theoretical corroboration⁴³ and experimental evidence⁴⁴ of such a fast cage effect for iodine atom recombination in solution.

When our results for the two phases of water are compared, there are a number of differences. The most significant difference is the increase in importance of ionization in the liquid compared to the gas. The variation of the entity-specific W value for ionization with energy shows the same trends in the two phases: a trough corresponding to events where only one ionization is possible followed by a long tail extending to an asymptotic value. However, in the liquid phase the trough is shallower and the asymptote is smaller. The distribution of ionizations and excitations for low-LET radiolysis shows the same effect. Ionization dominates excitation in the liquid while in the gas phase excitation exceeds ionization somewhat. In addition to the increased importance of ionization, the size of a typical event also increases in the condensed phase. This change will have a significant effect on the nonhomogeneous period of reaction that immediately follows radiolysis as the kinetics are strongly influenced by statistical effects upon encounter of the reactants.

Finally, it may be pointed out that while the satisfactory comparison of the calculated initial yields with the primary experimental yields of ionization and excitation is necessary, a more stringent test of the theory would require the comparison of the evolution of the yields of the primary species on the picosecond to nanosecond time scale. Kinetic calculations are currently in progress along these lines, and the results will be presented in the future. Meanwhile, we present the ionization and excitation distributions based on the available experimental information, which is a necessary link between the energy deposition statistics and the computation of the evolution of the yields.

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Kinetic Study of the Reaction $CCI_3 + O_2 + M \rightarrow CCI_3O_2 + M$ from 1 to 760 Torr and from 233 to 333 K

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The kinetics of reaction 1, $CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$, has been investigated in detail as a function of temperature and over a large pressure range. At low pressure, 0.8-12 Torr, the reaction was investigated by laser photolysis and time-resolved mass spectrometry, while at high pressure (760 Torr), flash photolysis with UV absorption spectrometry was employed. At the low-pressure limit, the rate expression, $k_1(0) = (1.6 \pm 0.3) \times 10^{-30} (T/298)^{-(6.3\pm0.5)}$ cm⁶ molecule⁻² s⁻¹ (M = N₂), exhibits a quite strong negative temperature coefficient. The obtained strong collision rate expression, $7.0 \times 10^{-30} (T/298)^{-4.3}$ cm⁶ molecule⁻² s⁻¹, using either RRKM calculations or Troe's factorized expression, is unable to reproduce the experimental temperature dependence, unless an unreasonably strong temperature dependence is assigned to the collisional efficiency factor: $\beta_c = 0.23(T/298)^{-2.0}$ (M = N₂). Similar results are obtained for other chlorofluoromethyl radicals. The falloff curves were constructed by using RRKM calculations obtained by adjusting β_c and the transition-state model, in order to reproduce the experimental data. The rate expression at the high-pressure limit was derived from these calculations $k_1(\infty) = (3.2 \pm 0.7) \times 10^{-12} (T/298)^{-(1.2\pm0.4)}$ cm³ molecule⁻¹ s⁻¹. All the parameters to be used in Troe's analytical expression for calculating the bimolecular rate constant at any pressure and temperature are given. The rate constant at the low-pressure limit $k_1(0)$ is more than an order of magnitude lower than for the CF₃ radical. The RRKM calculations show that this arises from a large difference in the C-O bond dissociation energies in the corresponding peroxy radicals: 81.9 kJ mol⁻¹ for CCl₃O₂ instead of ≈ 145 kJ mol⁻¹ for CF₃O₂.

Introduction

The reactions of halogenated radicals have received considerable interest in recent years as they are relevant to current problems in atmospheric chemistry, such as the release of chlorine in the stratosphere from CFC's and the release of chlorinated compounds from chlorinated plastics in the degradation and incineration of urban wastes. Haloalkyl radicals are oxidized in air according to a fairly well established reaction mechanism¹ in which the first step is the combination reaction of the radical with molecular oxygen.

A few studies of the combination reactions of chlorofluoromethyl radicals with O₂ have been reported in the literature. These studies were limited to either room temperature or small pressure ranges. The reactions of CF₃ and CCl₃ have been studied by pulse radiolysis at high pressure, 700 Torr, and at room temperature² but, as ethane was used as a Cl atom scavenger, it is likely that the observed kinetics of the formation of CCl₃O₂ were perturbed

by the UV absorption of the ethylperoxy radical. The reactions of CF₃,^{3,4} CCl₂F,⁵ and CCl₃⁶ have been studied at pressures under 12 Torr; only the reaction of CF_3 has been studied as a function of temperature.⁴ These studies revealed an interesting feature, since the reaction rate constant at the low-pressure limit increases by a factor of about 15 from CCl_3 to CF_3 . Calculations based on unimolecular reaction theories^{6,7} have indicated that this should

⁽¹⁾ Simonatis, R. In Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone; Nicolet, M., Aikin, A. C., Eds.; Algave: Portugal, 1979; p 501. Cox, R. A.; Lesclaux, R. Scientific assessment of stratospheric ozone, Vol. II: AFEAS Report; World Meteorological Organization, Report No. 20, 1989.

⁽²⁾ Cooper, R.; Cumming, J. B.; Mulac, W. A. Radiat. Phys. Chem. 1980, 16, 169.

⁽³⁾ Ryan, K. R.; Plumb, I. C. J. Phys. Chem. 1982, 86, 4678. (4) Caralp, F.; Lesclaux, R.; Dognon, A. M. Chem. Phys. Lett. 1986, 129,

⁴³³

[.] (5) Caralp, F.; Lesclaux, R. Chem. Phys. Lett. **1983**, 102, 54. (6) Ryan, K. R.; Plumb, I. C. Int. J. Chem. Kinet. **1984**, 16, 591. (7) Batt, L.; Stewart, P. Proc. 9th Int. Symp. Gas Kinet., Bordeaux, **1986**,

E48.

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Figure 1. Typical time-resolved mass spectrometric signal of the CCl₃O₂ radical buildup at m/e = 114 (CCl₂O₂⁺). The solid line is calculated by adjusting k_1 , after subtraction of the background.

arise from a significantly lower bond dissociation energy in CCl₃O₂ than in CF_3O_2 . This was corroborated by a recent determination of the enthalpy of the reaction of CCl_3 with O_2 , from the investigation of the equilibrium constant as a function of temperature.⁸

In this paper, we present a detailed investigation of the kinetics of reaction 1, over a large range of pressure and temperature.

$$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$$
 (1)

This study forms a part of our work on the reactions of chlorofluoromethyl radicals in order to understand how the reactivity varies from one compound to another in the series and if the theories of unimolecular reactions can account for the experimental results.

