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Vacuum–ultraviolet (147 nm) photodecomposition of 1,1,2trichloro-2,2-difluoroethane

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The 147 nm photolysis of CF₂ClCHCl₂ has been investigated at 25°C as a function of reactant pressure, conversion, and nitric oxide as additive. In the absence of NO the observed reaction products are CF2CHCl, CF2CCl2, and the diastereomers of (CF2ClCHCl)2. At constant reactant pressure the quantum vields of the olefin decrease with increasing conversion and there is a corresponding increase in the quantum yield of the C4 product. For fixed values of conversion the olefin quantum yields decrease with increasing reactant pressure and approach limiting values at ~100 Torr. The addition of NO completely suppresses the formation of the chlorofluorobutanes, while it enhances the olefin quantum yields at higher conversion. These observations are interpreted in terms of reactions of chlorine atoms which result either directly (by near simultaneous expulsion of two Cl atoms), or via the dissociation of an excited Cl₂* molecule produced by molecular elimination in the primary process. Chlorine atoms abstract hydrogen from the parent or add to the product olefins. These processes provide the principal source of halo-ethyl radicals in the system. The addition reaction leads to chemically activated radicals with a mean lifetime of $\tau \simeq 0.8 \times 10^{-8}$ sec which is commensurate with RRKM-theory predictions. The addition of nitric oxide provides a competing channel for chlorine atom removal by way of their NO-catalyzed recombination. The functional dependence of the olefin quantum yields with conversion in the absence and presence of NO suggests that the major fraction of the principal product, CF2CHCl, derives directly from a primary process, while CF₂CCl₂ is formed via both, the molecular elimination of HCl and from radical precursors. The limiting quantum yields of CF₂CHCl and CF₂CCl₂ are found to be $\phi_0 \simeq 0.68$ and $\phi_0' \simeq 0.19$, in the absence of NO, respectively, and $\phi_{0,NO} \simeq 0.56$ and $\phi'_{0,NO} \simeq 0.087$ in the presence of NO. The extinction coefficient for CF2ClCHCl2 at 147 nm and 25°C has been determined: $\epsilon = (1/PL) \ln(I_0/I_t) = 404 \pm 40 \text{ atm}^{-1} \text{ cm}^{-1}$.

INTRODUCTION

Our previous studies of the vacuum-ultraviolet photochemistry of chloro- and chlorofluoroethanes have shown that the photodecomposition processes depend on the identity, degree, and position of halogen substitution, as well as wavelength. Thus in the 147 nm photolyses of CH₃CHCl₂, ¹ CH₃CCl₃, ² and CH₃CF₂Cl³ the predominant decomposition channel is HCl elimination, while in the case of $C_2H_5Cl^4$ the photochemistry is very complex. Substitution of chlorine or fluorine in the β position as in CH₂FCH₂Cl⁵ or CF₃CH₂Cl⁶ leads to a decrease in the quantum yield of HCl and an increase in dehalogenation processes. A surprising feature in most of these studies (except C_2H_5Cl) has been the absence, or only very low yield, of products originating from radical precursors. These observations have led us to postulate the possibility of molecular elimination of Cl₂ or FCl from electronically excited states attributed to Rydberg-type transitions.⁷ However, with increasing (α, β) halogen substitution, e.g., CF₃CH₂Cl,⁶ a trend towards C-Cl bond scission has been observed, with a concomitant decrease in molecular elimination processes. Most recently, in the 147 nm photolysis of $CF_2ClCH_2Cl^8$ we have observed the product olefins CF₂CH₂ and CF₂CHCl and have also obtained evidence for the production of Cl atoms in one or more of the primary steps. These chlorine atoms are removed by competitive reactions which include hydrogen abstraction from the parent molecule as well as addition to the product olefins. The former process results in the production of thermal CF₂ClCHCl radicals, while the Cl-atom addition reactions lead to corresponding chemically activated halogenated ethyl radicals, which can redissociate or be collisionally stabilized.

In the present communication we report on the 147 nm photolysis of $CF_2ClCHCl_2$ which further exemplifies and corroborates the intriguing reaction kinetics of our recent study.

EXPERIMENTAL SECTION

Apparatus

The apparatus and experimental procedure have been described previously.⁸ Photolyses were carried out at room temperature in a spherical Pyrex cell of 215 cm³ volume. A titanium gettered xenon resonance lamp operated by a microwave generator (Kiva Instruments, Model MPG4M) was used as the light source. The lamp was similar, in principle, to that described by Gorden et al.9 but was equipped with two 1 mm thick LiF windows at opposing ends of the discharge tube. This modification was an improvement over previous designs as it allowed monitoring and adjustment for lamp intensity fluctuation during the photolyses, i.e., one end of the light source was connected by means of a ground glass joint to the photolysis cell, while the opposing window was similarly connected to a photoionization cell,¹⁰ which was filled with a trimethylamine (TMA)-helium mixture (3 Torr TMA/35 Torr He). With this arrangement photolysis of the test gas and physical actinometry by measuring the saturation ion current in TMA could be conducted simultaneously. By monitoring the stability of the ion current and adjusting the microwave power output, the control of lamp intensity was improved to $\pm 5\%$. The emission spectrum of the lamp was checked

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routinely with a McPherson (Model 218-0.3 m) vacuumultraviolet monochromator, and the contribution from the 129.5 nm line was found to be minimal. Photolysis quantum yields were determined by chemical actinometry based on the production of C_2H_2 in the photolysis of ethylene¹⁰ ($\phi_{C_2H_2} = 1.0$ at 147 nm). In separate experiments, the extinction coefficient of CF₂ClCHCl₂ at 147 nm was determined as $\epsilon = (1/PL) \ln(I_0/I_t) = 404 \pm 40$ atm⁻¹ cm⁻¹ using the double-cell method of Gorden *et al.*¹¹

Product analysis

Product analysis was carried out by flame-ionization gas-chromatography (Hewlett-Packard, Model 5830 A). The lower molecular weight C_2 products (CF₂CHCl, CF_2CCl_2) were separated with either a 3.6 m Porapak N column at 130 °C, or a 1.8 m Durapak (n-octane/Porasil C) column at 60 °C, with a He flow rate of 30 cm³/min. Identification and quantitative determination of the olefins was by comparison of their retention times and peak areas with those of authentic samples. The Durapak column with temperature programming (60-150 °C) was also used to isolate the C4 compounds. Two isomeric chlorofluorobutanes were inferred to be the diastereomers of $(CF_2ClCHCl)_2$ based on our recent work.⁸ The structure was also confirmed from the mass-spectral cracking pattern using a GC-MS instrument (Hewlett-Packard, Model 5992 A). Since an authentic sample of $(CF_2ClCHCl)_2$ was not available, its relative sensitivity in gas-chromatographic analysis was arbitrarily taken as equal to that of acetylene, which is adequate for the purpose of establishing qualitative trends.

