Photodissociation of 1,1,1-Trifluorodichloroethane at 147 nm. Evidence for Chlorine Atom Reactions

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The 147-nm photolysis of CF_3CHCl_2 has been investigated at ~23 °C as a function of reactant pressure and conversion (It/N), with and without nitric oxide as additive. The principal reaction product is CF_2CHF, with lesser yields of CF_2CFCl, CF_2CHCl, and four chlorofluorobutanes. At constant CF_3CHCl_2 pressure the observed quantum yields of the olefins decrease with increasing It/N and there is a corresponding increase in the yields of the C_4 products. The quantum yields of the olefins also decrease with increasing reactant pressure at the same values of It/N. The addition of NO completely suppresses the formation of the chlorofluorobutanes, but there is a marked *increase* in the olefin quantum yields. These observations are interpreted in terms of reactions of chlorine atoms which derive, primarily, from the α,α elimination of the elements of $(Cl)_2$ in the primary process. Chlorine atoms so produced abstract hydrogen from the parent and add to the product olefins, processes which are the source of haloethyl radicals in the system. Nitric oxide provides an additional and dominant channel for chlorine atom removal by way of their NO-catalyzed recombination which proceeds through ClNO as an intermediate. A reaction mechanism consistent with the observations is proposed and, from the functional dependence of the olefin quantum yields on It/N, limiting values have been obtained by extrapolation. The rate constant ratio for hydrogen abstraction from CF_3CHCl_2 by Cl atoms to Cl addition to CF_2CHF was found to be $k_5/k_6^\infty = (2.2 \pm 0.5) \times 10^{-4}$. The extinction coefficient for CF_3CHCl_2 at 147 nm (296 K) has been determined as $\epsilon = (1/PL) \ln (I_0/I_t) = 590 \pm 60$ atm^{-1} cm^{-1}.

Introduction

Our recent studies of the 147-nm photodecomposition of CF_2ClCH_2Cl[1] and $CF_2ClCHCl_2$[2] have shown that the principal mode of decomposition is associated with the production of chlorine atoms and the corresponding olefins. HCl elimination also occurs but to a minor extent. Based on experimental evidence and thermochemical considerations we inferred that chlorine atoms are formed either directly by near simultaneous (i.e., very rapid sequential) C-Cl bond scission reactions or from the dissociation of an excited Cl_2^* molecule produced by molecular elimination in the primary process. The chlorine atoms so generated are removed by competitive reactions involving hydrogen abstraction from the parent molecule and Cl addition to the product olefins, both processes yielding halogenated ethyl radicals. This interpretation was based on the identification of some chlorofluorobutanes among the reaction products and the dependence of the product quantum yields on pressure and conversion. The primary processes in the photolysis of CF_2ClCH_2Cl and $CF_2ClCHCl_2$ thus differ from those of other chloro- and chlorofluoroethanes in which the halogen substitution is in the α position. Thus in the 147-nm photolysis of CH_3CHCl_2,[3] CH_3CCl_3,[4] and CH_3CF_2Cl,[5] the predominant decomposition channel is HCl elimination. Hydrogen chloride elimination is also the most important process in the photolysis of C_2H_5Cl, though the photochemistry of this compound at 147 nm is very complex, with a large number of products having been observed.[6] Halogen (F or Cl) substitution on the second carbon atom as in CH_2FCH_2Cl,[7] CF_3CH_2Cl,[8] and CH_2ClCH_2Cl[9] leads to a decrease in HCl elimination relative to the dehalogenation processes, and the appearance of some secondary products with radical precursors. In our continuing effort to gain further insight into the photochemistry of the chloro- and chlorofluoro-C_2 hydrocarbon series, we report here on the 147-nm photolysis of CF_3CHCl_2.

Experimental Section

The apparatus and experimental procedure have been described previously.[1,2] Photolyses were carried out at room temperature (~23 °C) in a spherical Pyrex vessel of 215-cm^3 volume. The reactant, CF_3CHCl_2 (Peninsular Chemresearch), was purified to better than 99.95% by preparative gas chromatography with a 2-m SE-30 column at 25 °C with nitrogen as carrier. The residual impurities were not identified but were ascertained not to interfere with product analysis. In experiments with nitric oxide as additive, the NO was purified by trap-to-trap distillation at 77 K prior to its use.