Two techniques were used for investigating the kinetics of reaction 1. At low pressures (8-12 Torr) pulsed laser photolysis coupled with time-resolved mass spectrometric detection of radicals was used, while flash photolysis with UV absorption detection was used at pressures of around 1 atm. The results allowed the falloff curves to be constructed from 1 to 760 Torr at different temperatures and extrapolations, either to the low- or to the highpressure limits, could be obtained with good accuracy. RRKM calculations have been carried out and are compared with experimental data. These calculations, as well as those performed according to Troe's simplified formalism,⁹ help understand the differences in reactivity between CCl₃ and CF₃ near the lowpressure limit.

Experimental Results

A. Low-Pressure Measurements Using Mass Spectrometric Detection. Apparatus. A detailed description of the experimental setup has been reported in a previous publication.¹⁰ Only the principal features are given here including some particular details concerning the present study.

CCl₃ radicals were produced by pulsed laser photolysis of CCl₄ at 193 nm, using an excimer laser (Lambda Physics, Model EMG 500), which was fired at a frequency of about 1 Hz. The gas mixture was continuously flowed into the reactor, so that it was renewed after a few shots. The concentrations were obtained from the flow rates and the total pressure in the reactor. The temperature of the reactor could be varied from -40 to 150 °C and controlled to within ± 2 °C. The carrier gas was nitrogen.

Radical species were detected by time-resolved mass spectrometry (Balzers, Model QMG 500), using molecular beam sampling. All kinetic measurements were performed by monitoring the time-resolved formation profile of the CCl_3O_2 radical at m/e= 114, corresponding to the $CCl_2O_2^+$ fragment. The signals were stored in a multichannel analyzer and transferred to a microcomputer for data analysis. Generally, 4000-5000 shots were accumulated for an acceptable signal to noise ratio. The experimental data were analyzed by numerical integration of the reaction mechanism coupled with nonlinear least-squares fitting.

Products. Nitrogen (99.995%) and oxygen (99.995%), from l'Air Liquide were used directly from the cylinder. CCl₄ (99.9%) from Prolabo, was degassed and used without further purification.

Results. A typical trace, shown in Figure 1, shows the timeresolved buildup of the CCl_3O_2 radical. The initial concentration of CCl₃ radicals was around 10¹² molecules cm⁻³. The decay of the signal could be recorded over a longer time than shown in the figure, so that the loss of radicals during the occurrence of reaction 1 could be evaluated by simulating the reaction mechanism shown in eqs 2-7. R includes all radicals present in the reaction system

$$CCl_4 + h\nu \rightarrow CCl_3 + Cl$$
 (2a)

$$\rightarrow CCl_2 + 2 Cl$$
 (2b)

$$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M \tag{1}$$

$$CCl_3 + R \rightarrow products$$
 (3)

$$CCl_3O_2 + R \rightarrow products$$
 (4)

$$R + R \rightarrow \text{products}$$
 (5)

$$CCl_3 + walls \rightarrow products$$
 (6)

$$CCl_3O_2 + walls \rightarrow products$$
 (7)

and the products are supposed to be unreactive molecules. The rate constants k_3 , k_4 , k_5 , k_6 , and k_7 were adjusted in order to fit the decay of CCl₃O₂ over a period of 50 ms (by computer simulation of the above reaction mechanism). The first-order contribution, due to reactions at the walls, was the most important (> \approx 70%). Typical values of k_7 were around 50 s⁻¹. It was assumed that $k_3 = k_4 = k_5$ and that $k_6 = k_7$. These approximations seemed reasonable since radical-radical reactions were unimportant and the loss of radicals during the formation of CCl_3O_2 , which takes place over a much shorter time scale of a few milliseconds, was only of the order of 10%. Therefore, reaction 1 was by far the principal rate-determining process of the CCl₃O₂ buildup. No physical significance could be given to the values of k_3 , k_4 , and k_5 , since the radical concentration was not known accurately and changed from one experiment to another. The reaction of CCl_2 radicals with oxygen is very slow¹¹ and was ignored. In addition, it is very unlikely that the radical CCl₂O₂, which eventually could be formed in this reaction, interferes with the fragment $CCl_2O_2^+$, since parent ions of peroxy radicals have never been detected by mass spectrometry.

Preliminary experiments were found to be poorly reproducible, particularly when the initial concentration of radicals was changed by varying the laser pulse intensity. This was attributed to the fast reactions of Cl atoms with CCl₃ and CCl₃O₂ radicals⁸ and was overcome by scavenging Cl atoms with small amounts of propane, which instantaneously converted chlorine atoms into less reactive radicals

$$Cl + C_3H_8 (+ O_2) \rightarrow HCl + R$$
(8)

thus allowing Cl atoms to be included in the radicals R.

The experimental conditions were the following: (1) total pressure, 0.5-12 Torr; nitrogen was the buffer gas, except at the lowest pressures where oxygen was preponderant (the collisional deactivation efficiencies were assumed to be the same for O_2 and N_2 ; (2) temperatures of experiments: 233, 263, 298, and 333 K; at higher temperature, the reaction becomes equilibrated,⁸ thus preventing the kinetics of reaction 1 to be studied under clean conditions; (3) concentration of CCl₄, (3–10) \times 10¹⁴ molecules cm⁻³; (4) concentration of oxygen, $(2-100) \times 10^{14}$ molecules cm⁻³, which resulted in pseudo-first-order rate constants for reaction 1, ranging from 300 to 2000 s^{-1} ; (5) concentration of propane,

⁽⁸⁾ Russel, J. J.; Seetula, J. A.; Gutman, D.; Danis, F.; Caralp, F.; ightfoot, P. D.; Lesclaux, R.; Melius, C. F.; Senkan, S. M. J. Phys. Chem. 1990, 94, 3277.

⁽⁹⁾ Gardiner, W. C.; Troe, J. In Combustion Chemistry; Gardiner, W. C., Ed.; Springer-Verlag: New York, 1984; p 173. (10) Lesclaux, R.; Caralp, F. Int. J. Chem. Kinet. 1984, 16, 1117.

⁽¹¹⁾ Meunier, H.; Purdy, J. R.; Thrush, B. A. J. Chem. Soc., Faraday Trans. 2 1980, 76, 1304



Figure 2. Plots of the pseudo-first-order formation rate of CCl₃O₂ at 233, 298, and 333 K, obtained for a total gas density of 1.25×10^{17} molecules cm⁻³ (buffer gas, nitrogen).



