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Kinetics of the Association Reactions of NO with the Series of Chlorofluoromethyl Radicals CF_xCl_{3-x}

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The kinetics of the reactions $CF_2Cl + NO + M \rightarrow CF_2ClNO + M$ and $CFCl_2 + NO + M \rightarrow CFCl_2NO + M$ have been investigated using pulsed laser photolysis/time-resolved mass spectrometry in the pressure range 1–12 Torr and at the temperatures of 233, 298, and 333 K, using N_2 as the buffer gas. The results, along with those obtained in preceding works for the homologous reactions $CF_3 + NO + M \rightarrow CF_3NO + M$ and $CCl_3 + NO + M \rightarrow CCl_3NO + M$ (refs 5 and 7), were analyzed by a variational RRKM method. This analysis shows that all kinetic, structural, and thermochemical data of this series of species and of their corresponding reactions are internally consistent within the framework of the variational RRKM model used. By fitting the usual Troe's expression to the RRKM calculated rate constants values, themselves based on the experimental data, the broadening factor $F_c \approx 0.6$ was obtained. Setting $F_c = 0.6$ for all reactions, the following rate expressions have been obtained (units of cm^6 $molecule^{-2}$ s^{-1} for k_0 and cm^3 $molecule^{-1}$ s^{-1} for k_∞): $k_0(CF_3) = (2.0 \pm 0.4) \times 10^{-29}(T/298)^{-3.2}$; $k_\infty(CF_3) = (1.9 \pm 0.4) \times 10^{-11}(T/298)^{-1.0}$; $k_0(CF_2Cl) = (1.8 \pm 0.35) \times 10^{-29}(T/298)^{-4.4}$; $k_\infty(CF_2Cl) = (1.9^{+1.0}_{-0.5}) \times 10^{-11}(T/298)^{-1.5}$; $k_0(CFCl_2) = (1.0 \pm 0.25) \times 10^{-29}(T/298)^{-4.8}$; $k_\infty(CFCl_2) = (1.9^{+1.0}_{-0.5}) \times 10^{-11}(T/298)^{-1.5}$; $k_0(CCl_3) = (0.85 \pm 0.2) \times 10^{-29}(T/298)^{-5.5}$; $k_\infty(CCl_3) = (0.55 \pm 0.12) \times 10^{-11}(T/298)^{-1.6}$. It appears that in the low-pressure part of the falloff, the RRKM theory may be used in a predictive way for association reactions forming nitroso compounds: from the experimental determination of k_0, a reliable evaluation of the enthalpy of reaction can be obtained (within ±8 kJ mol^{-1}), using $\beta_c \approx 0.2$ and vice versa. The values of k_∞ have been found equal within uncertainties for those species containing fluorine. This is to be compared to the almost equal enthalpies of their corresponding reactions. In the case of CCl_3, both k_∞ and the reaction enthalpy have lower values than those obtained for the other species of the series. In contrast, k_0 decreases regularly in the series, from CF_3 to CCl_3, and this trend is well accounted for by the calculations.

Introduction

Kinetic studies of three-body recombination reactions of radicals provide data bases of interest in applications of theories of unimolecular reactions. Comparison of reactivity changes from one reaction to the other is generally more accurate than in the case of the reverse dissociation reactions, whose rate constants generally exhibit strong temperature dependencies as a result of large activation energies. On the contrary, association reactions of radicals generally proceed with no activation energy, and thus, interpretations of reactivity changes arising from differences in structural parameters are much easier.

Recently, several series of association reactions involving homologous radicals, generally of interest in atmospheric chemistry and in combustion processes, have been investigated in our laboratory.[1-3] Kinetic data concerning such series of reactions are of particular interest for testing theories. In fact, once the evolution of the kinetic behavior along the series is established experimentally, the challenge is to connect this trend to that of thermochemical and structural properties of the radicals, using a particular kinetic theory. Such an approach needs, of course, a good knowledge of these properties, but in some cases a good kinetic data base may reveal erroneous or unexpected thermochemical data. This has been the case in the preceding studies of the CCl_3–O_2[4] and CCl_3–NO[5] bond dissociation energies, and the latter case is discussed again in the present work. Another advantage of dealing with series of homologous radicals is to add more constraints to the applications of theories, since the whole series must be treated with a single theoretical model.

This paper deals with the series of association reactions of chlorofluoromethyl radicals with NO:

$$CF_3 + NO + M \rightarrow CF_3NO + M \quad (1)$$

$$CF_2Cl + NO + M \rightarrow CF_2ClNO + M \quad (2)$$

$$CFCl_2 + NO + M \rightarrow CFCl_2NO + M \quad (3)$$

$$CCl_3 + NO + M \rightarrow CCl_3NO + M \quad (4)$$

This series of reactions is of particular interest as the nitroso molecules produced have well-defined spectroscopic and thermochemical properties which are important input parameters in RRKM calculations. This is particularly true for CF_3NO, CF_2ClNO, and $CFCl_2NO$. These molecules exhibit structured electronic absorption spectra which have provided accurate data on low vibrational frequencies and on C–N bond dissociation energies. The dissociation energies are almost the same for all the above fluorinated molecules (167, 164, and 171 kJ mol^{-1}, respectively)[6] but significantly smaller for CCl_3NO (120 kJ mol^{-1}).[5] Thus, another interesting feature of this study is to verify the consistency between the kinetic parameters and the particular thermochemical properties of CCl_3NO, compared to those of other species.