Photolysis quantum yields were determined by chemical actinometry based on the production of C_2H_2 in the photolysis of ethylene[10] ($\phi_{C_2H_2} \simeq 1.0$ at 147 nm), and actinometric measurements were conducted just prior to each photolysis of the test gas. The extinction coefficient of CF_3CHCl_2 at 147 nm and 296 K was found to be $\epsilon = (1/PL) \ln (I_0/I_t) = 590 \pm 60$ atm^{-1} cm^{-1} by use of the double-cell method of Gorden et al.[11] Thus under our experimental conditions virtually all incident radiation was absorbed.

Product analysis was carried out by flame-ionization gas chromatography (Hewlett-Packard, Model 5830A). The lower molecular weight C_2 products were separated at 125 °C with a 3.6-m Porpak N column and identified as CF_2CHF, CF_2CFCl, and CF_2CHCl from their elution times. Quantitative determination of these olefins was carried out by comparison of peak area with those of authentic samples. A 1.8-m Durapak (*n*-octane/Porasil C) column at 100 °C with a He flow rate of 30 cm^3/min was used to isolate the higher molecular weight compounds. At the highest conversions up to eight product peaks were observed, of which only four, however, were of any significance in terms of their yields. Identification of these four products was based on their mass-spectral cracking pattern with a GC-MS instrument (Hewlett-Packard, Model 5992A). The two most prominent of the higher molecular weight products were identified as $CF_2ClCHFCCl_2CF_3$ (Cl_3-B) and $CF_3CCl_2CCl_2CF_3$ (Cl_4-B). The other two C_4 products with a shorter retention time were not well resolved by gas chromatography, but mass spectrometrically they were found to contain a CF_2ClCHF group at least. These compounds were inferred to be the diastereomers of CF_2ClC-

TABLE I: Product Quantum Yields in the 147-nm Photolysis of CF_3CHCl_2

run no.	$P_{CF_3CHCl_2}$, torr	P_{NO}, torr	$10^{-13}I$, photons s^{-1}	$10^4(It/N)$	ϕ^a					
					CF_2CHF	CF_2CFCl	CF_2CHCl	$Cl_2\text{-}B_{1,2}$[b]	$Cl_3\text{-}B$	$Cl_4\text{-}B$
1	1.2		0.91	3.13	0.332	0.041	0.059	c	c	c
2	1.3		0.93	6.42	0.284	0.064	0.070	c	0.094	0.147
3	1.2		3.0	12.4	0.224	0.027	0.035	~0.019	0.095	0.174
4	1.2		3.2	22.2	0.183	0.022	0.030	0.026	0.101	0.148
5	1.2	0.11	1.9	6.59	0.323	0.047	0.050	0	0	0
6	1.2	0.11	1.1	7.94	0.295	0.040	0.060	0	0	0
7	1.2	0.10	2.0	14.0	0.293	0.039	0.039	0	0	0
8	1.2	0.12	3.2	22.2	0.277	0.046	0.042	0	0	0
9	3.1		0.93	2.57	0.359	0.069	0.057	c	0.081	0.217
10	3.1		2.1	4.13	0.263	0.043	0.048	c	0.132	0.233
11	3.1		2.1	5.79	0.254	0.047	0.047	~0.019	0.141	0.262
12	3.1		4.6	12.8	0.178	0.032	0.035	0.039	0.186	0.273
13	3.1	0.21	0.98	1.35	0.390	0.045	0.062	0	0	0
14	3.1	0.20	1.4	3.93	0.354	0.054	0.051	0	0	0
15	3.1	0.21	1.3	7.27	0.310	0.053	0.043	0	0	0
16	6.2		2.0	1.38	0.335	0.070	0.078	c	0.140	0.307
17	6.4		2.1	2.37	0.298	0.058	0.050	c	0.152	0.308
18	6.4		2.0	2.65	0.312	0.053	0.055	c	0.146	0.293
19	6.2		4.5	13.2	0.160	0.031	0.027	0.028	0.235	0.272
20	6.2	0.61	1.9	2.70	0.387	0.065	0.063	0	0	0
21	6.2	0.62	3.0	4.22	0.374	0.064	0.037	0	0	0
22	6.2	0.62	3.1	8.67	0.299	0.053	0.051	0	0	0
23	13.3		2.1	0.667	0.405	0.071	0.103	c	0.118	0.287
24	13.2		3.4	2.22	0.310	0.075	0.061	c	0.199	0.352
25	13.3		5.1	4.94	0.229	0.054	0.043	0.013	0.215	0.317
26	13.3		3.5	5.76	0.218	0.048	0.042	0.010	0.219	0.310
27	12.8	0.71	3.3	3.93	0.369	0.075	0.065	0	0	0
28	23.8		3.2	1.15	0.355	0.077	0.085	c	0.149	0.308
29	23.8		8.9	3.27	0.279	0.058	0.052	c	0.202	0.305

