of 99.9% purity was supplied by Sigma and was also degassed before use. Dry grade N$_2$ and O$_2$ of 99.9% purity were supplied by the Toll Company while NO of 99.9% purity was obtained from Matheson. NOCl was synthesized and purified as described by Wu and Carr [6].

3. Results and discussion

3.1. Kinetics and mechanism of the $CHClFO_2 + NO$ reaction

The data presented below show that the reaction of $CHClFO_2$ with NO converts NO quantitatively to NO_2. The rate of formation of NO_2 and the rate of decay of NO were monitored mass spectrometrically to determine the rate constant for reaction (5) (see Table 1). NO_2 molecular ions at $m/z = 46$ and NO molecular ions at $m/z = 30$ were monitored in this laboratory before [2,3]. This technique of using the reactant (NO) and the product signal (NO_2) to determine the kinetics also gives information about the stoichiometry of the reaction. Fig. 1 shows the growth of NO_2 at 15, 20 and 25 Torr of a mixture of constant composition, while Fig. 2 shows a typical decay of NO. The decrease of the [NO_2] risetime with increasing pressure in Fig. 1 is due to the increasing [NO]. The kinetics were determined by a non-linear least-squares fit of the experimental data with the reaction scheme indicated in Table 1. The mean value of k_5 by using the experimental growth curves of NO_2 was determined to be $(1.30 \pm 11) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} while the mean value of k_5 arrived at by fitting the experimental profile of NO was found to be $(1.32 \pm .19) \times 10^{-11}$ cm^3 mole-

Fig. 2. A typical NO decay curve.

cule^{-1} s^{-1}. These two values are in an excellent agreement. No pressure dependence of the rate constants was observed in the range 6–25 Torr. We recommend $k_5 = (1.31 \pm .20) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (the error represents a 90% confidence interval and includes uncertainties in the determination of pressure control and gas mixture composition) at $(26 \pm 1)°C$. Fig. 3 shows the simultaneous formation of NO_2 and decay of NO. The calculated curves for NO and NO_2 were generated by using the recommended value of k_5, showing the goodness with which both sets of data are fit by a common
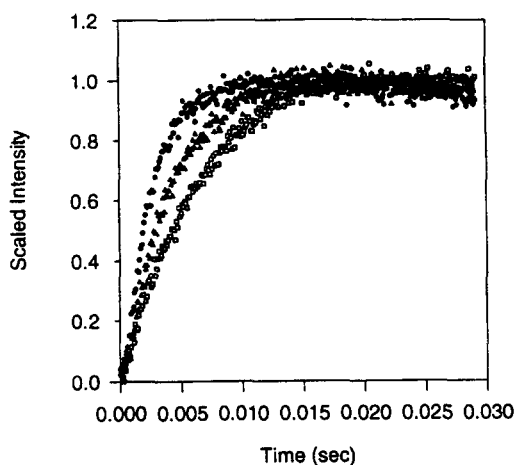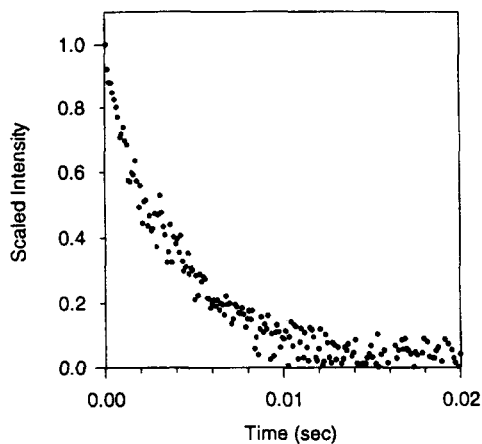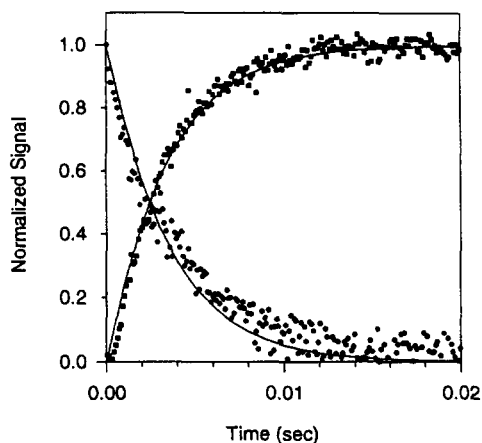

Fig. 1. Experimental NO_2 formation profile at different pressures. Gas mixture composition in N_2 HCFC-31: 21.81%; O_2: 9.18%; Cl_2: 9.14%; NO: 0.0048%. (□) 15 Torr, (△) 20 Torr, (●) 25 Torr.


Fig. 3. The experimental profile for (■) the formation of NO_2 and the (●) decay of NO, obtained by simultaneously monitoring of NO_2 and NO signals. The solid lines are the calculated profiles obtained by using the same value of k_5 for both the signals.