As a test for the presence of chlorine atoms in the system a diagnostic experiment was performed by photolyzing 2.3 Torr of $CF_2ClCHCl_2$ in the presence of 18.5 Torr of DI. In this photolysis, which was carried out to relatively high conversion (~ 0.9%), the contents of the reaction vessel were first condensed at 77 °K and then submitted to a separation train in an attempt to isolate DCl and HCl from the other products and reactants. The volatile components from an ethanol slush (- 112 °C) were finally collected at liquid nitrogen temperature and analyzed by mass spectrometry.

Chemicals

The reactant, $CF_2ClCHCl_2$, was obtained from Peninsular Chemresearch and purified to better than 99.8% by fractional distillation using a spinning band column (B/R glass, Inc.). Nitric oxide (Matheson) was purified by trap to trap distillation at 77 °K prior to its use. The DI (Merck, Sharp and Dohme) of 98 at. % D was used without further purification. Precise low pressure measurements were obtained using an electronic, fused quartz Bourdon gauge (Texas Instruments, Model 145).

RESULTS

The observed reaction products are CF_2CHCl , CF_2CCl_2 , and relatively small, but mechanistically significant quantities of the diastereoisomers of $CF_2ClCHClCHClCF_2Cl$ (Cl_4-B). The two other anticipated⁸ halogenated butanes, $CF_2ClCHClCCl_2CF_2Cl$ (Cl_5-B) and $CF_2ClCCl_2CCl_2CF_2Cl$ (Cl_6-B) were not found,



FIG. 1. Plot of the reciprocal of the quantum yield of CF_2CHCl versus It/N for small values of conversion, at different reactant pressures. Solid lines: Experiments without NO; $CF_2ClCHCl_2$ pressures (Torr): •, 3.5; o, 10; Δ , 20; \Box , 50; \blacktriangle , 100. Broken line: Experiments with 1 Torr NO and 10 Torr $CF_2ClCHCl_2$.

which is not unexpected, in view of their low volatility and consequently peak broadening and long retention times. Table I summarizes the product quantum yields as a function of the reactant pressure, the additive NO, and the conversion, It/N. The latter is an important correlation function,⁸ where I is the total absorbed light intensity (number of photons absorbed per second in the cell), t is the irradiation time (sec), and $N(=PVN_0/RT)$ is the total number of parent molecules in the reaction cell of volume V and pressure P. At the very low conversions in this study, N can be assumed to be a constant at any given pressure.

With reference to Table I it may be seen that at any fixed pressure of $CF_2ClCHCl_2$ and in the absence of NO the quantum yields of the olefins *decrease*, while the quantum yields of Cl_4 -B *increase* with increasing It/N. Also perceptible is a slight decrease in the quantum yield of the principal olefin, CF_2CHCl , with increasing $CF_2ClCHCl_2$ pressure at approximately the same values of It/N (runs 1, 4, and 22, for example). The addition of NO completely suppresses the formation of the chlorofluorobutanes, and there is a distinct and significant relative *increase* in the quantum yields of the olefins at the *same* conversion and reactant pressure. Conversely, the addition of NO effectively diminishes the decrease in $\phi_{CF_2CHC_1}$ and $\phi_{CF_2CCl_2}$ with increasing It/N (cf. runs 4-8 and 9-13, respectively).

Figure 1 shows plots of the reciprocal quantum yield of CF₂CHCl as a function of conversion for different reactant pressures. Four important features may be pointed out in Fig. 1: (i) there exists a linear relationship between $1/\phi_{\rm CF_2CHC1}$ and It/N at constant reactant pressures; (ii) the slopes of the straight lines are pressure dependent, i.e., the slopes increase with increasing reactant pressure; (iii) the limiting values of $1/\phi_{\rm CF_2CHC1}^{\rm C}$ (corresponding to zero conversion) at differ-

Run No.	P _{CF2} ClCHCl2 (Torr)	P _{NO} (Torr)	Quantum Yield, ϕ			I× 10 ⁻¹³	
			CF ₂ CHCl	CF ₂ CCl ₂	$Cl_4 - B_{1,2}^{a}$	(photons s ⁻ⁱ)	$(It/N) \times 10^4$
1	3.4	•••	0.705	b	с	0,598	1.51
2	3.5	•••	0.533	b	с	0.858	8.57
3	3.5	•••	0.450	b	0.024	2.63	12.5
4	10.1	•••	0.614	0.158	С	0.833	1.07
5	10.3	•••	0.548	0.149	с	1,37	2.31
6	10.2	•••	0.487	0.111	~ 0.03	5.28	4.49
7	10.1	•••	0.349	0.077	0.057	4.38	10.1
8	10.1	•••	0.247	0.055	0.064	7.13	18.1
9	10.4	1.0	0.548	0.083	0	1.72	1.44
10	10.4	0.99	0.450	0.074	0	9.33	7.90
11	10.4	1.0	0.418	0.075	0	10.7	8.87
12	10.5	0,98	0.377	0.070	0	5.92	14.6
13	10.4	1.0	0.369	0.063	0	10.1	16.8
14	20.1	•••	0.527	0.128	с	2.08	1.79
15	20.0	•••	0.435	0.099	0.016	3.15	4.09
16	20.0	•••	0,353	0.082	0.034	15.5	6.72
17	48.7	•••	0.665	b	с	1.46	0.258
18	48.1	•••	0.710	b	с	1.62	0.292
19	48.7	•••	0.498	b	с	3.78	2.02
20	48.7	•••	0.430	b	0.017	3,63	3.23
21	103.6	•••	0.612	b	с	5.25	0,526
22	102.1	•••	0.529	b	с	12.1	1.05
23	101.8	•••	0.404	b	0.014	12.2	3.35

TABLE I. Product quantum yields in the 147 nm photolysis of CF₂ClCHCl₂.

^aSum of the two diastereoisomers of CF₂ClCHClCHClCF₂Cl. ^bNot determined; see text.