[a] Quantum yields for chlorofluorobutanes are relative to C_2H_2, the actinometric standard (see text). [b] Sum of two diastereoisomers of $CF_2ClCHFCHFCF_2Cl$. [c] Trace amounts, ϕ could not be determined.

$HFCHFCF_2Cl$ ($Cl_2\text{-}B_{1,2}$). The yields of the residual trace products were too small to be analyzed, but, on the basis of their elution times, are likely to be other chlorofluoro-C_4 compounds. In the absence of bona fide samples of the various chlorofluorobutanes, their relative sensitivities in gas-chromatographic analysis were arbitrarily taken as equal to that of acetylene (actinometric standard). This is adequate for establishing relative yields and qualitative trends.

Results

Table I summarizes the product quantum yields as a function of reactant pressure, the additive NO, and the conversion, It/N. The latter quantity has been shown[1,2] to provide an important diagnostic correlation function, where I is the total light absorbed per unit time in the reaction cell (photons/s), t is the irradiation time (s), and N ($= PVN_0/RT$) is the total number of reactant molecules. As the conversions in this study were very low, N is effectively a constant at any given pressure.

Inspection of Table I shows that at any fixed pressure of CF_3CHCl_2 and in the absence of NO the quantum yields of the olefins *decrease*, while the quantum yields of the chlorofluorobutanes, $Cl_2\text{-}B_{1,2}$ and $Cl_3\text{-}B$, *increase* with increasing values of It/N. In the case of $Cl_4\text{-}B$ the trend is less discernable and the quantum yield appears to remain more or less constant with conversion. Also to be noted is a decrease in the quantum yield of the principal olefin, CF_2CHF, with increasing CF_3CHCl_2 pressure at approximately the same values of It/N (runs 3, 12, and 19, for example). The addition of NO completely inhibits the formation of the chlorofluorobutanes, and produces a significant increase in the quantum yields of the olefins at the same reactant pressure and (approximately) same conversion (cf. runs 4 and 8; 10 and 14; 18 and 20).

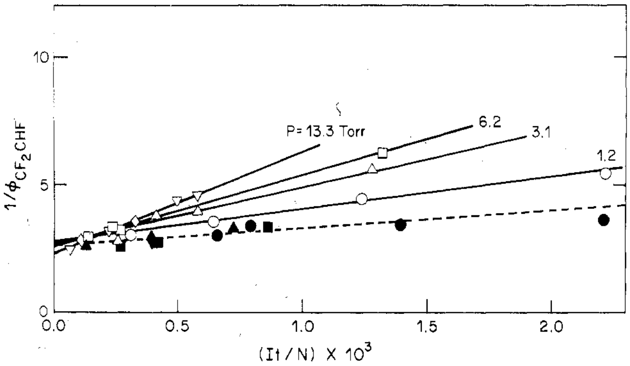

Figure 1. Plot of the reciprocal quantum yield of CF_2CHF vs. It/N for small values of conversion, at different reactant pressures: (open symbols) experiments without NO; (solid symbols and broken line) all experiments with NO.