Figure 3. Pressure dependence of the bimolecular rate constant for reaction 1. The low-pressure data (open symbols) were obtained by laser photolysis and time-resolved mass spectrometry. The high-pressure data (closed symbols) were obtained by flash photolysis and time-resolved UV absorption. Full lines are the results of RRKM calculations, fitted to experimental data (see text). The dashed line represents the data obtained at 298 K in helium by Ryan and Plumb (ref 6).

 $(3-5) \times 10^{14}$ molecules cm⁻³; (6) initial radical concentration, around 10¹² molecules cm⁻³.

Since CCl₃ concentrations were always much smaller than those of oxygen, all experiments were performed under pseudo-first-order conditions.

The experimental values of the bimolecular rate constant k_1 are given in Table I for each pressure and each temperature. Many of these values were obtained from several runs performed with different concentrations of oxygen. An example of a plot of the pseudo-first-order rate constant as a function of oxygen concentration is given in Figure 2, for three temperatures and for a total gas density of 1.25×10^{17} molecules cm⁻³. Reasonable linear plots going through the origin were obtained, showing that conditions of measurements were satisfactory and that loss of radicals was correctly taken into account. The plots show the strong negative temperature coefficient observed for this reaction at low pressure.

All the data given in Table I are represented in the form of falloff curves in Figure 3 (open symbols). The plots show that these data are located at the low-pressure end of the falloff and cannot therefore be extrapolated to the high-pressure limit with an acceptable accuracy. Thus, measurements at higher pressure, as presented in next section, were necessary.

The dashed line in Figure 3 represents the results obtained by Ryan and Plumb⁶ at 298 K, in the same pressure range as the present measurements, but using helium as the buffer gas. The rate constants at a given pressure are about twice as low as those obtained in this work, using nitrogen as the buffer gas. Such a

TABLE I: Experimental Results Obtained by Laser Photolysis and Time-Resolved Mass Spectrometry at Low Pressure: <12 Torr

	total gas		
	density ×	$k_1 \times 10^{13} / \text{cm}^3$	no.
<i>T/</i> K	10 ⁻¹⁷ /molecules cm ⁻³	molecule ⁻¹ s ⁻¹	of runs ^a
233	0.37	1.5	1
	0.62	2.0	1
	0.83	2.5	2
	1.25	3.6	8
	1.66	4.7	2
	2.08	5.4	2
	2.49	5.5	2
	3.32	6.5	1
	4.15	7.0	7
	5.03	7.7	4
263	0.37	0.7	1
	0.74	1.1	1
	0.92	1.2	1
	1.29	1.8	1
	2.21	2.5	1
	2.94	3.5	1
200	4.41	4.0	1
298	0.26	0.27	1
	0.35	0.35	3
	0.49	0.43	3
	0.05	0.33	3
	0.97	0.0	4
	1.23	0.9	2
	1.43	1.05	5
	2.6	1.25	2
	2.0	1.5	2
	3.25	2.0	5
333	0.38	015	1
555	0.44	0.19	1
	0.58	0.25	1
	1.02	0.43	2
	1.25	0.49	8
	1.31	0.57	2
	1.45	0.5	1
	1.9	0.82	2
	2.32	0.77	2
	2.91	1.1	1
	3.49	1.2	2

^a Performed with different concentrations of oxygen; the corresponding value of k_1 is an average.

difference is expected¹² and was corroborated by recent results.¹³

Fitting these low-pressure data using Troe's equation¹⁴ yields the following expression for the low-pressure limiting rate constant for reaction 1 $(M = N_2)$:

$$k_1(0) =$$

 $(1.6 \pm 0.3) \times 10^{-30} (T/298)^{-(6.3 \pm 0.5)} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$

More details on the derivation of this expression are given in the Discussion section. It should be noticed that it can be slightly influenced by the value of the high-pressure limiting rate constant used in Troe's equation. This expression was actually obtained after measurements at high-pressure and RRKM calculations had been carried out, as reported in the following sections. Note that the value of $k_1(0)$ at room temperature is more than an order of magnitude smaller than the value found for the equivalent reaction of the CF₃ radical: 19×10^{-30} cm⁶ molecule⁻² s⁻¹.⁴

B. High-Pressure Measurements Using Flash Photolysis and UV Absorption Detection. Apparatus. The flash photolysis setup has been described in detail in a recent publication.¹⁵ In brief,

⁽¹²⁾ Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr,

⁽¹²⁾ Atkinson, R.; Bauicn, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Troe, J. J. Phys. Chem. Ref. Data **1989**, 18, 881. (13) Experiments in Prof. D. Gutman's laboratory on the reactions of the series CH₂Cl, CHCl₂, and CCl₃ with O_2 , using both nitrogen and helium bath gases, have confirmed this result, with $k_1(0)(N_2)/k_1(0)(\text{He}) \approx 1.6$ for CCl₃ at room temperature. The absolute values of k_1 are, however, around a factor of 1.5 lower than the present values, over the same pressure range. Lightfoot, P. D.; Niiranen, J.; Gutman, D. To be submitted for publication.

⁽¹⁴⁾ Troe, J. Ber. Bunsen-Ges. Phys. Chem. 1983, 87, 161.

The $CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$ Reaction

the reactor consisted of a thermostated Pyrex cell, surrounded by two flash lamps, dissipating 300-500 J of electrical energy in about $5 \ \mu s$. The cell was provided with two quartz windows for monitoring the radical concentrations by UV absorption. The analysis beam, provided by a deuterium lamp, passed twice through the cell (139 cm path length) and impinged on a monochromatorphotomultiplier unit. The signals were stored in a transient recorder and transferred to a microcomputer for averaging and data processing. Ten to thirty shots were usually averaged.

Trichloromethyl radicals were generated by flashing molecular chlorine in the presence of chloroform:

$$Cl_2 + h\nu \rightarrow 2Cl$$
 (9)

$$Cl + CHCl_3 \rightarrow HCl + CCl_3 \tag{10}$$

 $k_{10} = 1.45 \times 10^{-11} \exp(-1380/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 16)}$

The concentration of chloroform was sufficient for making reaction 10 complete during the flash duration and to prevent Cl atoms from reacting with CCl_3 and CCl_3O_2 , as discussed in a previous publication.⁸

The UV absorption spectrum of CCl₃ and CCl₃O₂ have been reported in previous publications.^{8,17} CCl₃ has an absorption band peaking at 211 nm while CCl₃O₂ exhibits a broad and flat absorption between 200 and 260 nm. Most kinetic measurements were performed at 220 nm where the signal-to-noise ratio was maximum. At this wavelength, the absorption cross sections of CCl₃ and CCl₃O₂ are 9.9×10^{-18} and 1.65×10^{-18} cm² molecule⁻¹, respectively. The large difference between these values allowed the conversion of CCl₃ into CCl₃O₂ to be easily monitored by UV absorption.