^cNot observed at low conversion.

ent pressures converge to approximately the same average value (1/ $\phi^0_{CF_2CHC1}$ = 1.48 ± 0.07); (iv) the addition of NO affects both the slope and intercept of the linear relationship. Figure 2 shows the corresponding plot of $1/\phi_{CF_2CCI_2}$ versus It/N for the minor olefin. Again, qualitatively similar features can be pointed out, although in this case there are fewer data points owing to some analytical difficulties (CF₂CCl₂ was a residual trace impurity in the parent compound and for this reason it was not determined at low reactant pressures). Noticeable differences between the data in Figs. 1 and 2 at the same reactant pressure (10 Torr) are the higher value of the intercept and a much steeper slope for CF2CCl2, as well as a more pronounced effect with NO addition.

The above results are qualitatively rather similar to the 147 nm photolysis of CF₂ClCH₂Cl⁸ and strongly suggest involvement of chlorine atoms. In the latter study the reduction in the yields of the olefins with increasing coversion were attributed to the removal of the olefins by Cl atom addition. More direct evidence for photochemically produced Cl atoms was obtained in the present study in the photolysis of the $CF_2ClCHCl_2/DI$ mixture. Mass-spectrometric analysis of the irradiated and processed gases yielded a DCI/HCl ratio of $\sim 1/3$ (peak heights, m/e 39 and 38). Although owing to separation difficulties (see experimental section) this result must be regarded as qualitative, it appears to be conclusive with respect to the presence of Cl atoms, since other feasible processes leading to the formation of DCl are not important. For example, the isotopic exchange reaction between HCl and DI, or the direct reaction between $CF_2ClCHCl_2$ and DI, are negligible at room temperature (< 3%) as confirmed in separate dark experiments. Deuterium atoms produced in any possible photolysis of DI are expected to react, in the presence of excess DI, almost exclusively with DI itself. It is therefore concluded that the identification of DCl provides direct evidence for the presence of Cl atoms in the system.

DISCUSSION

As has already been indicated in the preceding section, the 147 nm photolysis of CF₂ClCHCl₂ parallels



FIG. 2. Plot of the reciprocal quantum yield of CF₂CCl₂ versus It/N for small values of conversion. Solid lines correspond to pure $CF_2ClCHCl_2$: 0, 10 Torr: Δ , 20 Torr. Broken line: Experiments with 1 Torr NO and 10 Torr CF₂ClCHCl₂.

closely the photolysis of CF₂ClCH₂Cl⁸ at this wavelength. The addition of NO, which normally serves as a scavenger for thermal radicals, confirms that the chlorofluorobutanes have radical precursors, and also supports that CF_2CHCl and CF_2CCl_2 are mainly molecular products. A more detailed consideration of the effect of NO on the quantum yields of these olefins is to be found later. In the absence of NO, the decrease in the olefin quantum yields with increasing conversion, It/N, can be well explained in terms of the removal of the olefins by Cl atom addition, a process which, as will be shown, competes with the hydrogen abstraction by chlorine atoms from the parent. These reactions are the main source of the halogenated ethyl radicals which, on combination, yield the chlorofluorobutanes, and provide an explanation for the observed dependence of the Cl₄-B quantum yield on It/N. In the light of these observations, and for the purpose of initiating the discussion, we consider the following reaction mechanism,

 $CF_2ClCHCl_2 + h\nu \longrightarrow CF_2ClCHCl_2^{\dagger}$, (R1)

$$CF_{2}CICHCl_{2}^{+} \rightarrow CF_{2}CHCl + 2Cl \qquad (R2)$$

$$\rightarrow$$
 CF₂CCl₂ + HCl, (R3)

$$Cl + CF_2ClCHCl_2 \longrightarrow CF_2ClCCl_2 + HCl$$
, (R4)

$$C1 + CF_2CHC1 \xrightarrow{M} CF_2CICHC1$$
, (R5)

$$Cl + CF_2CCl_2 \xrightarrow{M} C_2F_2Cl_3 \cdot , \qquad (R6)$$

$$2 \operatorname{CF}_{2}\operatorname{ClCHCl} \longrightarrow \operatorname{Cl}_{4} - \operatorname{B}, \qquad (R7)$$

$$CF_2ClCHCl + CF_2ClCCl_2 \rightarrow Cl_5 - B$$
, (R8)

$$2 \operatorname{CF}_{2} \operatorname{ClCCl}_{2} \longrightarrow \operatorname{Cl}_{6} - B , \qquad (R9)$$

where the dagger (†) denotes electronic excitation upon photon absorption. In Reaction (R2) three energetically possible processes are implied: (i) the "nearly" simultaneous expulsion of two Cl atoms, as written; (ii) the concerted molecular elimination of an excited Cl2 molecule followed by its rapid dissociation; or (iii) a rapid, sequential expulsion of two chlorine atoms. Our experiments cannot distinguish between these possibilities, and for the purpose of this discussion no distinction between these fine processes will be, or need be, made. For the present we omit from the reaction scheme single carbon-chlorine bond scission leading to stable CF₂ClCHCl and/or CF₂CHCl₂ radicals based on thermochemical considerations. For these precesses ΔH_{Rx} $\simeq D(C-C1) \sim 80$ kcal mol⁻¹, and since the photon energy is 194 kcalmol⁻¹, the residual energy to be distributed is ~ 114 kcal mol⁻¹. From the heats of formation^{12a} of CF2ClCHCl2 and Cl we obtain, for the haloethyl radical, $\Delta H_{f,298}^{\circ} (C_2 F_2 C I_2 H \cdot) \sim -74 \text{ kcal mol}^{-1}$, and with $\Delta H_{f,298}^{\circ}$ $(CF_2CHCl) = -75$ kcal mol⁻¹, ^{12b} the enthalpy change to break the second C-Cl bond is ~ 28 kcal mol⁻¹. For the $C_2F_2Cl_2H$ · radical to be stable would thus require 84-86 kcal mol⁻¹ to be apportioned in the form of translational energy. Nevertheless, some evidence for contributions from collisionally (partially) stabilized radicals originating in the primary process will be considered later.