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TABLE 1: Thermochemical Parameters Related to Reactions 1−4[a]

CX_3	CF_3	CF_2Cl	$CFCl_2$	CCl_3
$\Delta H^\circ_{f298}(CX_3)$	-460 ± 4[b]	-279 ± 8[c]	-96 ± 4[d]	71 ± 2.5[e]
$\Delta H^\circ_0(CX_3+NO)$	-167 ± 1[f]	-164 ± 5[g]	-171 ± 3[g]	-120 ± 8[h]
$\Delta H^\circ_{f298}(CX_3NO)$	-540 ± 5	-355 ± 13	-181 ± 7	38 ± 10
$\Delta H^\circ_{298}(CX_3+NO)$	-171 ± 1[i]	-168 ± 5[j]	-176 ± 3[j]	-125 ± 8[h]

$\Delta H^\circ_{f298}(NO) = 91.3 \pm 0.2$[k]

[a] Units of kilojoules mole^{-1}. [b] From ref 12. [c] From ref 13. [d] From ref 14. [e] From ref 15. [f] From ref 11. [g] From ref 16. [h] From ref 5. [i] Calculated from ΔH°_0 using molecular parameters given in ref 8. [j] Calculated from ΔH°_0 using molecular parameters given in Table 4. [k] From ref 17.

In preceding papers, we have reported kinetic studies of reaction 1 (CF_3)[7] and 4 (CCl_3)[5] complemented with nonvariational RRKM calculations. Concerning reaction 1, data were obtained in the range 1−12 Torr and 253−373 K, and the largest part of the falloff curve could be described at 298 K by joining our data to those of Vakhtin et al.,[8] who measured the rate constants from 20 to 455 Torr. In this case, vibrational frequencies and the C−N bond dissociation energy were available from IR and Raman spectroscopy[9] and from visible spectra of jet-cooled CF_3NO ($D_0(C-N) = 13980 \pm 60$ cm^{-1} = 167 ± 1 kJ mol^{-1}.[10,11]

Reaction 4 (CCl_3) was studied in the ranges 0.5−760 Torr and 263−373 K, using two complementary techniques.[5] In this case, the nine highest vibrational frequencies of CCl_3NO were available from IR spectroscopy,[9] but due to the unstructured spectrum of the jet-cooled CCl_3NO, neither the lowest vibrational frequencies nor the C−N bond dissociation was available. The latter was then measured by studying the equilibrium 4,-4: $D_0(CCl_3-NO) = 120 \pm 8$ kJ mol^{-1}[,5] and the lowest vibrational frequencies were calculated using the semiempirical MNDO-UHF method. In both cases RRKM calculations could account correctly for the experimental results. All thermodynamical parameters related to reactions 1−4 are collected in Table 1.

In this paper, we report measurements of the kinetics of reactions 2 and 3. Rate constants were measured between 1 and 12 Torr and from 233 to 333 K, using pulsed laser photolysis coupled to time-resolved mass spectrometry and by monitoring the rate of formation of CF_2ClNO and $CFCl_2NO$. Measurements at higher pressures, as performed in the study of the CCl_3 reaction,[5] were not possible in the present study of reactions 2 and 3. The results obtained for the whole series of reactions 1−4 have been analyzed using variational RRKM calculations, according to the procedure developed by Forst.[18] Rate expressions have been derived by fitting Troe's expression to the calculated RRKM falloff curves.

Experimental Section

The apparatus has already been described in detail,[19] and hence only a brief summary is presented here. The $CFCl_2$ and CF_2Cl radicals were produced by pulsed laser photolysis at 193 nm of $CFCl_3$ and CF_2Cl_2, respectively, using an excimer laser (Lambda Physics, EMG 101). The photolysis of CF_2Cl_2 at 193 nm has recently been shown to result exclusively in $CF_2Cl + Cl$, in which CF_2Cl does not undergo further decomposition.[20] The study of the photodissociation of $CFCl_3$ at 193 nm[21] has shown that the single C−Cl bond rupture is the predominant dissociation process. No evidence was found for molecular chlorine elimination ($CFCl_3 \rightarrow CFCl + Cl_2$) nor the three-body elimination ($CFCl_2 \rightarrow CFCl + Cl + Cl$), which are estimated to occur with a quantum yield lower than 5%. The $CFCl_2$ radicals formed are too cold to undergo unimolecular decomposition. Secondary dissociation of $CFCl_2$ might be possible through the absorption of a second photon at 193 nm. However, this can only occur at much higher laser fluence than that used in this work, and in addition, it is shown in ref 22 that the CFCl radicals that might be formed in this process cannot interfere with our kinetic measurements.

The initial radical concentrations of $CFCl_2$ and CF_2Cl were around 10^{11} molecule cm^{-3}. They were evaluated by introducing butane into the reaction mixture at low concentrations ($\sim 10^{14}$ molecule cm^{-3}) and by measuring its consumption after 10 laser pulses, due to reaction with chlorine atoms formed by the photolysis of the precursor. For a better sensitivity, the concentration of the precursor was about 10 times higher than that normally used in experiments. The gas mixture was continuously flowing through the reactor and was renewed every two/three laser pulses. The concentration of each component was determined by measuring both its flow rate and the total pressure in the reactor. The time-resolved buildup of CF_2ClNO and $CFCl_2NO$ was monitored by mass spectrometry (quadrupole Balzers QMG511), using molecular beam sampling. Signals were detected at m/e = 80 and 96, corresponding to the fragments CF_2NO^+ and $CFClNO^+$, respectively. No signal could be detected at the parent ion masses, in contrast to that observed in the case of CF_3NO.[7] The time-resolved concentration profiles of the CF_2ClNO and $CFCl_2NO$ formation were stored in a multiscaler (TRACOR) and transferred to a microcomputer for data processing. Generally, 1500 to 3000 shots were accumulated for an acceptable signal to noise ratio. The buffer gas was nitrogen in all cases. At the lowest pressure (≈ 1 Torr), care was taken to maintain a large excess of nitrogen by using very small concentrations of precursors (<10 mTorr).

N_2 (99.995%) and NO (99.9%) were provided by l'Air Liquide and used without further purification. CF_2Cl_2 (PCUK) and $CFCl_3$ (Fluka, purity 99.5%) were carefully degassed at low temperature.