Figure 1 shows plots of the reciprocal quantum yield of CF_2CHF as a function of conversion for different reactant pressures in the absence and presence of NO. Though the data show some scatter, several important features can be pointed out in Figure 1: (1) there exists a linear relationship between $1/\phi_{CF_2CHF}$ and It/N at constant CF_3CHCl_2 pressure; (2) the slopes of the straight lines are pressure dependent and increase with increasing reactant pressure; (3) the limiting values of the reciprocal quantum yield (extrapolated to zero conversion) at different pressures converge to approximately the same average value: $1/\phi^0_{CF_2CHF} \simeq 2.5 \pm 0.4$; (4) the addition of NO affects the linear relationship in two ways: the slopes of the lines at any given reactant pressure are decreased dramatically from their values in the absence of NO, and, more curious, in the presence of NO, the data at all pressures fall, within experimental error, on the same straight line with a (positive) nonzero slope.

Analogous plots to Figure 1 for the minor olefins (CF_2CFCl and CF_2CHCl) show qualitatively similar features, although in this case the data are much scattered owing to the very low yields of these products and the associated analytical difficulties. Extrapolation of the data to $It/N = 0$ suggests limiting quantum yield values of $1/\phi^0_{CF_2CFCl} \simeq 12 \pm 2$ and $1/\phi^0_{CF_2CHCl} \simeq 10 \pm 2$.

The effect of NO on the reciprocal olefin quantum yield vs. conversion data at *different* reactant and NO pressures has not been examined in our previous studies, and this aspect requires some further consideration.

Discussion

The main features in the 147-nm photolysis of CF_3CHCl_2 are qualitatively rather similar to those of other α,β-substituted chlorofluoroethanes, specifically CF_2ClCH_2Cl[1] and $CF_2ClCHCl_2$.[2] The complete suppression of the formation of chlorofluorobutanes by nitric oxide shows that these products derive from radical precursors. Moreover, the experiments with added NO support the view that CF_2CHF, CF_2CFCl, and CF_2CHCl are associated with primary processes, though very minor contributions resulting from possible radical disproportionation reactions could well be masked by compensating processes. A more detailed discussion of the effect of NO on the quantum yields of these olefins is given later. In the absence of NO the decrease in the olefin quantum yields with increasing conversion is linked with the production of the chlorofluorobutanes. This dependency of the product quantum yields on conversion is readily explained in terms of reactions of atomic chlorine, specifically hydrogen abstraction from the parent compound and Cl addition to the product olefins. All these processes lead to the formation of halogenated ethyl radicals and provide the source of the chlorofluorobutanes. Based on these observations we therefore propose a similar reaction mechanism to those described in recent publications.[1,2]

Olefin Formation. The formation of the principal product, CF_2CHF, must occur from the rearrangement of the $CF_3\ddot{C}H$ diradical, which is produced in a primary process by the α,α elimination of the elements of $(Cl)_2$:

$$CF_3CHCl_2 + h\nu \rightarrow CF_3CHCl_2{}^{\dagger} \qquad (R1)$$

$$CF_3CHCl_2{}^{\dagger} \rightarrow CF_3\ddot{C}H + 2Cl \text{ (or } Cl_2{}^{*} \rightarrow 2Cl) \qquad (R2a)$$

$$CF_3\ddot{C}H \rightarrow CF_2CHF \qquad (R2b)$$

where the dagger denotes electronic excitation. In reaction R2a the rapid sequential (or nearly simultaneous) expulsion of two chlorine atoms is implied. An alternative process may involve the concerted molecular elimination of an excited $Cl_2{}^{*}$ molecule followed by its rapid dissociation. Our experiments cannot distinguish between these two processes, but both lead to the formation of chlorine atoms, since $Cl_2{}^{*}$ cannot be expected to be stabilized in view of the energetics involved. Parenthetically we note, however, that on the basis of our product analysis and thermochemical considerations we have excluded here, as a primary process, single C–Cl bond fission leading to stabilized $CF_3\dot{C}HCl$ radicals. In the ground state, the overall reaction (reaction R2) is endothermic by about 117 kcal mol^{-1}.[12a]

$$CF_3CHCl_2 \rightarrow CF_2CHF + 2Cl \qquad (R2)$$

Since the photon energy is 194 kcal mol^{-1}, the excess energy which must be distributed between the reaction products in reaction R2 is 77 kcal mol^{-1}. This energy is less than the estimated activation barrier for HF elimination from CF_2CHF, which is the expected decomposition channel, in analogy to the thermal decomposition of 1,1-difluoroethylene[13] ($CF_2CH_2 \rightarrow CFCH + HF$, $E_a \sim 86$ kcal mol^{-1}). The absence of C_2F_2 as a reaction product supports this prediction.