Reaction (R2) is endothermic by ~108 kcal mol⁻¹, ¹² and hence an excess energy of ~86 kcal mol⁻¹ must be distributed between the primary products. The absence of either CFCF or CFCCl among the reaction products

indicates that the energy content of CF₂CHCl does not exceed the respective activation barriers for HCl or HF eliminations, which are the expected decomposition channels. The activation energy for the latter process should be of the order of $E_a \sim 86 \text{ kcal mol}^{-1}$ in analogy to the HF elimination from CF₂CH₂,¹³ while for HCl elimination E_a is estimated in excess of 70 kcal mol⁻¹, which is the activation energy for the dehydrochlorination of $C_{2}H_{3}Cl$.¹⁴ This sets an upper limit on the internal energy content of CF₂CHCl and any residual excess energy must appear as relative translational energy of the products in Reaction (R2). The formation of the minor olefin, CF_2CCl_2 , in Reaction (R3) may proceed via the direct or sequential elimination of the elements of HCl. The conserted molecular elimination of HCl is endothermic by ~ 27 kcalmol⁻¹, 12 while for the overall reaction leading to the cofragments H and Cl, $\Delta H_{Rx} \simeq 130 \text{ kcal mol}^{-1}$.¹² The corresponding excess energies are 167 and 64 kcal kcal mol⁻¹, respectively. Based on the observed product distribution, CF_2CCl_2 evidently does not undergo further dissociation reaction such as C-Cl bond cleavage, which is the anticipated mode of decomposition in this case, in analogy of C_2Cl_4 or $CHClCCl_2$, for which the respective C-Cl bond dissociation energies are 80-84 kcalmol⁻¹.¹⁵ If the latter value is taken as an upper limit of the energy content of CF_2CCl_2 one obtains $\approx 83-87 \text{ kcal mol}^{-1}$ as the lower limit of the energy content of HCl produced in Reaction (R3), assuming zero relative energy of translation. Since $D(H-C1) = 103 \text{ kcal mol}^{-1}$, ^{12c} the production of H and Cl atoms in Reaction (R3) would impose the condition that the CF_2CCl_2 molecule possess less than ~ 38% of the total available energy. On the basis of this estimate we prefer here the molecular elimination of HCl and omit, at this point, from further consideration possible contributions to secondary reactions as a result of H and Cl atoms which may be generated in Reaction (R3). This neglect is further justified on the basis of the *relative* importance of Reaction (R3), which is a minor process, in the first instance.

In the absence of NO, Reactions (R4) to (R6) provide the principal sink for the removal of chlorine atoms, since the direct three-body recombination (Cl+Cl+M $-Cl_2+M$) is negligible in our system. Hydrogen abstraction by chlorine atoms from alkanes and partially substituted halo-alkanes is known to proceed at or near room temperature.^{16,17} In the case of some fluoro- and chloroethanes it has been shown^{18,19} that the activation energies increase and the A factors decrease with (a) increasing halogen substitution on the same carbon atom, and (b) with H-abstraction occurring from the carbon atom adjacent to the halogen-substituted one. As will be shown later, from an examination of our data in the presence and absence of nitric oxide, we obtain $k_4 \sim 1.3 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ at 298 °K. If we assume a normal pre-exponential factor of $A_4 \simeq 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, then $E_1 \sim 3.9 \text{ kcal/mol}^{-1}$, which is a plausible value in the light of the variation of this quantity with the degree and position of chlorine/fluorine substitution. The fate of the thermal CF₂ClCCl₂ radical produced in Reaction (R4) may include metathetical reactions with the parent, combination, and cross combination with other radicals, and possibly disproportionation reactions. Parenthetically it may be noted, however, that the most likely rate process of H abstraction from $CF_2ClCHCl_2$ leads to no *net* change, since the parent molecule is regenerated, while Cl-atom abstraction is apparently not competitive since no CF_2ClCCl_3 product was observed.

The addition of chlorine atoms to chloroethylenes^{20,21} and chlorofluoroethylenes²² is known to proceed rapidly with near-zero activation energy to produce the corresponding vibrationally excited halogenated ethyl radicals. Thus the reaction of Cl atoms with the product olefins in Reactions (R5) and (R6) explains the decrease in the quantum yields of these olefins with increasing conversion. While the rate constants for these particular reactions have apparently not been reported, a reasonable estimate can be obtained from a consideration of Cl-atom addition to tri- and tetrachloroethylene.²¹ We thus estimate $k_5 \sim k_8 \sim 10^{13 \cdot 3}$ cm³ mol⁻¹ sec⁻¹ at 298 °K.

The relative rates of the principal addition to abstraction reactions of chlorine atoms is given by

$$R_{5}/R_{4} = \frac{1}{2} \frac{k_{5}}{k_{4}} \frac{[CF_{2}CHC1]_{f}}{[CF_{2}ClCHC1_{2}]} , \qquad (1)$$

where $[CF_2CHC1]_f$ is the final concentration and the factor $\frac{1}{2}$ corrects for the average concentration of the olefin assuming a linear dependence of its rate of production with phololysis time. Using the above values of k_4 and k_5 yields $R_5/R_4 \sim 0.076$ for $[CF_2CHC1]_f/[CF_2CICHCl_2] = 10^{-4}$. This shows that despite considerable uncertainties in the Arrhenius parameters the chlorine addition to the olefin is significant even at conversions of ~ 0.01%

Linear dependence of $1/\phi$ on It/N

Based on the proposed mechanism, the rate of production of CF_2CHCl is given by

$$d[CF_2CHC1]/dt = \phi_0 I_a - k_5[C1][CF_2CHC1]$$
 , (2)

where ϕ_0 is the true quantum yield of CF₂CHCl, and I_a is the absorbed light intensity per unit length (einsteins/ cm³ sec). Since chlorine atoms are highly reactive, the quasi-stationary-state approximation will be valid⁸; hence, in the absence of NO the chlorine atom concentration is approximately given by

$$[C1]_{s.s.} = \frac{2\phi_0 I_a}{k_4 [CF_2 CICHCI_2] + k_5 [CF_2 CHCI]} , \qquad (3)$$

which neglects Cl-atom removal by Reaction (R6). Introducing Eq. (3) in Eq. (2) and making the substitution $X = [CF_2CHC1]$, $\alpha = k_4[CF_2ClCHCl_2]$, and $\beta = k_5$, we obtain

$$\frac{dX}{dt} = \phi_0 I_a \frac{(\alpha - \beta X)}{(\alpha + \beta X)} \quad . \tag{4}$$