Experimental Results

The experimental results reported in this work concern reactions 2 and 3 of CF_2Cl and $CFCl_2$, respectively. Nitric oxide was always present in large excess over the CX_3 (X = F or Cl) radical concentrations, resulting in pseudo-first-order kinetics. The values of rate constants were obtained by recording the time-resolved buildup of the CX_3NO species. The time profile of signals and their analysis procedure were the same as those already presented for CF_3 and CCl_3 radicals.[5,7] The particular experimental conditions used in this work for the study of reactions 2 and 3 are the following: total gas concentration $(0.3-4.5) \times 10^{17}$ molecule cm^{-3} (1−12 Torr); N_2 buffer gas; temperature 233, 298, and 333 K; CF_2Cl_2, $CFCl_3$ concentrations $(2-10) \times 10^{14}$ molecule cm^{-3} (5−30 mTorr); radical concentrations ($CFCl_2$ or CF_2Cl) < 10^{12} molecule cm^{-3}; NO concentrations $(0.8-80) \times 10^{14}$ molecule cm^{-3}, corresponding to pseudo-first-order rate constants varying from 500 to 2000 s^{-1}; flow rate varied from 3 to 100 cm^3 s^{-1}; laser pulse frequency 0.2−1 Hz.

Due to the low radical concentrations, radical−radical recombination reactions could be neglected. However, at the lowest temperature, the recombination of chlorine atoms with CF_2Cl or $CFCl_2$ radicals became faster and could perturb measurements, as observed in previous studies.[5] In those cases, small quantities of propane ($\sim$20 mTorr) were introduced into the gas mixture to scavenge chlorine atoms and convert them into less reactive propyl radicals. At the lowest temperatures, the addition of propane resulted in an approximately 10% decrease in the rate constant. No effect could be detected at higher temperature.

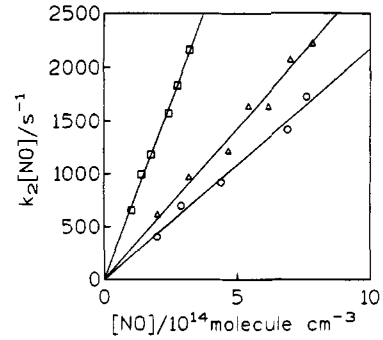

Figure 1. Pseudo-first-order rate constants for the CF$_2$Cl reaction with NO, plotted as a function of NO concentration: total gas density 3.25 × 10^{17} molecule cm^{-3}; buffer gas N$_2$; (□) 233 K; (△) 298 K; (○) 333 K.

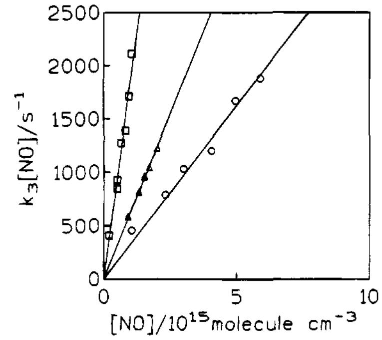

Figure 2. Pseudo-first-order rate constants for the CFCl$_2$ reaction with NO, plotted as a function of NO concentration: total gas density 7.0 × 10^{16} molecule cm^{-3}; buffer gas N$_2$; (□) 233 K; (△) 298 K; (○) 333 K.

As explained in ref 5 and 7, the rates of CX$_3$ radical losses to the walls were estimated from the intercepts of plots of the pseudo-first-order rates of CX$_3$NO production vs [NO] and averaged at a given temperature. The average value of intercepts was always around 100 s^{-1}.

The pseudo-first-order rate constants of CX$_3$NO formation, corrected for wall losses of CX$_3$ radicals, are plotted against NO concentration in Figures 1 and 2 for the radicals CF$_2$Cl (total gas density 3.25 × 10^{17} molecule cm^{-3}) and CFCl$_2$ (total gas density 7 × 10^{16} molecule cm^{-3}), respectively. Linear plots passing through the origin were obtained, suggesting that the experimental conditions of experiments were appropriate. Bimolecular rate constants for reactions 2 and 3 were obtained from the slopes of the lines using a least-squares treatment of the data. The values obtained at different pressures for the three experimental temperatures are listed in Tables 2 and 3 (the number of runs corresponding to each value also being indicated), and the corresponding falloff curves are plotted in Figures 3 and 4. It is clear that the rate constants measured between 1 and 12 Torr are close to the third-order limit and far from the high-pressure limit. The solid lines in the figures are the results of RRKM calculations described below.

RRKM Calculations

In our previous work,[5,7] the experimental results concerning CCl$_3$ and CF$_3$ were analyzed using a nonvariational RRKM procedure (program "FALLOFF"[23]). The representation of the experimental results, which included low- and high-pressure data obtained from different techniques, was satisfying and only necessitated short extrapolations to the limits. In the cases of CF$_2$Cl and CFCl$_2$, investigated in the present work, rate constants could only be measured at low pressures, and thus a long and uncertain extrapolation to the high-pressure limit was necessary. The curvature of the calculated falloff curves is obviously critical in performing such extrapolations, and we have thus taken great care in the procedure used to extrapolate our data. In this particular study, additional information which may help in such extrapolations can be gained from the fact that we are dealing with a series of homologous radicals in which results for the two species of interest, CF$_2$Cl and CFCl$_2$, are flanked by two others, CF$_3$ and CCl$_3$, for which experimental data exist at high pressure. Consequently, the results of extrapolations must present a certain internal consistency and continuity along the present series of homologous species.

Extrapolations to high-pressure limits, from the low-pressure data obtained in the present work for CF$_2$Cl and CFCl$_2$, were performed with the help of RRKM calculations. We have first tested RRKM models with the objective of obtaining shapes of falloff curves which correspond to the best representation of the experimental results obtained over large pressure ranges for the CF$_3$ and CCl$_3$ reactions.