The formation of CF_2CFCl must occur by a process similar to reaction R2 and involve the α,α elimination of HCl, followed by the rapid rearrangement of the $CF_3\ddot{C}Cl$ diradical, the overall reaction being

$$CF_3CHCl_2{}^{\dagger} \rightarrow CF_2CFCl + HCl^{*} \; (HCl^{*} \rightarrow H + Cl) \qquad (R3)$$

The enthalpy change for HCl elimination in reaction R3 is $\sim 30 \pm 4$ kcal mol^{-1} and hence the excess energy is roughly 164 ± 4 kcal mol^{-1}, though the heat of formation of CF_2CFCl is not well known.[12b] Based on our product analysis, the CF_2CFCl evidently does not undergo further dissociation such as C–Cl bond cleavage (in analogy to $C_2Cl_4 \rightarrow C_2Cl_3 + Cl$, $E_a \simeq 80$ kcal mol^{-1} [14]) which suggests that the HCl^{*} must carry a large fraction (>50%) of the excess energy. It is therefore feasible that in this system some dissociation of HCl does occur, despite its high bond dissociation energy.[12c]

The molecular production of CF_2CHCl is readily explained in terms of the α,β elimination of the elements of FCl:

$$CF_3CHCl_2{}^{\dagger} \rightarrow CF_2CHCl + FCl^{*} \; (FCl^{*} \rightarrow F + Cl) \qquad (R4a)$$

$$\rightarrow CF_2CHCl + F + Cl \qquad (R4b)$$

Again, the CF_2CHCl is stable with respect to further decomposition, and it is not possible to distinguish between the concerted FCl^{*} elimination followed by its dissociation or rapid sequential carbon–halogen bond scission reactions. The heat of reaction R4a is ~ 90 kcal mol^{-1} [12d] and the excess energy is therefore ca. 104 kcal mol^{-1}. In view of the relatively low value of $D(F\text{–}Cl) = 59.8$ kcal mol^{-1},[12c] the constraints on the energy partitioning would have to favor the decomposition of the FCl^{*} molecule.

In concluding this section we note, however, that though the question as to the cofragments in the production of CF_2CFCl and CF_2CHCl remains unsettled, these processes are minor in relation to reaction R2 in the first instance, and we omit from further consideration possible contributions to secondary reactions as a result of H, Cl, or F atoms which may be generated in reactions R3 and R4, respectively.

Chlorine Atom Reactions and Production of Chlorofluorobutanes. Metathetical reactions of chlorine atoms with chlorinated[15] and fluorinated ethanes[16] are known to proceed at, or near, room temperature. The observed general trend for hydrogen abstraction is that the activation energies *increase* and the preexponential factors *decrease* with increasing halogen substitution. Moreover, in the case of some fluoroethanes, Cadman et al.[16] have found that the abstraction of a hydrogen atom in the β position to the fluorine substituents is considerably slower than for hydrogen in the α position. The situation with mixed chlorofluoro substitution has apparently not been investigated in detail, but our recent studies[1,2] indicate that the general trend is the same: the rate of H abstraction decreases with progressive halogen substitution.