Some further underlying assumptions in the derivation of Eq. (4) have been discussed elsewhere.⁸ Subject to the initial condition of X = 0 at t = 0, Eq. (4) has the solution

$$\frac{1}{2}(\beta/\alpha)X + \ln[1 - (\beta/\alpha)X] = -\frac{1}{2}\phi_0(\beta/\alpha)I_at \quad , \tag{5}$$

where we identify $(\beta/\alpha)X = R_5/R_4$ as the rate ratio of the addition/abstraction reactions and, from our definition of the conversion, It/N,

$$(\beta/\alpha)I_a t = (k_5/k_4)It/N \equiv \theta \qquad (6)$$

For the purpose of facilitating comparison with experiment, Eq. (5) may be first recast into the exponential form

$$X = (\alpha/\beta) \left\{ 1 - \exp\left[-\frac{1}{2} (\beta/\alpha) (X + \phi_0 I_a t) \right] \right\} \quad , \tag{7}$$

which simplifies to

$$\phi = (1/\theta) \{ 1 - \exp[-(\theta/2)(\phi + \phi_0)] \}$$
(8)

using the definition of θ in Eq. (6), and upon noting the identity $X/I_a t = \phi$, which is the *observed* quantum yield. If the conversion is very low, then, necessarily θ is very small (i.e., $\theta \to 0$ as $It/N \to 0$). Upon expansion of the exponential term in Eq. (8) and neglecting terms of order 3 and higher, we obtain

$$\phi = (1/\theta) \left[-(2 + \theta \phi_0) + 2(1 + 2\theta \phi_0)^{1/2} \right] , \qquad (9)$$

which is within ~ 3% for $(\theta/2)(\phi + \phi_0) < 0.5$. Further power series expansion of the square root term in Eq. (9) leads to

$$\phi \approx \phi_0 [1 - \theta \phi_0 + \theta^2 \phi_0^2 - \theta^3 \phi_0^3 + \dots]$$
$$\approx \phi_0 [1 - (\theta \phi_0)^4] / [1 + \theta \phi_0] \qquad (10)$$

For $0 < \theta \phi_0 \ll 1$, Eq. (10) reduces to

$$\phi \approx \phi_0 / (1 + \theta \phi_0) . \tag{11}$$

Substitution for θ and taking the inverse gives

$$\frac{1}{\phi} = \frac{1}{\phi_0} + \left(\frac{k_5}{k_4}\right) \left(\frac{It}{N}\right) \qquad (12)$$

An analogous expression to Eq. (12) can also be derived for the quantum yield (ϕ') of the minor product olefin, CF₂CCl₂. Subject to similar approximations we obtain

$$\frac{1}{\phi'} = \frac{1}{\phi'_0} + \left(\frac{\phi_0}{\phi'_0}\right) \left(\frac{k_6}{k_4}\right) \left(\frac{It}{N}\right) \quad . \tag{13}$$

Equations (12) and (13) predict that the reciprocal of the observed quantum yields is a linear function of conversion, for small values of It/N, and in the limit of $It/N \rightarrow 0$, $\phi \rightarrow \phi_0$, and $\phi' \rightarrow \phi'_0$.

A plot of $1/\phi_{CF_2CHC1}$ versus conversion for different reactant pressures is shown in Fig. 1 for $It/N \le 2 \times 10^{-3}$. The experimental data support the predicted linear relationship at any constant $CF_2ClCHCl_2$ pressure. Moreover, within experimental error, the straight lines (isobars) converge to roughly the *same* value of the intercept. From the intercept in Fig. 1 we obtain an average value of $\phi_0 \simeq 0.68$ for the true quantum yield of CF_2CHCl . Similarly, Fig. 2 shows a plot of $1/\phi'$ versus It/N and from the intercept we obtain $\phi'_0 \simeq 0.19$ for the limiting quantum yield of CF_2CCl_2 .

Pressure dependence of the slope

With reference to Fig. 1, the slopes of the isobars increase with increasing reactant pressure and approach a limiting value above 100 Torr. This may be readily explained in terms of a chemical activation mechanism: the addition of Cl atoms to the olefins produces vibrationally excited, electronic ground state, haloethyl radicals which may either redissociate or be collisionally



FIG. 3. Plot of the reciprocal of the slopes of the isobars in Fig. 1 versus inverse pressure [cf. Eq. (17)].

stabilized. Thus we can consider Reaction (R5) in terms of the detailed processes

$$C1 + CF_{2}CHC1 \stackrel{a_{a}}{\stackrel{\leftarrow}{\rightarrow}} CF_{2}CI\dot{C}HC1^{*}$$
$$CF_{2}CI\dot{C}HC1^{*} + M \stackrel{k_{s}}{\rightarrow} CF_{2}CI\dot{C}HC1 + M$$

Making the customary steady state assumption with respect to the vibrationally excited (*) radical concentration, the net rate of disappearance of CF_2CHCl is given by

$$-\frac{d[CF_{2}CHC1]}{dt} = \frac{k_{a}[C1][CF_{2}CHC1]}{1 + (k_{d}/k_{s}[M])}$$
$$= k_{a}[C1][CF_{2}CHC1]/(1 + k_{d}/\lambda ZP) , (14)$$

where Z is the gaskinetic collision frequency per unit pressure, and λ is a collisional efficiency factor. From Eq. (14) and with reference to Reaction (R5) we can identify

$$k_5 = k_a / (1 + k_d / \lambda ZP) \quad , \tag{15}$$

which shows that k_5 is pressure dependent and increases with P. In the limit, as $P \rightarrow \infty$, $k_5 \rightarrow k_a$, the rate constant for activation. Introducing Eq. (15) in (12) we obtain

$$\frac{1}{\phi} = \frac{1}{\phi_0} + \frac{(k_a/k_4)}{1 + k_d/\lambda ZP} (It/N) , \qquad (16)$$

which provides an explanation of the observed pressure dependence of the slopes in Figs. 1 and 2. Equation (16), predicts a zero slope in the limit of very low pressures $(\lim P \rightarrow 0)$, while the high pressure limiting slope, $\lim_{p\to\infty} [\partial \phi^{-1}/\partial (It/N)] = k_a/k_4$, provides a direct measure of the ratio of rate constants for the addition/abstraction reactions in the high pressure limit. In the intermediate pressure range, where the slopes are pressure dependent as given by Eq. (16), k_a/k_4 (or its inverse) can be obtained from a plot of the reciprocal of the slope for each isobaric line against the reciprocal of the corresponding pressure which is predicted to be a linear relationship, based on Eq. (16):

$$\frac{1}{\text{slope}} = \frac{k_4}{k_a} + \left(\frac{k_4}{k_a}\right) \left(\frac{k_d}{\lambda Z}\right) \frac{1}{P} \quad . \tag{17}$$

Figure 3 shows a plot of the data for CF_2CHC1 and confirms the linear relationship given by Eq. (17).