TABLE 2: Experimental Bimolecular Rate Constant k_2, for the Reaction CF$_2$Cl + NO + M → CF$_2$ClNO + M

temperature, K	total gas density, 10^{16} molecule cm^{-3}	number of runs	k 10^{-12} cm^3 molecule^{-1} s^{-1}
233	4.2	3	1.5 ± 0.2
	8.3	5	3.0 ± 0.2
	16.6	6	5.2 ± 0.5
	24.9	6	5.7 ± 0.3
	33.3	6	6.8 ± 0.2
	41.6	7	7.5 ± 0.5
	49.9	5	8.0 ± 1.5
298	3.3	4	0.40 ± 0.04
	6.5	5	0.90 ± 0.16
	9.8	8	1.20 ± 0.04
	13.0	8	1.90 ± 0.1
	19.5	6	1.80 ± 0.1
	26.0	7	2.60 ± 0.2
	32.5	7	2.80 ± 0.2
	39.0	8	3.20 ± 0.4
333	2.9	4	0.30 ± 0.03
	5.8	6	0.50 ± 0.03
	8.7	5	0.80 ± 0.06
	11.6	5	1.0 ± 0.1
	17.4	8	1.3 ± 0.1
	23.2	6	1.7 ± 0.1
	29.1	7	1.9 ± 0.2
	34.8	5	2.2 ± 0.2

TABLE 3: Experimental Bimolecular Rate Constant k_3, for the Reaction CFCl$_2$ + NO + M → CFCl$_2$NO + M

temperature, K	total gas density, 10^{16} molecule cm^{-3}	number of runs	k, 10^{-12} cm^3 molecule^{-1} s^{-1}
233	4.2	6	0.9 ± 0.1
	7.1	7	1.7 ± 0.2
	11.2	6	2.7 ± 0.3
	18	7	3.4 ± 0.5
	27	6	4.9 ± 0.6
	54	6	6.7 ± 0.4
298	2.6	1	0.26
	2.8	2	0.27
	3.2	1	0.3
	3.5	6	0.30 ± 0.06
	7	7	0.5 ± 0.1
	14.1	7	1.2 ± 0.1
	21.1	11	1.7 ± 0.1
	28.3	9	1.9 ± 0.1
	35.2	8	2.4 ± 0.2
	42.4	6	2.6 ± 0.1
333	4.3	7	0.20 ± 0.05
	7	6	0.30 ± 0.02
	12.6	10	0.50 ± 0.03
	18.9	8	0.9 ± 0.1
	37.8	7	1.4 ± 0.1

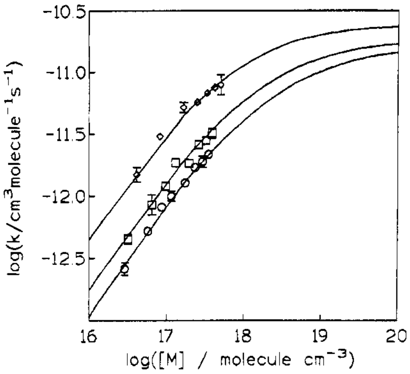

Figure 3. Pressure dependence of the bimolecular rate constant of the CF_2Cl reaction with NO, at three temperatures: (◇) 233 K; (□) 298 K; (○) 333 K; buffer gas N_2. Solid lines are the results of variational RRKM calculations fitted to experimental data.

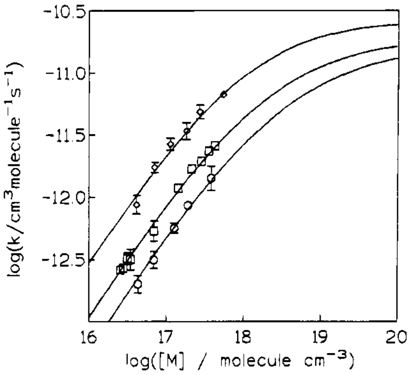

Figure 4. Pressure dependence of the bimolecular rate constant of the $CFCl_2$ reaction with NO, at three temperatures: (◇) 233 K; (□) 298 K; (○) 333 K; buffer gas N_2. Solid lines are the results of variational RRKM calculations fitted to experimental data.

We have at our disposal two RRKM-type routines: the nonvariational[23] and variational[18,24] procedures developed by Forst. The latter was already tested with a variety of systems.[25,26] When applied to the same reaction, it is observed that these two routines yield different shapes for the fall off curves, resulting in significantly different extrapolations to the high-pressure limit from the fit to low-pressure experimental data, as shown for example in Figure 5a for the CF_2Cl reaction. The extrapolation performed using the nonvariational routine yields k_∞ values about 50% higher than those obtained with the variational method. In the case of the CCl_3 + NO reaction, the best fit to low-pressure experimental data (obtained with the same experimental method as that used in the present work), which can be obtained by the nonvariational routine, does not pass through the high-pressure data (obtained independently by flash photolysis), as shown in Figure 5b. In contrast, the variational routine reproduces much better all the data. Similar behavior seems to be observed for the CF_3 reaction, but not as clearly as for the case of CCl_3, due to a larger dispersion in the experimental points at low pressure.

Apparently, the same trend is observed in the cases of CF_2Cl and $CFCl_2$ reactions, when the results of extrapolations are compared to the more reliable high-pressure-limit rate constants, derived from the high-pressure measurements available for the CF_3 and the CCl_3 reactions (see Table 4). Obviously, the nonvariational routine yields a value of k_∞ that is too high for the CF_2Cl and $CFCl_2$ reactions (around 3×10^{-11} cm^3 molecule^{-1} s^{-1}), whereas intermediate values of $(1-2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} would have been expected by comparison with the k_∞ values obtained for CF_3 and CCl_3. In contrast, the variational routine yields values in better agreement with the above expectation, as also presented in Table 4. It is worth noting that irrespective of the extrapolation method used, similar values of k_∞ are obtained for the three fluorine-containing radicals, whereas the value obtained for CCl_3 is a factor of 2−3 lower. The distinct value which seems to characterize the CCl_3 reaction will be discussed further below.