Chlorine atoms produced in the system will abstract hydrogen from the parent molecule to form thermal $CF_3\dot{C}Cl_2$ radicals (reaction R5) and, as noted earlier, they

$$Cl + CF_3CHCl_2 \rightarrow CF_3\dot{C}Cl_2 + HCl \qquad (R5)$$

will also react with the product olefins. The addition of chlorine atoms to chloroethylenes[17] and chlorofluoroethylenes[18] proceeds rapidly with nearzero activation energy to produce the corresponding vibrationally excited haloethyl radicals which may be collisionally stabilized. It has been shown previously[1,2] that, at room temperature, the addition reaction is competitive with hydrogen abstraction even at very low olefin concentration, owing to the significant increase in the activation energy for the abstraction reaction with increasing degree of α,β-halogen substitution. Thus in the present system we may consider the following addition reactions which inhibit olefin formation and which explain the decrease in the olefin quantum yields with increasing conversion:

$$Cl + CF_2CHF \xrightarrow{(+M)} CF_2Cl\dot{C}HF \qquad (R6)$$

$$\xrightarrow{(+M)} \dot{C}F_2CHFCl \qquad (R6a)$$

$$Cl + CF_2CFCl \xrightarrow{(+M)} CF_2Cl\dot{C}FCl \qquad (R7)$$

$$\xrightarrow{(+M)} \dot{C}F_2CFCl_2 \qquad (R7a)$$

$$Cl + CF_2CHCl \xrightarrow{(+M)} CF_2Cl\dot{C}HCl \qquad (R8)$$

$$\xrightarrow{(+M)} \dot{C}F_2CHCl_2 \qquad (R8a)$$

In the absence of nitric oxide reactions R5–R8a provide the sink for the removal of chlorine atoms, since the direct three-body recombination ($Cl + Cl + M \rightarrow Cl_2 + M$) is negligible.

The association of the haloethyl radicals produced in reactions R5–R8a leads to the corresponding chlorofluorobutanes. Other conceivable reactions of these radicals, such as disproportionation or metathetical reactions, are not important as evidenced by our product analysis. Also, in view of the low yields of CF_2CFCl and CF_2CHCl, the corresponding radical concentrations (reactions R7–R8a) must also be very low and are neglected from further consideration, except to note that some of the unidentified trace products are likely to be the combination products involving these radicals. Furthermore, from the GC-MS analysis of the chlorofluorobutanes we conclude that the much more preferred site of chlorine atom addition is to the CF_2 group in CF_2CHF. A similar observation has been made in previous studies.[1,2] Thus, from a practical point of view we need only consider the radicals produced in reactions R5 and R6. The combination and cross combination of these radicals gives rise to the observed chlorofluorobutanes:

$$2CF_2Cl\dot{C}HF \rightarrow CF_2ClCHFCHFCF_2Cl \quad (Cl_2\text{-B}) \qquad (R9)$$

$$CF_2Cl\dot{C}HF + CF_3\dot{C}Cl_2 \rightarrow CF_2ClCHFCCl_2CF_3 \quad (Cl_3\text{-B}) \qquad (R10)$$

$$2CF_3\dot{C}Cl_2 \rightarrow CF_3CCl_2CCl_2CF_3 \quad (Cl_4\text{-B}) \qquad (R11)$$

Since the formation of Cl_2-B and Cl_3-B involves the $CF_2Cl\dot{C}HF$ radical originating from the addition reaction R6, the increase in the quantum yields of these chlorofluorobutanes with a concomitant decrease in the quantum yield of CF_2CHF with the progress of reaction is readily understood. In contrast, as may be seen from Table I, the yield of Cl_4-B is approximately constant with conversion, as it should, since the production of the $CF_3\dot{C}Cl_2$ radical is not directly linked with the olefin yield.

Dependence of ϕ_{CF_2CHF} on It/N and Pressure. On the basis of the proposed reaction scheme and the foregoing discussion, the rate expression for the principal product, CF_2CHF, is given by

$$d[CF_2CHF]/dt = \phi_0 I_a - k_6[Cl][CF_2CHF] \qquad (1)$$

where ϕ_0 is the *true* quantum yield of CF_2CHF, and I_a is the absorbed light intensity per unit length (einsteins/cm^3 s). Replacing the chlorine atom concentration in eq 1 by its quasi-stationary state value[1,2] (with reactions R6a–R8a neglected) and making the substitution X = [CF_2CHF], A = [CF_3CHCl_2], and $y = k_6X/k_5A$, we obtain