From the intercept and slope of the plot in Fig. 3 we obtain $k_4/k_a = 3.76 \times 10^{-4}$ and $k_d/\lambda Z = 11.9$ Torr, respectively. Using, as earlier, $k_4 = 1.3 \times 10^{10}$ cm³ mol⁻¹ sec⁻¹ leads to $k_a \sim 3.4 \times 10^{13}$ cm³ mol⁻¹ sec⁻¹, which is comparable to the rate constants for Cl atom addition to triand tetrachloroethylene.²¹ Finally, if we assume $\lambda = 1.0$ and $Z = 10^7$ Torr⁻¹ sec⁻¹, then the average rate constant for decomposition of vibrationally excited radicals is $k_d \sim 1.2 \times 10^8$ sec⁻¹, corresponding to a mean radical life time of $\tau \sim 0.8 \times 10^{-8}$ sec.

RRKM theory prediction of $k_d(E)$

As indicated in the preceding section, k_d represents an average rate constant for the decomposition of chemically activated haloethyl radicals. In general, k_d will be a function of the internal energy of the adduct. It is instructive to compare the experimental value with the theoretical prediction based on the RRKM theory of unimolecular reactions. Accordingly, if hindered internal rotations of the active radical are treated as low frequency vibrations, the rate constant for the reverse of the addition reaction is given by²³

$$k_{d}(E) = \frac{1}{h} \frac{Q_{1}^{\dagger}}{Q_{1}} \frac{\sum P(E_{v}^{\dagger})}{N^{*}(E_{v})} \quad ,$$
(18)

where $\sum P(E_v^{\dagger})$ is the sum of vibrational quantum states of the activated complex with a nonfixed energy E_v^{\dagger} ; $N^*(E_v)$ is the density of states of the active radical at a nonfixed energy $E_v(=E_0+E_v^{\dagger})$, and Q_1^{\dagger}/Q_1 , the ratio of partition functions for adiabatic rotations, provides a rough, but for present purposes adequate, correction for centrifugal effects. Using the approximation of Whitten and Rabinovitch^{23,24} for the sum and density of states, we obtain for the reaction in question

$$k_d(E) \simeq c \frac{\prod_{i=1}^{15} \omega_i}{\prod_{i=1}^{14} \omega_i^{\dagger}} \left(\frac{Q_1^{\dagger}}{Q_1}\right) \left(\frac{E_v^{\dagger} + a^{\dagger} E_x^{\dagger}}{E_v + a E_x}\right)^{14} \quad , \tag{19}$$

where c is the velocity of light, and ω_i denotes the vibrational frequencies expressed in wave numbers. Table II summarizes the input data for the evaluation of Eq. (19). Based on thermochemical estimates, ^{12b} the addition reaction (R5) for ground state reactants is exothermic by about 27 kcal mol⁻¹. Assuming an activation energy of 1-2 kcal mol⁻¹ for this process, the critical energy for the reverse dissociation reaction is therefore $\sim 28-29$ kcalmol⁻¹. Allowance for an average thermal energy of ~2 kcal mol⁻¹ leads to 30-31 kcal mol⁻¹ as the lower limit of the energy content of the chemically activated $CF_2ClCHCl^*$ radicals. Table III lists the calculated values of $k_d(E)$ as a function of energy. At $E_{\rm p} = 36 \text{ kcal mol}^{-1}, k_d(E) \simeq 1.5 \times 10^8 \text{ sec}^{-1}, \text{ which compares}$ favorably with the experimental value of $k_d \simeq 1.2 \times 10^8$ sec⁻¹. In view of the uncertainties in the thermochemical data, this suggests that the CF2CICHCl* radicals are nearly "thermal" above the chemical activation threshold, and lends support that these radicals are produced mainly in a secondary reaction rather than in the initial photochemical process where the $CF_2ClCHCl^*$

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would be expected to carry a significant fraction of the roughly 114 kcal mol⁻¹ of excess energy.

Effect of nitric oxide

The observed relative increase in the quantum yields of CF_2CHCl and CF_2CCl_2 with the addition of NO is the result of the suppression of the inhibition reactions (R5) and (R6) by the NO enhanced recombinative removal of chlorine atoms. Hippler and Troe²⁵ have studied the NOcatalyzed recombination of Cl atoms in helium over the pressure range 0.5–100 atm and have attributed the increase in the recombination rate to reactions involving nitrosyl chloride as an intermediate,

$$Cl + NO + M \rightarrow ClNO + M$$
, (R10)

$$Cl + ClNO \rightarrow Cl_2 + NO$$
 . (R11)

Assuming the ClNO to be quasistationary, the rate of removal of Cl atoms by recombination is given by $R_{10} = 2k_{10}[M][C1][NO]$, where the pressure dependent rate constant may be evaluated from the corresponding limiting low- and high-pressure rate constants: $k_{10}[M] \simeq k_{10}^{\circ}/[1 + k_{10}^{\circ}/k_{10}^{0}[M]]$. For helium as diluent, Hippler and Troe reported the values $k_{10, He}^{0} = 1.4 \times 10^{16}$ cm⁶ mol⁻² sec⁻¹ and $k_{10}^{\circ} = 4 \times 10^{13}$ cm³ mol⁻¹ sec⁻¹. These data can be used to estimate the relative rates of the abstraction and addition reactions to the NO-catalyzed chlorine atom recombination in the present system. Thus, assuming the deactivation efficiency of CF₂ClCHCl₂ is 10 times larger than that of He, the rate ratio for H abstraction/Cl recombination for the experiments with nitric oxide

TABLE II. Properties of the active radical and activated complex.

Frequencies ^a (cm ⁻¹)	Active Ra	Complex	
CCl	650 (2)		650 (1)
			r.c. ^b
C-F	1100 (2)		1100 (2)
С-Н	3000 (1)		3000 (1)
CC	1000 (1)		1400 (1)
C-C-F	440 (2)		440 (2)
C-C-C1	400 (2)		400 (1)
			280 (1)
С-С-Н	700 (1)		800 (1)
F-C-F	470 (1)		470 (1)
F-C-Cl	430 (1)		280 (1)
H-C-Cl	1035 (1)		1035 (1)
Hind. rot.	150 (1)	Torsion	200 (1)
$\langle \omega \rangle$, cm ⁻¹	79 8		828
E_{g} , kcal mol ⁻¹	17.10		16,58
s ^c	15		14
β_1^{d}	1,56		1.593
$Q_1^{\dagger}/Q_1 \sim 2$			

^aAssigned frequencies for normal and partial bonds. ^bReaction coordinate.