Table 2
Rate constants of the reaction of C_1 peroxy radicals with NO

Peroxy radical	$k(298 \text{ K})$ [a]	Reference
CH_3O_2	0.8	[1]
CCl_3O_2	1.8	[1]
CF_3O_2	1.6	[1,5]
$CHClFO_2$	1.3	this work
CH_2FO_2	1.3	[12]
CHF_2O_2	1.3	[12]
$CFCl_2O_2$	1.5	[1]
CF_2ClO_2	1.5	[1]
CH_2ClO_2	1.9	[1]

[a] Units are 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

rate coefficient. The lack of any pressure dependence of k_5 indicates that alkyl nitrate(s) formation by the following reactions [8,9]

$$CHClFO_2 + NO + M \rightarrow CHClFO_2NO + M$$

$$\rightarrow CHClFONO_2 + M$$
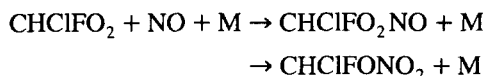
is negligible. The direct mass spectrometric monitoring of the decay rate of NO, in conjunction with the formation of NO_2, is significant as the correspondence of the two rates unequivocally demonstrates that NO_2 is the only product under the existing experimental conditions and reaction (5) is the dominant pathway. The rate constant determined in this study is compared with other rate constants for the reaction of C_1 peroxy radicals (derived from other HCFCs and HFCs) with NO in Table 2. It is evident that k_5 is commensurate with all of the literature data on the C_1 peroxy radicals, and that the rate coefficients are only modestly sensitive to the substitutional pattern of the halogens. For comparison, the $CH_3O_2 + NO$ reaction is also included in Table 2. It is interesting to note that the rate constant is 38% smaller than the slowest of the halogenated methylperoxy radicals $CHClFO_2$, CH_2FO_2, and CHF_2O_2, suggesting that halogen substituents weaken the O–O bond.

In the kinetic model used in this study (as indicated in Table 1), k_3, k_4 and k_6 were estimated from the currently available literature values for the reactions of similar radicals. The rate constants for the reaction of halogenated alkyl radicals with O_2 are all around 10^{-12} cm^3 $molecule^{-1}$ s^{-1} [1] and k_3 was estimated to be 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

All the experiments were done in the presence of excess O_2 so that the rate of reaction (3) was approximately three orders of magnitude faster than reaction (5), and the determination of k_5 was insensitive to k_3. Similarly, k_4 was estimated to be 2.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, which is typical of $RO_2 + RO_2$ reactions of this kind [1]. The rate constant for Cl elimination, reaction 6, is not known but by analogy with the unimolecular elimination of Cl from the α-position of other oxy radicals, $k_6 = 1 \times 10^5$ s^{-1} was adopted. Reaction of CHClFO with O_2 is unimportant, as shown in the next section, and is not included in the mechanism.

The uncertainties in the determination of k_5 due to the changes in the values of k_3, k_4 and k_6 were calculated and are plotted in Fig. 4. It is evident that the determination of k_5, under the existing experimental conditions, is not sensitive to the values of these rate constants. Using a very liberal 75% change in these rate constants resulted in a maximum of 2% change in the determined k_5, which is well within the experimental error range (10%). This method also allowed us to estimate the lower limit of k_6. The value of k_6 at which k_5 becomes sensitive ($\geqslant 15\%$ change in k_5) to k_6 was determined to be 3.11×10^3 s^{-1}. This sets the lower limit for the Cl atom elimination reaction (6) rate constant at around 3×10^3 s^{-1}.
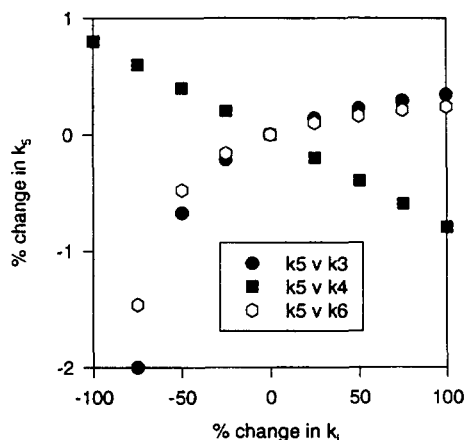

Fig. 4. A plot of uncertainties in the determination of k_5 due to uncertainties in the values of k_3, k_4 and k_6.

Secondary reactions of Cl atoms with O_2 and/or $CHClFO_2$ were found to be unimportant in the present analysis. Cl atoms can react with O_2 to form ClO_2 [1]. In these experiments, the $[HCFC-31]/[O_2]$ ratio was 2.4 and with $k(Cl + O_2 \rightarrow ClO_2) = 1.75 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} more than 99% of Cl atoms will react with HCFC-31. Cl atoms can also react with peroxy radicals according to reaction (7):

$$CHClFO_2 + Cl \rightarrow CHClFO + ClO \qquad (7)$$

In past work we have been able to detect ClO down to 10^{12} molecules cm^{-3} [6]. No signal from ClO was observed in these experiments, indicating that complications due to the formation of ClO are insignificant. Though the rate constant of reaction (7) is unknown, k_5 was found to be insensitive to changes in the partial pressure of HCFC-31, giving further evidence that the reaction of Cl atoms with peroxy radicals is not important in the present analysis. The reactions of Cl atoms with NO and NO_2 were also found to be unimportant due to the low pressure of the experiments. The excellent correspondence between the decay rate of NO and the formation rate of NO_2 also argues against secondary reactions of NO and NO_2 with Cl atoms.