$$dy/dt = C(1 - y)/(1 + y) \qquad (2)$$

where $C = (k_6/k_5)\phi_0 I_a/A$ is a constant in view of the very low conversions in this study (i.e., $A \simeq$ constant). Integration of eq 2 with the initial conditions $X = 0$, $y = 0$ at $t = 0$ yields

$$y = 1 - e^{-1/2(Ct+y)} \qquad (3)$$

From the definition of y we note that eq 3 describes the time dependence of the *rate ratio* of the addition/abstraction reactions. Rewriting eq 3 in terms of X we obtain

$$\phi = (1/\xi)\{1 - \exp[-(\xi/2)(\phi + \phi_0)]\} \qquad (4)$$

where $\phi = X/I_a t$ is the *observed* quantum yield, and $\xi = (k_6/k_5)I_a t/A \equiv (k_6/k_5)It/N$ follows from the definition of the conversion, It/N. Equation 4 expresses the dependence of the observed quantum yield on conversion. For low conversions, the exponential in eq 4 may be expanded in a power series leading to the simple relationship[2]

$$\phi^{-1} = \phi_0^{-1} + (k_6/k_5)It/N \qquad (5)$$

Equation 5 predicts that the reciprocal of the observed quantum yield is a linear function of conversion, for *small* values of It/N, and in the limit $(It/N) \rightarrow 0$, $\phi \rightarrow \phi_0$.

A plot of ϕ^{-1} vs. conversion for different sets of reactant pressure is shown in Figure 1 for $It/N \leq 2.3 \times 10^{-3}$. The experimental data support the predicted linear relationship for photolyses at *constant* CF_3CHCl_2 pressure, however, it is also evident that for experiments at different concentrations the slopes are pressure dependent. An explanation of this pressure dependence is readily provided by noting that the adduct formed in reaction R6 is chemically activated, and, hence, the rate constant k_6 is pressure dependent. This can be shown from a consideration of the detailed processes

$$Cl + CF_2CHF \underset{k_d}{\overset{k_a}{\rightleftharpoons}} CF_2Cl\dot{C}HF^* \xrightarrow{k_s[M]} CF_2Cl\dot{C}HF$$

where k_a, k_d, and k_s are, respectively, the rate constants for activation, (re)-dissociation, and stabilization of the chemically activated radical, $CF_2Cl\dot{C}HF^*$. Assuming the deactivation is directly proportional to the collision frequency, $k_s[M] = \lambda ZP$, the overall rate constant for the addition reaction is therefore given by

$$k_6 = k_a/(1 + k_d/\lambda ZP) \qquad (6)$$

where Z is the gas kinetic collision frequency per unit pressure, and λ is a collisional deactivation efficiency factor. Equation 6 shows that k_6 is pressure dependent and increases with pressure. In the limit as $P \rightarrow \infty$, $k_6 \rightarrow k_a \equiv k_6^\infty$. Substitution of eq 6 in eq 5 leads to

$$\begin{aligned}\phi^{-1} &= \phi_0^{-1} + (k_6^\infty/k_5)(1 + k_d/\lambda ZP)^{-1}(It/N) \qquad (7)\\ &= \phi_0^{-1} + m(P)It/N\end{aligned}$$

Equation 7 provides an explanation of both the linear relationship between ϕ^{-1} and It/N at any *fixed* pressure and the observed pressure dependence of the slopes (cf. Figure 1). At high pressures such that $k_d/\lambda ZP \ll 1$ the limiting slope gives directly k_6^∞/k_5, the rate constant ratio for the addition/abstraction reactions, while at sufficiently low pressures ($k_d/\lambda ZP \gg 1$) the slope is directly proportional to pressure. Neither of the limiting cases were ac-