 $c_s =$ number of vibrational degrees of freedom.

 ${}^{d}\beta_{i} = (s-1) \sum \omega_{i}^{2} / (\sum \omega_{i})^{2}$ is the modified frequency dispersion parameter for the evaluation of $a = 1 - \beta_{i} W(E')$, where a [cf.Eq. (19)] is a correction to the zero point energy $E_{g} = \frac{1}{2} \sum \omega_{i}$ and W(E') is an analytic function of the reduced energy E' $= E_{v} / E_{g}$ (Ref. 24).

TABLE III. Calculated rate constants $k_d(E)$ for the reaction $CF_2CICHCI^* \rightarrow CF_2CHCI+CI$.

E [†] _v , kcal mol ⁻¹	2.0	3.0	5.0	8,0	10.0
E ^{"a} , kcal mol ⁻¹	30.0	31.0	33.0	36.0	38.0
$10^{-6} k_d(E)$, sec ⁻¹	1.45	4.6	25.6	156	337

 ${}^{a}E_{u} = E_{0} + E_{u}^{\dagger}$, where E_{0} (critical energy) = 28 kcal mol⁻¹.

 $[P(CF_2CICHCl_2) = 10 \text{ Torr}, F(NO) = 1 \text{ Torr}]$ is found to be $R_4/R_{10} \sim 0.7$. From the earlier estimate of R_5/R_4 at $[CF_2CHCl]_f/[CF_2CICHCl_2] = 10^{-4}$ it follows that the rate ratio for Cl-olefin addition/Cl-recombination is $R_5/R_{10} \sim 0.05$.

The effect of NO on the olefin quantum yields may be expressed quantitatively by expressions analogous to Eqs. (12) and (13). Under our experimental conditions $k_{10}^{\infty}/k_{10, H_0}^{0} \lambda' [CF_2ClCHCl_2] \gg 1$, and it can be shown that based on the proposed mechanism the reciprocal quantum yield of CF₂CHCl is given by

$$\frac{1}{\phi} = \frac{1}{\phi_0} + \frac{k_5}{k_4 + 2k_{10,\text{He}}^0 \lambda'[\text{NO}]} \left(\frac{lt}{N}\right) \quad , \tag{20}$$

where λ' is the collisional deactivation efficiency of the third body in Reaction (R10) (i.e., $\lambda' k_{10, He}^0 = k_{10, CF_5CICHCI_2}^0$, where we have assumed $\lambda' = 10$). A corresponding relation holds for the minor olefin, CF_2CCl_2 . Equation (20) shows that at a *constant* pressure of NO, $1/\phi$ is still a linear function of It/N, but the slope is decreased corresponding to the magnitude of $2k_{10,He}^0\lambda'$ [NO]. Comparison of the 10 Torr experiments in Fig. 1 in the presence and absence of NO supports this prediction, though the agreement must be considered to be only qualitative. First we note that the quantum yield of CF₂CHCl still shows a significant decline with increasing conversion, which indicates that, in the amount added, the NO does not remove all the chlorine atoms. More important, the intercept at zero conversion is higher, and hence the limiting quantum yield, $\phi_{0,NO}$ is lower in the presence of NO by an amount which is outside the experimental error. These effects are even more pronounced in the case of CF_2CCl_2 , and possible explanations are briefly considered below. Despite these noted difficulties, a semiquantitative estimate of the rate constant for the abstraction reaction (R4) can be obtained from the data in Fig. 1. The experimental ratio of slopes for the 10 Torr experiments in the absence and presence of NO is $S_0/S_{NO} \sim 2.13$, while from Eqs. (12) and (20) this slope ratio is given by $S_0/S_{NO} = 1 + 2k_{10,He}^0 \lambda' [NO]/k_4$. Using the literature value²⁵ for $k_{10,\text{He}}^0$ with $\lambda' = 10$, we obtain k_4 = 1.3×10^{10} cm³ mol⁻¹ sec⁻¹, which has been used in earlier discussion.

The lower *limiting* quantum yields of the olefins are indicative of some other processes involving radical precursors which are scavengeable by nitric oxide. In the case of CF₂CHCl this suggested radical contribution to the quantum yield is relatively minor, but is quite significant in the case of CF₂CCl₂. Thus, from Fig. 1 we obtain $\Delta\phi_0 = \phi_0 - \phi_{0,NO} \approx 0.12$ as the radical contribution which corresponds to ~17% of the total limiting quantum yield of CF₂CHCl. Similarly, from Fig. 2,

 $\Delta \phi'_0 = \phi'_0 - \phi'_{0,NO} \simeq 0.10$ or ~ 52% of the total quantum yield of CF₂CCl₂.

Preliminary to the discussion of the free radical reactions the question which now arises is as to the origin of these radicals at low conversions. While there is no conflict with the production of CF₂ClCCl₂ by Reaction (R4), Reactions (R5) and (R6) cannot be the source of the other haloethyl radicals in the limit as $It/N \rightarrow 0$. On the other hand, earlier in this discussion we had indicated that it is unlikely that $CF_2ClCHCl$ (and/or CF_2CHCl_2) radicals which may be produced as a first step in the primary photochemical process (R2) will be sufficiently long lived to undergo stabilizing or reactive collisions, and evidently, this restriction may have to be relaxed. We note, however, a possible alternate source of these radicals at or near thermal energies which could be provided by the H-atom abstraction of chlorine from the parent molecule, where the H atoms themselves are produced in the primary process: $CF_2ClCHCl_2 - H$ $+ CF_2ClCCl_2$, which is energetically possible.