The gas mixture, Cl_2 , $CHCl_3$, and O_2 diluted in N_2 , was continuously flowed through the reactor with a residence time of around 30 s, so that it was renewed after each flash. Concentrations were determined for each component from its flow rate and from the total pressure. All experiments were performed at 760 Torr.

Products. Nitrogen (99.995%) oxygen (99.995%) and chlorine (5% in nitrogen), from l'Air Liquide were used directly from the cylinder. Chloroform, spectroscopic grade from Aldrich, contained 0.5-1% of ethanol for stabilization. Ethanol was removed, either by distillation or by storing chloroform over molecular sieves, under nitrogen atmosphere.

Results. Fairly high radical concentrations $((4-10) \times 10^{13} \text{ molecules cm}^{-3})$ had to be used in this system, for good signal to noise ratio. Thus, the following reaction mechanism, including radical-radical reactions, was taken into account in simulations of the decay curves of the CCl₃ radical:

$$CCl_1 + CCl_2 + M \rightarrow C_2Cl_4 + M \tag{11}$$

$$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M \tag{1}$$

$$2CCLO_{2} \rightarrow 2CCLO + O_{2} \qquad (12)$$

$$CCl_3 + CCl_3O_2 \rightarrow 2CCl_3O$$
 (13)

$$CCl_{2}O \rightarrow CCl_{2}O + Cl \qquad (14)$$

$$Cl + CHCl_3 \rightarrow HCl + CCl_3 \tag{10}$$

As the CCl_3O_2 radical builds up, the above chain reaction starts, regenerating CCl_3 , in which the main terminating step is reaction 11. The principal absorbing species are CCl_3 and CCl_3O_2 radicals. In order to obtain a good simulation until the very end of the decay trace, the absorption of other reactants and products was taken into account: formation of C_2Cl_6 and CCl_2O and consumption of $CHCl_3$, which resulted in a small contribution to the absorption at long reaction times. Nevertheless, the first stages of the decay were the most important for the determination of k_1 which was



Figure 4. Time-resolved signal recorded at 240 nm, showing the formation of CCl₂O in the chain reaction (reactions 10, 1, 12, and 14) initiated by the flash. The full line was obtained by simulation of the reaction mechanism, by adjusting k_{12} (see text).

therefore only slightly influenced by these small contributions to absorption.

A second chain reaction took place owing to the presence of the CCl₃ radical in the reacting system:

$$CCl_3 + Cl_2 \rightarrow CCl_4 + Cl$$
 (15)

 $k_{15} = 6.7 \times 10^{-13} \exp(-2500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 18)}$

$$Cl + CHCl_3 \rightarrow HCl + CCl_3$$
 (10)

Reaction 15 is fairly slow in the temperature range of the study (253-333 K), therefore limiting the extent of the chain. These reactions did not have any effect on the overall kinetics since any CCl₃ radical reacting in reaction 15 was instantaneously recovered in reaction 10. However, this chain reaction was included in the reaction system for taking into account the additional very small change in absorption due to the consumption of CHCl₃ and to the formation of CCl₄. The absorption cross sections of the stable molecules were either known, 1.7×10^{-19} and 1.15×10^{-19} cm² molecule⁻¹ for CCl₄ and CCl₂O, respectively, ¹⁹ or were measured in the laboratory, 1.8×10^{-20} and 1.5×10^{-18} cm² molecule⁻¹ for CHCl₃ and C₂Cl₆, respectively, all at 220 nm. An uncertainty of a factor 2 on these absorption cross-sections would result in an uncertainty smaller than 1% in k₁.

It should be emphasized that only reactions 1 and 11 had an important contribution to the decay rate of CCl_3 . The contribution of reaction 11 was significant, particularly at low oxygen concentrations, as fairly high initial concentrations of radicals had to be used. The kinetics of this reaction was investigated in detail in this laboratory,¹⁷ yielding the following rate expression

$$k_{11} = 3.3 \times 10^{-12} (T/298)^{-1.0} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

independent of pressure in the temperature range of this study. An uncertainty of 20% in k_{11} results in an error smaller than 2% in k_1 .

Reaction 14 is very fast²⁰ and was considered as instantaneous. The rate constant of reaction 12 could not be measured directly by using our chemical system, since the reaction is part of the chain which regenerates the CCl₃O₂ radical through reactions 12, 14, 10, and 1. Indeed, no significant decay of the CCl₃O₂ absorption could be observed at 260 nm, in the presence of an excess of oxygen, during a period of time up to 100 ms. If the absorption is recorded at 240 nm during 500 ms, the generation of CCl₂O can be clearly seen, as shown in Figure 4. Reaction 12 is the rate-limiting step of the chain reaction and, therefore, its rate constant can be derived from the rate of formation of CCl₂O. By use of the known absorption cross section of CCl₂O ($\sigma_{240 nm} = 1.10 \times 10^{-19} \text{ cm}^2$ molecule⁻¹),¹⁹ the trace shown in Figure 4 was fitted by simulating the above reaction mechanism. The only adjustable

⁽¹⁵⁾ Lightfoot, P. D.; Lesclaux, R.; Veyret, B. J. Phys. Chem. 1990, 94, 700.

⁽¹⁶⁾ Clyne, M. A.; Walker, R. F. J. Chem. Soc., Faraday Trans. 1 1973, 69, 1547.

⁽¹⁷⁾ Danis, F.; Caralp, F.; Veyret, B.; Loirat, H.; Lesclaux, R. Int. J. Chem. Kinet. 1989, 21, 715.

⁽¹⁸⁾ Timonen, R. S.; Russel, J. J.; Gutman, D. Int. J. Chem. Kinet. 1986, 18, 1193.

⁽¹⁹⁾ Okabe, H. Photochemistry of Small Molecules; Wiley: New York, 1978.

⁽²⁰⁾ Lesclaux, R.; Dognon, A. M.; Caralp, F. J. Photochem. Photobiol. A 1987, 41, 1.



Figure 5. UV absorption decay traces of CCl₃ radical obtained at 220 nm by flash photolysis: total pressure, 760 Torr (buffer gas, nitrogen); [CHCl₃] = 2.4×10^{17} molecules cm⁻³; [Cl₂] = 6.4×10^{16} molecules cm⁻³; [CCl₃]₀ = 7.4×10^{13} molecules cm⁻³. Trace a, no oxygen; trace b, [O₂] = 9.0×10^{14} molecules cm⁻³; trace c, excess of oxygen. Solid lines are the results of simulations.

parameters were k_{12} , which determined the initial slope of the curve, and a factor, which arbitrarily took into account a first-order loss of radicals, for reproducing the curvature of the trace. The following expression

$$k_{12} = (1.6 \pm 0.8) \times 10^{-12} (T/298)^{(-3\pm1)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

was derived from a few runs performed at the temperatures of experiments given below.