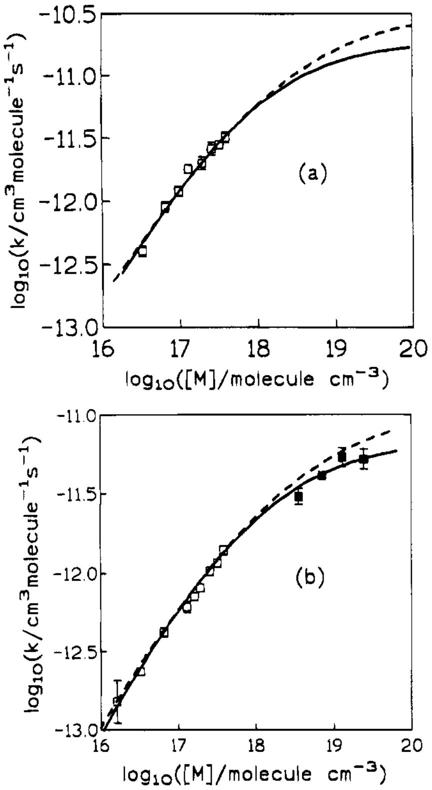

Figure 5. Comparison of calculated falloff curves obtained from nonvariational (dashed line) and variational routines (solid line) at 298 K: (a) for the CF_2Cl reaction; (b) for the CCl_3 reaction. Experimental data are from ref 5: the low pressure data (open symbols) were obtained using the same technique as in the present work, and the high pressure data (solid symbols) were obtained by flash photolysis.

TABLE 4: Values of k_∞ Obtained by the Different Extrapolation Procedures (Units of 10^{-11} cm^3 Molecule^{-1} s^{-1})

	CF_3	CF_2Cl	$CFCl_2$	CCl_3
a	3.0 ± 1.3	3.0 ± 0.8	3.0 ± 0.8	1.0 ± 0.4
b	2.0 ± 1.0	1.8 ± 0.6	1.8 ± 0.6	0.7 ± 0.3
c	1.8 ± 0.3			0.65 ± 0.1

[a] Extrapolated from low-pressure data only, using the nonvariational RRKM procedure. [b] Extrapolated from low-pressure data only, using the variational RRKM procedure. [c] Extrapolated from both low- and high-pressure data, using either the nonvariational or the variational RRKM procedures.

In conclusion, we believe that the variational routine offers the best representation of available experimental data for the particular series of CF_xCl_{3-x} + NO reactions considered in this work, and thus, the variational RRKM calculation was preferred for the representation of kinetic data of the entire series. The calculational procedure has been described previously.[18] It is only recalled here that the variational transition state is determined by using a switching function characterized by an adjustable parameter "c", allowing an interpolation between the partition function of products and those of reactants. As the calculations are carried out in the strong collision hypothesis, the collisional efficiency factor β_c is introduced to shift the calculated falloff curve along the pressure axis for best agreement with the low experimental results. β_c is the second adjustable parameter of the analysis, "reasonable" values of this

TABLE 5: Molecular Parameters for Reactants and Products of the Recombination Reactions 2 and 3

	CF_2ClNO^a	CF_2Cl	$CFCl_2NO^a$	$CFCl_2$
frequencies/cm^{-1}	1600	1208^c	1614	1143^c
	1244	1148^c	1139	919^c
	1149	761^c	943	747^c
	925	599^c	823	407^d
	768	477^d	756	378^d
	644	366^d	646	265^d
	439		527	
	439		399	
	353		362	
	283		306	
	225		232	
	70.7^b		71^e	
rotational constant/cm^{-1}	0.1217^d	0.109^d	0.0806^d	0.235^d
	0.085^d	0.153^d	0.0749^d	0.107^d
	0.069^d	0.386^d	0.0524^d	0.074^d
symmetry number	1	1	1	1
$\Delta H°_0$/kJ mol^{-1}	164 ± 4^b		171 ± 3^e	
Lennard-Jones parameters	$\sigma(CF_2ClNO) = 4.49$ Å $\epsilon/k(CF_2ClNO) = 392$ K		$\sigma(CFCl_2NO) = 4.96$ Å $\epsilon/k(CFCl_2NO) = 402$ K	
		$\sigma(N_2) = 3.63$ Å $\epsilon/k(N_2) = 91.5$ K		

[a] From ref 9. [b] From ref 28. [c] From ref 25. [d] Calculated using MNDO semiempirical method. [e] From ref 16.

parameter being $0.1 < \beta_c < 0.4$, with nitrogen as bath gas. These calculations are carried out using the program INTERVAR, which has been described recently.[18,24] The critical energy for dissociation, E_0, is taken to be equal to the negative of enthalpy change of reaction at 0 K, $\Delta H°_0$ as given in Table 1, the assumption being that there is no potential barrier to adduct formation for such association reactions.

Table 5 lists the molecular parameters of reactants and products used as input data in calculations related to reactions 2 and 3, along with the enthalpy changes of the reactions. The parameters used for reactions 1 and 4 are the same as those used in previous work.[5,7] Studies of the vacuum ultraviolet photolysis of CHF_2Cl and $CHFCl_2$[27] have led to the infrared determination of the value of the four highest vibrational frequencies for CF_2Cl and of the three highest for $CFCl_2$. The lowest frequencies and the principal moment of inertia were obtained from semiempirical MNDO calculations. As these radicals are not planar,[28,29] their symmetry numbers (σ) are equal to 1. Ernsting and Pfab[9] determined the 11 highest of the 12 fundamental vibrational frequencies of CF_2ClNO and $CFCl_2NO$ by infrared spectroscopy. The lowest torsional frequencies were obtained for CF_2ClNO[30] and $CFCl_2NO$[16] from the study of the fluorescence excitation spectrum in the visible region for jet-cooled molecules, which also allowed the determination of the C−N bond dissociation energies ($D_0 = -\Delta H°_0$),

$$D_0(CF_2Cl{-}NO) = (13700 \pm 350)\ \mathrm{cm^{-1}} = (164 \pm 4)\ \mathrm{kJ\ mol^{-1}}$$

$$D_0(CFCl_2{-}NO) = (14300 \pm 300)\ \mathrm{cm^{-1}} = (171 \pm 3)\ \mathrm{kJ\ mol^{-1}}$$

The principal moments of inertia were obtained from semiempirical MNDO calculations.

The Lennard-Jones parameters were determined with the method of Stiel and Thodos,[31] which uses the critical constants, obtained from the experimental boiling point[32] and from tables of Lydersen's critical property increments.[33] The corresponding values are listed in Table 5.