An explanation of the radical contribution to the olefin yields may be sought in terms of the disproportionation reactions of the haloethyl radicals produced in the system. From amongst ten disproportionation reactions involving H- or Cl-atom transfer, which could arise, in principle, from the radicals CF₂ClCHCl, CF₂CHCl₂, and CF_2ClCCl_2 , five can be excluded on the basis of product analysis since none of the corresponding coproducts (CF₂ClCH₂Cl, CF₂HCHCl₂, CF₂ClCCl₃) were observed. The remaining reactions lead to the respective olefins and the parent molecule:

 $2CF_{2}CICHCI \rightarrow CF_{2}CHCI + CF_{2}CICHCI_{2}$ (R12) $CF_{2}CICHCI + CF_{2}CHCI_{2} \rightarrow CF_{2}CHCI + CF_{2}CICHCI_{2}$, (R13)

 $CF_2CICHCI + CF_2CICCI_2 - CF_2CCI_2 + CF_2CICHCI_2$, (R14)

 $2\dot{C}F_2CHCl_2 \rightarrow CF_2CHCl + CF_2ClCHCl_2$, (R15)

 $\dot{C}F_2CHCl_2 + CF_2Cl\dot{C}Cl_2 - CF_2CCl_2 + CF_2ClCHCl_2$ (R16)

where only Reaction (R16) involves a hydrogen transfer. While the reaction scheme above provides a feasible explanation for the olefin yields from radical sources, some difficulties should be pointed out. Firstly, it postulates "selective" disproportionations based, as stated, on product analysis. Secondly, assuming a total quantum yield of unity, it leads to the unusual result that the radical disproportionation/combination ratio is larger than unity, as may be seen from the limiting quantum yields in Figs. 1 and 2. Thus, introducing $\phi_0^{dis} = \Delta \phi_0 + \Delta \phi_0' = 0.22$ for the total limiting olefin quantum yield from radical (disproportionation) reactions, and assuming $\phi_0^{\text{tot}} = 1$, we obtain, by difference, in the light of lack of evodence for other processes, the limiting total quantum yield for haloethyl radical combination: $\phi_0^{\text{rec}} = \phi_0^{\text{tot}} - \phi_{0,NO} - \phi_{0,NO}' - \phi_0^{\text{dis}} \simeq 0.13$ where $\phi_{0,NO} = 0.56$ and $\phi_{0,NO}' = 0.087$ are the limiting quantum yields of the olefins formed molecularly as determined in the presence of NO. Hence, it follows that $\phi_0^{\text{dis}}/\phi_0^{\text{rec}} \simeq 0.22/$ 0.13>1.

served photolysis products which were attributed to similar "selective" disproportionation reactions, including chlorine atom transfer,⁶ and in which the radical combination products were quite low. In these cases "hot" radicals, originating in the primary process of carbon-chlorine bond cleavage, were implicitly invoked to explain the peculiar selectivity. It is also likely that a fraction of the radicals in the present system derives from a primary process, though the question of the efficiency with which hot radicals are scavenged by NO remains an area of concern. This latter consideration suggests that at least some partial collisional deactivation of the radicals must occur.

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- ¹D. Salomon, A. W. Kirk, and E. Tschuikow-Roux, Int. J. Chem. Kinet. 9, 619 (1977).
- ²D. Salomon, A. W. Kirk, and E. Tschuikow-Roux, J. Photochem. 7, 345 (1977).
- ³T. Ichimura, A. W. Kirk, and E. Tschuikow-Roux, Int. J. Chem. Kinet. 9, 697 (1977).
- ⁴T. Ichimura, A. W. Kirk, G. Kramer, and E. Tschuikow-Roux, J. Photochem. 6, 77 (1976).
- ⁵T. Ichimura, A. W. Kirk, and E. Tschuikow-Roux, Int. J. Chem. Kinet. 9, 743 (1977).
- ⁶T. Ichimura, A. W. Kirk, and E. Tschuikow-Roux, J. Phys. Chem. 81, 1153 (1977).
- ⁷C. Sanderfy, Z. Phys. Chem. 101, 307 (1976).
- ⁸T. Yano and E. Tschuikow-Roux, J. Phys. Chem. 83, 2572 (1979).
- ⁹R. Gorden, Jr., R. E. Rebbert, and P. Ausloos, Natl. Bur. Stand. (U.S.) Tech. Note 496 (1969).
- ¹⁰D. Solomon, and A. A. Scala, J. Chem. Phys. 62, 1469 (1975).
- ¹¹R. Gorden, Jr., R. Doepker, and P. Ausloos, J. Chem. Phys. 44, 3733 (1966).
- ¹²(a) $\Delta H_{f,298}^{\circ}$ (CF₂ClCHCl₂) = -125 kcal mol⁻¹ based on group additivity data from S. W. Benson, Thermochemical Kinetics, 2nd ed. (Wiley, New York, 1976); (b) $\Delta H_{f,298}^{\circ}$ (CF₂CHCl) = -75.4, $\Delta H_{f,298}^{\circ}$ (CF₂CCl₂) = -76.3 kcal mol⁻¹ from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. Chem. Ref. Data 6, Suppl. 1 (1977); (c) D(H-Cl) = 103, and $D(C1-C1) = 58.2 \text{ kcal mol}^{-1}$, from B. de B. Darwent, Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. 31 (1970).
- ¹³J. M. Simmie and E. Tschuikow-Roux, J. Phys. Chem. 74, 4075 (1970).
- ¹⁴F. Zabel, Int. J. Chem. Kinet. 9, 651 (1977).
- ¹⁵F. Zabel, Ber. Bunsenges. Phys. Chem. 78, 232 (1974).
- ¹⁶(a) A. F. Trotman-Dickenson and G. S. Milne, Tables of Bimolecular Gas Reactions, Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. 9, (1967); (b) J. A. Kerr and E. Ratajczak, Second Supplementary Table of Bimolecular Gas Reactions (University of Birmingham, England, 1973); (c) J. A. Kerr and E. Ratajczak, Third Supplementary Table of Bimolecular Gas Reactions (University of Birmingham, England, 1977).
- ¹⁷V. N. Kondrat'ev, Gas-Phase Reaction Rate Constants (Akad. Nauk, Moscow, 1970).
- ¹⁸P. Cadman, A. W. Kirk, and A. F. Trotman-Dickenson, J. Chem. Soc. Faraday Trans. 1 72, 1027 (1976).

¹⁹C. Cillien, P. Goldfinger, G. Huybrechts, and G. Martens,

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- ²⁰P. B. Ayscough, A. J. Cocker, F. S. Dainton, and S. Hirst, Trans. Faraday Soc. 58, 318 (1962).
- ²¹P. C. Beadle and J. H. Knox, J. Chem. Soc. Faraday Trans. 1 70, 1418 (1974).
- 22 E. Sanhueza and J. Heicklen, Int. J. Chem. Kinet. 7, 399

(1975).

- ²³See, for example, P. J. Robinson and K. A. Holbrook, Unimolecular Reactions (Wiley, New York, 1972).
- ²⁴G. Z. Whitten and B. S. Rabinovitch, J. Chem. Phys. **38**, 2466 (1963).
- ²⁵H. Hippler and J. Troe, Int. J. Chem. Kinet. 8, 501 (1976).