The rate constant of reaction 13 was evaluated in a previous study of the equilibrium of reaction 1: $k_{13} = (1.0 \pm 0.5) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ and was assumed independent of temperature.⁸

The chain reaction composed of reactions 1, 12, 13, 14, and 10 distorded the shape of the CCl₃ decay, slightly from a pure pseudo-first-order behavior. It also tended to slow down the removal of the CCl₃O₂ radical, which thus appeared as a stable product on a time scale of a few milliseconds. As a result, the value of k_1 derived from simulations was only slightly dependent on the rates of the reactions involved in the chain. Reactions 10 and 14 had no influence, as they are very fast and thus not rate determining for the chain reaction. Concerning reactions 12 and 13, a variation of a factor 2 of their rate constant resulted in variations of k_1 of about 3% and 1% respectively, at the lowest oxygen concentrations, the influence was negligible.

The experimental conditions were the following: (1) total pressure, 760 Torr, nitrogen being the buffer gas; (2) temperatures of measurements: 253, 298, and 333 K; at higher temperatures, the reaction became equilibrated;⁸ (3) concentration of molecular chlorine, $(2-5) \times 10^{16}$ molecules cm⁻³; (4) concentration of chloroform, $(2-5) \times 10^{17}$ molecules cm⁻³; (5) initial concentration of CCl₃, $(5-10) \times 10^{13}$ molecules cm⁻³; (6) concentration of oxygen, $(1.8-15) \times 10^{14}$ molecules cm⁻³, resulting in pseudo-first-order rate constants varying from 300 to 2700 s⁻¹.

Typical signals are given in Figure 5 for three different experimental conditions. Figure 5a represents the decay of the CCl₃ radical in the absence of oxygen, according to second-order kinetics

TABLE II: Experimental Results Obtained by Flash Photolysis and Time-Resolved UV Absorption at 760 Torr

	10 1 × 10-14/		le lama	
T / 1 /		1	κ_1/cm^2	
<u>7/K</u>	molecules cm ⁻³	$\kappa_1 \times [O_2]/s^{-1}$	molecule" s	_
253	1.8	440		
	1.8	580		
	3.6	860		
	5.3	1300		
	7.1	1920		
	8.9	2050		
	9.1	2700		
			2.62×10^{-12}	
298	3.0	380		
	6.1	760		
	9.0	1160		
	9.0	1340		
	9.1	1440		
	10.1	1380		
	12.3	1860		
		1000	1.44×10^{-12}	
333	3.1	240		
555	5.8	480		
	85	860		
	10.5	1000		
	12.9	1160		
	150	1560		
	15.0	1500	0.07 × 10-12	
			0.7/ ~ 10	

^a From the slope of the plots in Figure 6.



Figure 6. Plots of the pseudo-first-order decay rates of CCl_3 at 253, 298, and 333 K, obtained at 760 Torr by flash photolysis and time-resolved UV absorption. Buffer gas, nitrogen.

due to reaction 11 alone. The trace obtained in the presence of an excess of oxygen is shown in Figure 5c where the absorption is essentially that of CCl_3O_2 , which does not decay significantly, as described above, as a result of the occurrence of the chain reaction. The decay trace shown in Figure 5b is obtained in the presence of an intermediate concentration of oxygen. The kinetics is complex since reactions 1, 11, and the chain reaction occurred at the same time, although reactions 1 and 11 were by far the dominant pathways for the CCl_3 decay. In addition, the consumption of oxygen was taken into account in calculations. The figure shows that the experimental trace could be well reproduced by computer simulation of the above reaction mechanism.

The experimental values of k_1 , obtained at three temperatures and for different concentrations of oxygen are given in Table II. The pseudo-first-order rate constants are plotted in Figure 6 as a function of oxygen concentration. The linear plots, going through the origin, indicate that the conditions of experiments and the reaction mechanism were satisfactory. The results show that, even at this high pressure, the reaction rate constant still exhibits a large negative temperature coefficient. The rate expression obtained at 760 Torr is

$$k_1(760 \text{ Torr}) =$$

$$(1.45 \pm 0.2) \times 10^{-12} (T/298)^{-(3.6\pm0.4)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The closed symbols on the falloff curves in Figure 3 represent the data obtained at 760 Torr, as calculated from the above expression for the same temperatures as those for which the low-pressure experiments were performed. It can be seen that both the rate constants and the temperature dependence are consistent with those obtained at low pressure, using a different technique. The negative temperature coefficient is still fairly high at this pressure, where the rate constant is about half the value at the high-pressure limit. This results in a negative temperature coefficient for the high-pressure limit, when fitting the whole data, as shown in the next section.

Theoretical Calculations

A. RRKM Calculations. The experimental data described above were obtained in two different pressure ranges: 760 Torr for the high-pressure measurements and <12 Torr for the lowpressure data. RRKM calculations were carried out and fitted to these experimental data in order to perform good extrapolations to the low- and high-pressure limits. In addition, the other important purposes of the RRKM calculations were the following: (1) to construct a theoretical model which accounts for the present experimental data, in particular the pressure dependence of the rate constant and its strong negative temperature coefficient; (2) to understand the large difference between the low-pressure limiting rate constants measured in the present work for the reaction of CCl₃ with O₂ and in a previous study for the equivalent reaction of CF₃.4

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M \tag{16}$$

For this purpose, similar calculations were performed for both reactions 1 and 16.

RRKM calculations were performed for the unimolecular dissociation of the peroxy radicals, according to the procedure developed by Forst and presented in detail in a previous paper.²¹ Rate constants for the association reaction were then derived by using the equilibrium constant which was itself determined from the partition functions of reactants and products and from the enthalpy ΔH°_{0} of the reaction. The previous procedure²¹ was slightly modified in this work: the external rotation around the C-O axis corresponding to the K rotational quantum number was taken to be active.

The parameters required for these calculations are the molecular parameters, i.e., vibrational frequencies and moments of inertia for all species involved in the reactions and the critical energy E_0 , which was identified to the enthalpy ΔH^{o}_{0} of the reaction since the experimental results indicate that there is no potential barrier on the reaction coordinate. In addition, a model for the transition state has to be chosen.