Results of Calculations

Since in our previous works, dealing with the reactions of CF_3[7] and CCl_3,[5] nonvariational RRKM calculations were used, the corresponding experimental results were reanalyzed together with those obtained in the present work for CF_2Cl and $CFCl_2$, in order to set a homogeneous representation of all the kinetic data of the series.

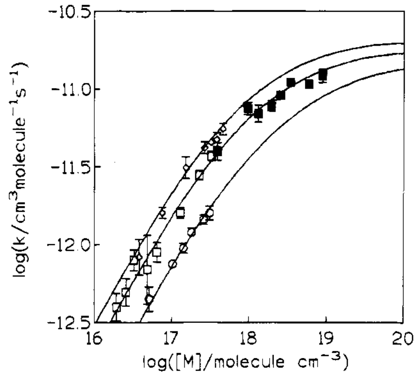

Figure 6. Pressure dependence of the bimolecular rate constant of the CF_3 reaction with NO: (◇) 253 K; (□) 298 K; (○) 373 K. Open symbols are from ref 7, buffer gas N_2. Closed symbols are from ref 8, buffer gas He. [M] is scaled by the factor 0.6, corresponding to the ratio $[k_0^{sc}(He)\beta_c(He)]/[k_0^{sc}(N_2)\beta_c(N_2)]$.

The parameters c (important at high pressure) and β_c (important at low pressure) were adjusted to obtain the best fit of the calculated curves to the experimental data obtained at 298 K. Calculations were then performed at other temperatures with the same value of c and fitted to experimental results by only adjusting β_c. The resulting curves are the solid lines shown in Figure 3, 4, 6, and 7, and the corresponding kinetic parameters are reported in Table 6. The experimental results shown in Figures 6 and 7 for the reactions of CF_3 and CCl_3 are reproduced from our previous studies.[5,7] It can be seen that the calculated falloff curves are good representations of all the experimental data, except for the data obtained for CCl_3 at 263 K between 4 and 12 Torr, where there were probably experimental complications, as already discussed in ref 5. For a better comparison of the reactions of the series, all falloff curves obtained at 298 K are presented together in Figure 8.

RRKM calculations return the third-order strong collision rate constants and their temperature dependences (in the form $k_0^{sc}(T) = k_0^{sc}(298)(T/298)^{n_0}$), which only depend on structural and thermochemical parameters of reactants and products. The

TABLE 6: Kinetic Parameters Resulting from the Variational RRKM Calculations

CF_xCl_{3-x}	$k^{sc}(298)$[b]	n_0[c]	$k_\infty(298)$[d]	n_∞[c]	$\beta_c(298)$[e]	p[e]
CF_3 (M = He)[a]	2.5 ± 0.1				0.06 ± 0.003	
(M = N_2)	1.8 ± 0.1	−2.9	1.8 ± 0.4	−0.8	0.14 ± 0.01	0
CF_2Cl	1.0 ± 0.3	−3.4	$1.8^{+1.0}{}_{-0.5}$	−1.1	0.19 ± 0.05	−0.9
$CFCl_2$	1.0 ± 0.2	−3.8	$1.8^{+1.0}{}_{-0.5}$	−1.4	0.13 ± 0.03	−1.0
CCl_3	$0.4^{-0.2}{}_{+0.4}$	−4.8	0.65 ± 0.12	−1.2	$0.3^{-0.15}{}_{+0.3}$	−0.7

[a] Calculations performed with $\sigma_{LJ}(He) = 3.608$ Å, $(\epsilon/k)_{LJ}(He) = 10.22$ K. [b] Units of 10^{-28} cm^6 molecule^{-2} s^{-1}. Error bars are only those resulting from the uncertainties on the values of $E_0 = -\Delta H°_0$ (see text). [c] Temperature dependencies of rate constants are expressed in the form $k_T = k(298)(T/298)^n$. [d] Units of 10^{-11} cm^3 molecule^{-1} s^{-1}. [e] Temperature dependence of $\beta_c = \beta_c(298)(T/298)^p$. Error bars are only those resulting from the uncertainties on the values of $E_0 = -\Delta H°_0$ (see text).

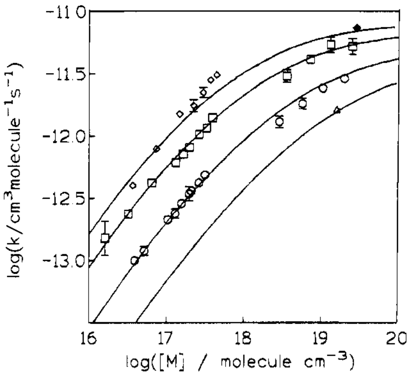

Figure 7. Pressure dependence of the bimolecular rate constant of the CCl_3 reaction with NO: experimental data are from ref 5; buffer gas N_2; (◇) 263 K; (□) 298 K; (○) 373 K; △ 465; (◆) extrapolated from experimental data obtained at higher temperatures and 1 atm of pressure, using the rate expression reported in ref 5. Solid lines are the results of variational RRKM calculations, fitted to experimental data.

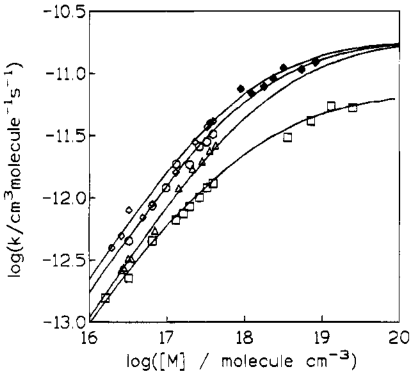

Figure 8. Pressure dependence of the bimolecular rate constant for the four reactions of the CF_xCl_{3-x} radicals at 298 K: buffer gas N_2; (□) CCl_3 + NO (ref 5); (△) $CFCl_2$ + NO (this work); (○) CF_2Cl + NO (this work); (◇) CF_3 + NO (ref 7). For this last reaction, the symbols (◆) represent the data from ref 8, buffer gas He. [M] is scaled by the factor 0.6, corresponding to the ratio $[k_0^{sc}(He)\beta_c(He)]/[k_0^{sc}(N_2)\beta_c(N_2)]$.

fitting to experimental data was obtained by adjusting β_c at each temperature and thus resulted in a temperature dependence for β_c ($\beta_{c(T)} = \beta_c(298)(T/298)^p$). For each reaction, a slight negative temperature dependence was observed for β_c ($p \approx -1$). It should be emphasized that the uncertainties quoted in Table 6 for k_0^{sc} and β_c are those resulting only from the uncertainties in $\Delta H°_0$, as discussed further in the next section.