3.2. The CHClFO radical

The reaction of $CHClFO_2$ radicals with NO produces NO_2 and CHClFO radicals. NO_2 was found to be a stable product of reaction (5) on the time scale of our experiments. On the other hand, CHClFO is expected to either react with O_2 (reaction (8)) or unimolecularly dissociate by eliminating the Cl atom (reaction (6)):

$$CHClFO + O_2 \rightarrow CCl(O)F + HO_2 \qquad (8)$$
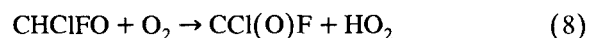
Recently, evidence has been obtained that HCl elimination can also occur from some α-Cl and α-H substituted oxy radicals [10]. Tuazon and Atkinson carried out a Cl initiated phooxidation product study of HCFC-31 in the absence of NO [4]. In their experiments, CHClFO was generated by the self reaction of peroxy radicals. They reported a 100% yield of HC(O)F as the primary product, which was attributed to the Cl atom elimination from the oxy radical (reaction (6)).

If Cl elimination from CHClFO takes place then Cl will further react with HCFC-31 and the cycle of reactions (2)–(6) would continue till NO is fully converted to NO_2 when $[NO]_0 > [Cl]_0$. In these experiments, the $[NO]_0/[Cl]_0$ ratio varied from 1 to 4.15 and complete conversion of NO was observed in every case, indicating that Cl elimination reaction is the dominant process for the decomposition of the CHClFO radicals. Moreover, if reaction (8) is the dominant reaction then HO_2 will be formed, and will react with the excess NO present to form NO_2 + OH. The OH radicals can initiate a chain reaction similar to the Cl atom chain, consuming CH_2FCl and NO. However, this will increase the time taken by the NO_2 signal to reach a maximum because of the difference in rate coefficients for $CHFClO_2$ + NO and HO_2 + NO, 1.3×10^{-11} and 8.6×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively, and the rate coefficients for OH + CH_2ClF and Cl + CH_2ClF, 4.5×10^{-14} and 1.1×10^{-13} cm^3 molecule^{-1} s^{-1}, respectively. In that case, the determined value of k_5 will depend on $[NO]_0/[Cl]_0$ and will vary with this ratio as it changes from 1 to $\geqslant 2$. No such dependence was observed, and thus no evidence to support the occurrence of CHFClO with O_2 was obtained. Furthermore, this reaction is not expected to be important, since k_8 would have to be significantly greater than the rate coefficient for reaction of O_2 with CH_3O, 2×10^{-15} cm^3 molecule^{-1} s^{-1}. If this value is assumed for k_8 and the upper limit estimate, $k_6 \geqslant 3 \times 10^3$ s^{-1} is used, then $k_8[O_2]/k_6 \leqslant 2$ to 4×10^{-2} is predicted over the range of O_2 pressures employed. We conclude that the dominant fate of the CHFClO radical is unimolecular decomposition by Cl atom elimination. This is in agreement with the product study of Tuazon and Atkinson [4] which was done at 298 K and 740 Torr.

4. Conclusions

Time-resolved mass spectroscopy with flash photolysis was used to investigate the kinetics and mechanism of the reaction of $CHClFO_2$ radicals with NO and the subsequent reaction of the CHClFO radicals. The rate constant for the title reaction was determined to be $(1.31 \pm .20) \times 10^{-11}$ cm^3 mole-

cule^{-1} s^{-1} and complete conversion of NO to NO$_2$ was observed in all the experiments. A good correspondence between the rates determined by monitoring the molecular NO and NO$_2$ signals indicated NO$_2$ and, by inference, CHClFO to be the only products. On the time scale of our experiments, CHClFO unimolecularly dissociates by Cl atom elimination reaction indicating a weak C–Cl bond.

CHClFO$_2$ radicals will be an important intermediate in the atmospheric degradation of HCFC-31. As mentioned earlier, these radicals can react with HO$_2$, NO$_2$, R'O$_2$ and NO in the atmosphere. Though, by analogy with reactions of other peroxy radicals derived from HCFCs and HFCs, their (CHClFO$_2$ radicals) reactions with NO will probably dominate over other reactions, and kinetic data for their reactions with HO$_2$, R'O$_2$ and NO$_2$ is needed to fully chart out the atmospheric chemistry of HCFC-31.

Acknowledgement

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