Few molecular parameters are known from experiments. As one of the principal aims of this work is to perform comparable calculations for both CCl₃ and CF₃ and also (currently and in the future) for other radicals, it is very important to carry out these calculations in the same way, using consistent sets of molecular parameters for all species in the two reactions. Such consistent sets were built by calculating all vibrational frequencies and moments of inertia by using the semiempirical SCF/UHF MNDO method. These semiempirical methods are known to produce fairly good geometries and force constants for molecular species. However, some systematic errors are obtained, particularly for the vibrational frequencies of the stretching modes, which are usually too high by 15-25%. This was the case for the present calculations, as seen by comparison of calculated and experimental data, when available. All the vibrational frequencies were then corrected according to the recommendations of Dewar et al.22 and are given in Table III, along with the values of moments of inertia. The calculated value of the O-O stretch frequency is always abnormally high in MNDO type calculations: 1800 cm⁻¹ instead of 1100 cm⁻¹ for the experimental value of peroxy radicals. This

TABLE III: Spectroscopic and Molecular Parameters Used in **RRKM Calculations**

	CF ₃	CCl ₃	CF ₃ O ₂	CCl ₃ O ₂	O ₂	N ₂
	V	ibrationa	I Frequen	cies/cm ⁻¹		
	1386	895	1100	1100	1590	
	1386	895	1292	1017		
	971	443	1270	815		
	660	251	1129	761		
	530	251	870	523		
	525	145	728	424		
			596	370		
			584	326		
			469	273		
			398	213		
			300	195		
			70	80		
	M	oments o	f Inertia/1	0^{-40} g cm^2		
I.	79	259	154	455		
I _B	79	259	268	506		
Ι _c	155	517	270	553		
		Lennard	-Jones Par	ameters		
σ/Å			4.96	5.95		3.68
$(\epsilon/k)/K$			188	323		91.5

last value was then chosen for both CCl_3O_2 and CF_3O_2 .

In our previous paper,⁸ dealing with the equilibrium constant of reaction 1, vibrational frequencies of CCl₃ and CCl₃O₂ radicals were calculated by Melius by using the SCF/UHF ab initio method. In spite of some differences in vibrational frequencies, compared to the values used in this work, both the MNDO and ab initio sets of frequencies yielded calculated entropies for the reactions, which were the same within uncertainties. Since, as explained above, we want to use in this work (and in other works performed in our laboratory) the MNDO sets of vibrational frequencies, we have used in the present calculations a value of the critical energy, $E_0 = \Delta H^0_0$, slightly different from that derived from the previous work:⁸ 81.9 instead of 80.6 kJ mol⁻¹. The difference is not significant but this was necessary for making consistent the value of E_0 , the MNDO set of vibrational frequencies and the experimental value of the equilibrium constant.

Concerning the equivalent reaction of CF₃, it appears that all authors have used Vedeneev's value,²³ $\Delta H^{o}_{0} = -141 \text{ kJ mol}^{-1}$, which was estimated from kinetic data, fitted by using RRKM calculations in which ΔH^{o}_{0} was an adjustable parameter. It would not be correct therefore to reintroduce this parameter into our own calculations. By studying the oxidation of CF₃Br in the temperature range 800-1100 K, Antonik²⁴ obtained a rough estimate of the activation energy for the thermal dissociation of CF_3O_2 of 157 kJ mol⁻¹. A reinterpretation of the results yielded $\Delta H_0^{\circ} = -(150 \pm 15) \text{ kJ mol}^{-1}$ for the association reaction of CF₃ with O_2 . This is slightly higher than Vedeneev's value but still much smaller than the estimate of Batt and Walsh²⁵ of 205 kJ mol⁻¹, obtained by using an additivity method. Since a large uncertainty exists on the critical energy E_0 for the reaction of CF₃ $+ O_2$, we have chosen to carry out the calculations in exactly the same way as for the reaction of $CCl_3 + O_2$, by just changing the molecular parameters and adjusting E_0 to reproduce the experimental data at low pressure, with the same collisional efficiency β_c . The resulting value of E_0 will be compared to the above estimates and discussed in connection with the difference in reactivity between CCl₃ and CF₃.

The model chosen for the activated complex was the modified Gorin model:^{26,27} the seven frequencies of the "conserved" degrees

⁽²³⁾ Vedeneev, V. I.; Propoi, V. I.; Sarkisov, O. M. Kinet. Catal. (Engl. Transl.) 1980, 21, 854. Teitel'Boim, M. A.; Gol'Denberg, M. Ya.; Vedeneev, V. I. Oxidation Commun. 1983, 3, 315.

 ⁽²⁴⁾ Antonik, S. Bull. Soc. Chim. Fr. 1983, I-117.
 (25) Batt, L.; Walsh, R. Int. J. Chem. Kinet. 1983, 15, 605.

⁽²⁶⁾ Benson, S. W. Thermochemical Kinetics, 2nd ed.; Wiley: New York, 1976.

⁽²¹⁾ Caralp, F.; Lesclaux, R.; Rayez, M. T.; Rayez, J. C.; Forst, W. J. Chem. Soc., Faraday Trans. 2 1988, 84, 569. (22) Dewar, A. J. S.; Ford, G. P.; KacKee, M. L.; Kzepa, H. S.; Thiel, W.; Yamamoochi, Y. J. Mol. Struct. 1978, 43, 135.

⁽²⁷⁾ Davies, J. W.; Pilling, M. J. Bimolecular Collisions. In Advances in Gas Phase Photochemistry and Kinetics; Ashfold, M. N. R., Baggott, J. E., Eds.; Royal Society of Chemistry: London, 1989; p 105.

of freedom were taken equal to those of the CX₃ (CCl₃ or CF₃) and O₂ fragments; the C–O stretch became the reaction coordinate; the deformation and torsional modes became two twodimensional restricted rotors. A hindrance parameter η was used to take into account the restriction of the rotation.²⁷ The effective moments of inertia of each restricted rotors were given by $I' = I(1 - \eta/100)^{1/2}$, where I is the moment of inertia for the isolated moiety $(I = (I_A I_B)^{1/2}$ for CX₃ and $I = I_{O_2}$ for oxygen).

Results of Calculations

Calculations were first carried out for CCl₃ since both an accurate value of E_0 and measurements of the rate constant at high pressure as a function of temperature were available. At each temperature, η and β_c were used as variable parameters in the RRKM calculations to fit both the high- and the low-pressure experimental results. Given the large pressure range explored in experiments, η and β_c were only slightly interdependent in the fitting procedure.