Since only measurements at total pressures lower than 12 Torr are available for reactions 2 (CF_2Cl) and 3 ($CFCl_2$), the uncertainties in the determination of k_∞(298 K) are larger than in the case of reactions 1 (CF_3) and 4 (CCl_3), where measurements are available up to 760 Torr. As the interpolation parameter *c*, adjusted at 298 K, is conserved at all temperatures, the negative temperature dependence of k_∞ reported in Table 5 (in the form $k_\infty = k_\infty(298)(T/298)^{n_\infty}$) is the one returned by calculations. It is satisfying to observe that the calculated temperature dependence is in good agreement with the one observed experimentally in the case of the CCl_3 reaction, where measurements were performed near the high-pressure limit.[5] Unfortunately, such a comparison is not possible for other reactions. It is observed that the variational calculations return negative temperature dependencies for k_∞, with $n_\infty \approx -1$ for all reactions, a value generally observed for association reactions of this type.[35]

TABLE 7: Kinetic Parameters Resulting from the Fitting of Troe's Expression[a,b] to RRKM Falloff Curves

CX_3	$k_0^{298} \times 10^{29}$ [c]	n[e]	$k_\infty^{298} \times 10^{11}$ [d]	m[f]
CCl_3	0.85 ± 0.02	5.5 ± 0.1	0.55 ± 0.02	1.6 ± 0.2
$CFCl_2$	1.0 ± 0.2	4.8 ± 0.2	1.9 ± 0.1	1.5 ± 0.2
CF_2Cl	1.8 ± 0.2	4.4 ± 0.2	1.9 ± 0.1	1.5 ± 0.3
CF_3	2.0 ± 0.2	3.2 ± 0.2	1.9 ± 0.1	1.0 ± 0.2

[a] The uncertainties given are the standard deviations resulting from the fitting of Troe's expression to the RRKM falloff curves (see text). [b] The expression used is from ref 34 ($F_c = 0.6$). [c] Units of cm^6 molecule^{-2} s^{-1}. [d] Units of cm^3 molecule^{-1} s^{-1}. [e] The temperature dependence for k_0 is $k_0(T) = k_0^{298}(T/298)^{-n}$. [f] The temperature dependence for k_∞ is $k_\infty(T) = k_\infty^{298}(T/298)^{-m}$.

For the purpose of rate constant compilations it is advantageous to express the rate constants using an analytic function of temperature and pressure, such as that derived from the method developed by Troe.[34] Therefore, we have fitted the parameters of Troe's expression to the calculated falloff curves obtained from a variational RRKM calculation (which were themselves ajusted for the best representation of experimental results). This has resulted in the following values of the broadening factor F_c: 0.57, 0.60, 0.65, and 0.48 for the CF_3, CF_2Cl, $CFCl_2$, and CCl_3 reactions, respectively. All these values do not differ significantly from 0.6, even when their temperature dependences are taken into account, and thus, we have chosen to set $F_c = 0.6$ for presenting all our results using Troe's expression, in the same way as in the NASA compilation.[35] The resulting optimized parameters are given in Table 7. Note that the uncertainties quoted in Table 7 are standard deviations which only characterize the precision of the representation of the RRKM falloff curves by Troe's expression. The small errors confirm the accuracy of this representation. The real uncertainties are given in the abstract.

Troe's method may also be used to fit experimental data and to extrapolate to the pressure limits. In this case, the F_c factor has to be calculated from structural and thermochemical parameters and from weak collision factors. However, this method is useless in our case, since it is a simplifcation of the RRKM procedure that we have used above for our extrapolations. Nevertheless, as a test, we have calculated the F_c parameters, according to Troe's method[34] and found values of 0.4 ± 0.02 for all reactions. Extrapolation of low-pressure experimental data, using Troe's expression[34] along with the above values of F_c, yields values of k_∞ varying from 3 × 10^{-11}

to 5×10^{-11} cm^3 molecule^{-1} s^{-1} for CF_3, CF_2Cl, and $CFCl_2$ and around 1.0×10^{-11} cm^3 molecule^{-1} s^{-1} for CCl_3. These values are obviously too high when compared to the high-pressure experimental data available for CF_3 and CCl_3 and also appear too high for CF_2Cl and $CFCl_2$ if it is considered that we should keep a certain internal consistency in the results for the series. This shows that k_∞ values determined by extrapolation of low-pressure experimental data have no real physical significance. They are only parameters used in a given fitting procedure that gives the best representation of a set of experimental data. This is certainly the case of our values derived for $k_\infty(CF_2Cl)$ and $k_\infty(CFCl_2)$, even though we have chosen the extrapolation method that gives the best representation of the low- and high-pressure experimental data available for the other species of the series. Nevertheless, the error bars on k_∞ given in Table 6 and in the abstract for the CF_2Cl and $CFCl_2$ reactions seem to us reasonable in estimating the real value of k_∞ for these reactions, considering the consistency of the results in the present series of reactions.

Discussion

Accuracy of Results. The experimental results presented above for reactions 2 (CF_2Cl) and 3 ($CFCl_2$) are obtained in the low-pressure part of the falloff curve. The standard deviation of individual determinations of k_2 and k_3 is typically 10%, and it is estimated that the extrapolation to the low-pressure limit, performed using the variational RRKM method, should result in an error in k_0 of <20%.

The third-order strong collision rate constants k_0^{sc} are derived from RRKM calculations using as input parameters the enthalpy change of the reaction $\Delta H°_0$ ($= -E_0$) and the structural properties of the species. The resulting values of k_0^{sc} are strongly dependent on the values of $\Delta H°_0$, and the uncertainties on k_0^{sc} mainly result from the uncertainties on this parameter. RRKM calculations performed using the uncertainty limiting values of $\Delta H°_0$ give the uncertainty limits of k_0^{sc} indicated in Table 6. It can be observed that an error of about 2% in $E_0 = -\Delta H°_0$ results in an error of about 20% in k_0^{sc}. This is the maximum uncertainty resulting from $\Delta H°_0$ that can be evaluated for reactions 1–3 (CF_3, CF_2Cl, and $CFCl_2$), but it is larger in the case of reaction 4 (CCl_3): 8% on $\Delta H°_0$, resulting in an uncertainty factor of 2 for k_0^{sc}. These uncertainities are transferred to the values of the collision efficiency factors β_c, which are the ratio k_0/k_0^{sc}. Thus, the overall uncertainties in β_c are a combination of the above uncertainties and those in k_0 resulting from errors in the experimental data.

As already stated, the values of k_∞ for reactions 2 and 3 are derived from a long extrapolation from low-pressure determinations, and consequently, the uncertainties are large (up to a factor of 2). However, in the cases of reactions 1 and 4, measurements at high pressures are available, resulting in a better accuracy (errors < 20%). We have demonstrated above the interest of working with a series of homologous radicals such as that described here, for which the analysis method must yield consistent results for the whole set of experimental data. Obviously, once it has been proved that the analysis method yields consistent results for the entire series, the accurate data that have been obtained for a particular reaction of the series can help to improve the data for another reaction, where the results are missing or have poor accuracy.

It is clear that, in spite of the fairly large uncertainty, the extrapolation of the data obtained at low pressure in the cases of CF_2Cl and $CFCl_2$ (reactions 2 and 3) yields values of k_∞ close to that of reaction 1 (CF_3), i.e. about a factor of 3 larger than the value of k_∞ obtained for reaction 4 (CCl_3), as shown in Figure 8. It is worth noting that this effect is still true when other methods are used for extrapolating the low-pressure results (nonvariational RRKM routine or Troe's method). We have therefore assigned to reactions 2 and 3 the same value of k_∞ as the more accurate value obtained for the reaction of CF_3.

Having obtained a complete set of kinetic data for the whole series of reactions 1–4, it is of interest to examine how the evolution of the kinetic behavior in the series can be related to the structural and thermodynamical parameters of reacting species, via a theoretical model.

It can be observed that the value of k_0 regularly decreases from CF_3 to CCl_3. This trend is predicted within the limits of uncertainties, by the RRKM calculations, as the values of β_c can be considered to be the same for all reactions (Table 6). The higher value of β_c obtained in the case of CCl_3 (0.3 instead of 0.15–0.20 for other radicals) is not significant since the larger uncertainty on $\Delta H°_0$ obtained in this particular case results in an uncertainty of about a factor of 2 on β_c, as discussed above. Thus, all kinetic, structural, and thermodynamic data are self-consistent in the framework of the RRKM theoretical model. In particular, in the case of the reaction of CCl_3, it would have been expected from the low vibrational frequencies observed in CCl_3NO and hence higher density of states that the value of k_0 would have been the largest of the series. In fact, the low value of $\Delta H°_0 = -E_0$ (about 40 kJ mol^{-1} less than the values observed for other reactions) results in a significant decrease in the density of states, compared to the other reactions, which accounts for the low value of k_0 observed experimentally.

The experimental data concerning the reaction $CH_3 + NO$[36] have been analyzed using the same procedure as above. Calculations have resulted in a value of β_c of about 0.1 in argon, which is consistent with the values found in this work for halogenated radicals in nitrogen. It therefore appears that the kinetics of association reactions forming nitroso compounds are well described near the low-pressure limit by statistical theories such as RRKM and that such theories may be used in a predictive way. This means that the determination of k_0 from experimental results may be used for a fairly reliable evaluation of the enthalpy of reaction, using $\beta_c(N_2) = 0.2 \pm 0.1$ and vice versa. It should be recalled that an error of a factor of 2 on β_c only results in an error of about 10% in $E_0 = -\Delta H°_0$.

In contrast, there is no regular evolution of the rate constant at the high-pressure limit, as mentioned above, the value of k_∞ for CCl_3 being a factor of about 3 lower than other values in the series. Consequently, there is no obvious relation between the steric hindrance in the transition state and the value of k_∞. This particular behavior of the kinetics of the CCl_3 reaction is to be compared to the particular enthalpy of the reaction, which is also much smaller than the enthalpy of other reactions (Table 1). Therefore, it is very likely that a relationship exists between the reaction enthalpies and the kinetics at the high-pressure limit. No quantitative details can be given about such a relationship, since this would require an accurate description of the potential energy surfaces. The only simple comment that can be made is that, in the present series of reactions, the reactant with the smallest potential well depth (i.e. $\Delta H°_0$) has the smallest high-pressure rate constant. This connection between the kinetics at high pressure and the enthalpies of reactions was already observed for the reactions of CF_3 and CCl_3 with O_2[4] (for $CCl_3 + O_2$, $\Delta H°_0 = -82$ kJ mol^{-1} and $k_\infty = 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; for $CF_3 + O_2$, $\Delta H°_0 \approx -140$ kJ mol^{-1} and $k_\infty = 9.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}). However, the above observations are too qualitative for presenting any predictive character.

Conclusion

The combination of experimental measurements and RRKM calculations has led to a comprehensive description of the kinetics of the series of reactions studied in this work, from the low- to the high-pressure limits. The variational RRKM model used seems to be adequate for describing the shape of the falloff for combination reactions of radicals with NO. This allows fairly reliable extrapolations of data to conditions where experimental measurements could not be performed. The present work demonstrates the interest of dealing with an entire series of homologous radicals: both the experimental data and the theoretical model used must yield an internally consistent set of kinetic parameters for the whole series, and in addition, the kinetic parameters themselves have to be consistent with structural and thermochemical parameters. Thus, compared to a single reaction, dealing with the series introduces additional constraints which result in a better reliability of the final results.

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