At high pressure, η was the most important parameter which determined the extrapolation to $k(\infty)$. Of course, different values of η had to be chosen for the different temperatures investigated, in order to reproduce the temperature dependence of the rate constant, particularly to 760 Torr. This procedure resulted in the following expression for the high-pressure limit of the rate constant:

 $k_1(\infty) =$

$$(3.2 \pm 0.7) \times 10^{-12} (T/298)^{-(1.2\pm0.4)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Note that this is not a calculated expression but rather an extrapolation of experimental data, with the help of RRKM calculations. More elaborate calculations, using variational transition state theory, are in progress, particularly in order to account for the temperature dependence of the high-pressure limiting rate constants for $CX_3 + O_2$ reactions.

At low pressure, the rate expression of $k(0)^{\infty}$ can be calculated without any assumption:

$$k_1(0)^{\text{sc}} = 7.0 \times 10^{-30} (T/298)^{-4.3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

Note that the equivalent rate expression, calculated according to the factorized expression of Troe,⁹ is only 15% higher, with the same temperature dependence. At 298 K, a good agreement between RRKM calculated and experimental data was obtained with a collisional efficiency factor $\beta_c = 0.23$, which is in the range of expected values for this parameter.

The calculated temperature dependence of the low-pressure limiting rate constant is obviously significantly smaller than the experimental observation, $T^{-4.3}$ instead of $T^{-6.3}$, respectively. No explanation can be found at the present time for this difference, except by assuming a strong negative temperature coefficient for the collisional efficiency factor: $\beta_c = 0.23(T/298)^{-2.0}$, which is rather unusual and difficult to account for, as discussed in the next section.

The RRKM falloff curves, calculated with the above expression for β_c are displayed on Figure 3 and compared to experimental data.

RRKM calculations were also performed for the reaction forming CF_3O_2 , using a similar model as the one described above and the experimental results reported in a previous publication.⁴ In this case, however, the critical energy E_0 is not known accurately and measurements of the rate constant at pressures higher than 12 Torr are not available.

At low pressure, where the critical energy is an important parameter, the collisional efficiency factor was fixed at the same value as in the case of CCl₃O₂, $\beta_c = 0.23$ at 298 K, and E_0 was taken as an adjustable parameter. It was found that $E_0 = 144 \pm 10$ kJ mol⁻¹ was the best value for reproducing the experimental data, resulting in the following expression for the calculated strong collision rate expression at the low-pressure limit:

$$k_{16}(0)^{\text{sc}} = 9.8 \times 10^{-29} (T/298)^{-2.9} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

As in the case of reaction 1, the calculated temperature dependence for the strong collision rate constant is much smaller

TABLE IV: Parameters To Be Used in Troe's Equation

	k ₀ ^{298 a}	n0 ^b	k_ ^{298 c}	n_ ^b	<i>C</i> , ^{<i>d</i>} K
CCl ₃	1.6 ± 0.3	6.3 ± 0.5	3.2 ± 0.7	1.2 ± 0.4	255
CF ₃	22 ± 4.0	4.7 ± 0.4	8 ± 3	0 ± 1	385

^aUnits 10^{-30} cm⁶ molecule⁻² s⁻¹. ^bTemperature dependence of rate constant $k(T) = k_{298}(T/298)^{-n}$. ^cUnits 10^{-12} cm³ molecule⁻¹ s⁻¹. ^dTemperature dependence of F_c ; $F_c = \exp(-T/C)$.

than the experimental observation $(T^{-4.7})$. This leads us again to a strong negative temperature coefficient for the collisional efficiency: $\beta_c = 0.23(T/298)^{-1.8}$.

The extrapolation to infinite pressure was not accurate in the case of this reaction since no measurements of the rate constant have been performed at high pressure. The expression for $k_{16}(\infty)$ is

$$k_{16}(\infty) = (8.0 \pm 3.0) \times 10^{-12} (T/298)^{0\pm 1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

in good agreement with the preceding value⁴ obtained by a simple fit of experimental data, using Troe's expression.¹⁴

For the purpose of rate constants compilations, it is useful to present the kinetic parameters in the form of an analytical rate expression, which permits a simple calculation of the rate constant at a given pressure and temperature. The commonly used rate expression developed by Troe¹⁴ was utilized to fit the RRKM falloff curves by adjusting the broadening factor F_c and by using the values of the parameters $k(0)^{298 \text{ K}}$, $k(\infty)^{298 \text{ K}}$ and the temperature coefficients determined above. The expression used for calculating the bimolecular rate constant k_{bi} is

$$\log k_{bi} = \log \left[\frac{k(0)[M]}{1 + k(0)[M]/k(\infty)} \right] + \frac{\log F_{c}}{1 + [(1/N_{c}) \log \frac{k(0)[M]}{k(\infty)}]^{2}}$$

with $N_c = 0.75 - 1.27 \log (F_c)$ and $F_c = \exp(-T/C)$, C being a constant. All parameters to be used to Troe's expression for calculating the bimolecular rate constant are given in Table IV for CCl₃ and CF₃.

Discussion

The principal aim of this work was to build a comprehensive description of the kinetics of the reaction of CCl_3 with O_2 over a large range of pressure and at different temperatures. Two different techniques were used for exploring the low- and the high-pressure regions. The experimental data were shown to be consistent with the results of RRKM calculations, which were also used for extrapolating the data to the high-pressure limit. In addition, these calculations may help understand the variation in reactivity from one radical to the other, for equivalent reactions.

Accuracy of Results and Comparison with Other Data. The uncertainties quoted for the limiting low- and high-pressure rate constants reported above are slightly larger than the extreme values that allow the experimental results to be reproduced acceptably. A more rigorous evaluation is not possible, given the procedure of fitting the experimental data using the RRKM calculations.

Besides the classical sources of errors concerning the determination of experimental parameters, the main source of uncertainties in the low-pressure measurements was probably an imperfect evaluation of the extent of wall reactions. The wall reaction rate could be determined for CCl₃O₂, but we had to assume that it was the same for CCl_3 . However, the results were apparently not greatly influenced by this uncertainty since fairly good linear plots, going through the origin, were obtained for the dependence of the CCl₃O₂ formation rate on the oxygen concentration (Figure 2). An overall uncertainty of 20% was estimated for $k_1(0)$. The only previous determination of $k_1(0)$ was performed by Ryan and Plumb⁶ in a fast flow reactor at room temperature, using helium as the carrier gas: $k_1(0) = 0.58 \times 10^{-30}$ cm³ molecule⁻¹ s⁻¹, i.e., a factor of about 2.5 smaller than the value found in this work, using nitrogen as the buffer gas. The value of this factor looks reasonable,^{12,13} which indicates a good

agreement between the present results and those reported by Ryan and Plumb.⁶ However, the equivalent ratio is much smaller in the case of the reaction of CF₃, 1.25.^{3.4} We have no explanation for this difference and it should be reminded that many apparent inconsistencies of this type can be found in the literature. This also indicates that the same value of 0.23 that we have assigned to β_c for the reactions of both CCl₃ and CF₃ may be a rough approximation.

The determination of the rate constant at 760 Torr was fairly straightforward and the uncertainty should not be much larger than about 10%. However, the extrapolation to infinite pressure results in a larger uncertainty on $k(\infty)$, 20–25%. The value of $k_1(\infty)$, 3.2×10^{-12} cm³ molecule⁻¹ s⁻¹ is significantly smaller than the value reported for the equivalent reaction of CF₃,^{3.4} (8–10) $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. This can be easily accounted for, at least qualitatively, with the model used for the activated complex, since the restriction of rotors (corresponding to rocking modes) is much less important in CF₃O₂ than in CCl₃O₂. In the case of CH₃ + O₂, however, the value of $k(\infty)$, 1.2×10^{-12} cm³ molecule⁻¹ s⁻¹,²⁶ is even smaller than that found in this work for CCl₃ + O₂. This abnormally low value has already been discussed in detail in relevant publications.^{28,29}

Temperature Dependence of the Rate Constant. A strong negative temperature coefficient had already been observed for k(0) in the case of the reaction of CF₃ with oxygen,⁴ $T^{-4.7}$. The negative temperature dependence is even stronger for the low-pressure limit of k_1 , $T^{-6.3}$. This is corroborated by preliminary results obtained in this laboratory for the equivalent reaction of CFCl₂, again showing a strong negative temperature dependence, $T^{-6.3}$.

Both RRKM calculations and Troe's factorized expression account for the stronger negative temperature dependence found for the reaction of CCl₃ compared to that for CF₃. This arises from the larger variation with temperature of the vibrational partition function of CCl₃, compared to that of CF₃, due to the lower vibrational frequencies in CCl₃. However, the calculated temperature coefficients for $k(0)^{\infty}$ are significantly smaller than the experimental ones. The difference could be accounted for by introducing a negative temperature coefficient in β_c expressions, but this coefficient would be abnormally high. The expressions of β_c derived from a simple ratio of the calculated (strong collision) and experimental rate expressions of k(0) are

$$\beta_c = 0.23(T/298)^{-2.0}$$
 for CCl₃
 $\beta_c = 0.23(T/298)^{-1.8}$ for CF₃

We have no explanation at this time for such a temperature dependence of the collisional efficiency factor. The commonly used expression proposed by Troe,⁸ which links β_c to the average energy $\langle \Delta E \rangle$ removed per collision, predicts a T^{-1} variation for β_c , which seems to be a maximum predictable variation for this factor.

This strong temperature dependence of β_c might arise from an overevaluated value of the experimental temperature coefficient of k(0). However, it should be emphasized that these coefficients, determined for CF₃, CFCl₂ (preliminary results), and CCl₃, using

different chemical systems, are all consistent with each other. In addition, in the case of CCl₃, the temperature coefficient obtained at 760 Torr with a completely different technique is still strong, in good agreement with the results obtained at low pressure. All these experimental results are therefore consistent and certainly correct, within experimental uncertainties. However, due to these uncertainties, it should be possible to fit the experimental data by using a smaller temperature coefficient for k(0). We have determined the smallest coefficient which could be used for fitting the data: any coefficient smaller than $T^{-6.0}$ for $k_1(0)$ would not allow an acceptable representation of the experimental data. This corresponds to a $T^{-1.7}$ temperature dependence for β_c , which is obviously still too large.

At the high-pressure limit, $k_1(\infty)$ exhibits a significant negative temperature coefficient, $T^{-1.2\pm0.4}$. The significance of this coefficient mainly results from the fairly high negative temperature coefficient that we have measured at 760 Torr. Indeed, taking into account this result, there is no way to fit correctly the experimental data with a temperature coefficient out of the uncertainty limits. On the contrary, in the case of the CF₃ reaction, the temperature dependence is close to zero, but the uncertainty is much larger, due to the long extrapolation from low pressures. Calculations using the variational transition state theory, which are in progress,³⁰ should account for these temperature dependences observed at high pressures.

Thermochemistry of Reactions. The kinetics and the thermochemistry of the reaction of CCl₃ with O₂ have now been described in detail in a large range of experimental conditions. Thus, this reaction can be taken as a model for obtaining information concerning other similar reactions. This was done above by treating the reaction of CF_3 with O_2 with the same RRKM model as for the CCl₃ reaction and adjusting the critical energy $E_0 = \Delta H^o_0$. The best value was $\Delta H^{\circ}_{0} = -(144 \pm 10) \text{ kJ mol}^{-1}$. Using a similar procedure, with the reaction of CH₃ with NO taken as a model, Vedeneev²³ obtained a very similar value, -141 kJ mol⁻¹. However, this agreement only shows that both Vedeneev's and the present experimental results are consistent. These values are also close to $\Delta H_0^{\circ} = -(150 \pm 15)$ kJ mol⁻¹, which can be derived from Antonik's work,²⁴ as described above, even though this last value was a rough estimate. The value estimated from an additivity method,²⁵ 205 kJ mol⁻¹, however, appears too high.

In any case, our calculations show that the large difference between CCl₃ and CF₃, in reactivity toward oxygen, can be accounted for by a significant difference between the C–O bond dissociation energies in CCl₃O₂ and CF₃O₂ radicals. The intermediate reactivity of CFCl₂, determined at room temperature,⁵ results in an intermediate value of the C–O bond dissociation energy in CFCl₂O₂, 120 ± 10 kJ mol⁻¹, if the same procedure as in the case of CF₃ is applied. However, since it was shown above that the value of β_c may change significantly from one reaction to the other, calculations using either the RRKM method or Troe's factorized expression can only yield a rough estimate of the critical energy of the reaction. Only a direct experimental determination can give an accurate value of E_0 for the reaction of CF₃ and other radicals with oxygen.

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⁽²⁸⁾ Keiffer, M.; Pilling, M. J.; Smith, M. J. C. J. Phys. Chem. 1987, 91, 6028.

⁽²⁹⁾ Cobos, C. J.; Hippler, H.; Luther, K.; Ravishankara, A. R.; Troe, J. J. Phys. Chem. 1985, 89, 4332.

⁽³⁰⁾ Forst, W.; Caralp, F. J. Chem. Soc., Faraday Trans., in press.