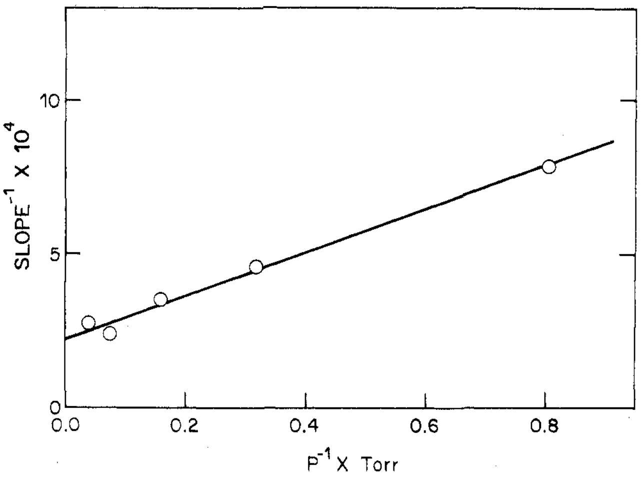

Figure 2. Plot of the reciprocal of the slopes of the isobars in Figure 1 for experiments without NO (cf. eq 8).

cessible under our experimental conditions. However, in the general pressure range eq 7 predicts a linear relationship when the inverse of the slope is plotted against the reciprocal pressure:

$$\frac{1}{m(P)} = \frac{k_5}{k_6^{\infty}} + \frac{k_5}{k_6^{\infty}}\left(\frac{k_d}{\lambda Z}\right)\frac{1}{P} \qquad (8)$$

Figure 2 shows a plot of this function for the CF_2CHF data derived from Figure 1 and the agreement with the theoretical prediction is most satisfactory. From the intercept we obtain $k_5/k_6^{\infty} = (2.2 \pm 0.5) \times 10^{-4}$ which is close to the corresponding rate constant ratio found in the $CF_2ClCHCl_2$ photolysis ($k_{abs}/k_{add} = 3.8 \times 10^{-4}$).[2] This is not unexpected since the compounds in the two systems are similar in terms of their structure and have common groups (cf. CF_3CHCl_2 vs. $CF_2ClCHCl_2$ and CF_2CHF vs. CF_2CHCl, respectively). In order to establish further trends, it is instructive to compare these results with other selected data on abstraction and addition reactions.[19] Arrhenius parameters have been reported for hydrogen abstraction by chlorine atoms from C_2H_6,[20] C_2HCl_5,[15] and chlorine addition to C_2H_4[21] and C_2HCl_3.[21,22] Using these literature data we calculate the rate constant ratios [denoted pairwise by R(i/j)] at 298 K as follows: $R(C_2H_6/C_2H_4) = 0.98$; $R(C_2H_6/C_2HCl_3) = 7.81$; $R(C_2HCl_5/C_2HCl_3) = 5.6 \times 10^{-3}$. The conclusion which can be drawn from these values is that, while chlorine substitution decreases the rate constants for both the abstraction and addition reactions, the decrease is much more pronounced in the case of the abstraction reaction. The very small values of the rate constant ratios in the present study and in the photolysis of $CF_2ClCHCl_2$ are in agreement with this general trend, and, further, suggest that fluorine substitution increases the activation energy for the abstraction of a β hydrogen somewhat more than does chlorine substitution.

From the slope and intercept of Figure 2 we obtain $k_d/\lambda Z = 3.2 \pm 1.1$ torr. If we assume the "usual" value of $Z \simeq 10^7$ torr^{-1} s^{-1} and $\lambda = 1$, the *average* rate constant for decomposition of the chemically activated $CF_2Cl\dot{C}HF^*$ radical is $k_d = (3.2 \pm 1.1) \times 10^7$ s^{-1}. This value may be compared with $k_d(E)$ predicted by the RRKM theory of unimolecular reactions.[23] Based on thermochemical estimates, the addition reaction R6 for ground state reactants is exothermic by ca. 21 kcal mol^{-1}.[12e] Assuming an activation energy for this process of ~1.0–1.5 kcal mol^{-1} gives a critical energy of $E_0 \simeq 22.5$ kcal mol^{-1} for the reverse dissociation reaction. Table II lists the necessary input data and the results of the calculation. The value of $k_d(E)$ nearest to the experimental k_d value is seen to correspond to an energy content of just below $E_v = 25.5$ kcal mol^{-1}, or a nonfixed energy of $E_v^{\dagger} \simeq 3$ kcal mol^{-1}, which indicates that the reactants forming the adduct are nearly thermal.

TABLE II: Input Data and Calculated Rate Constant $k_d(E)$ for the Reaction $CF_2Cl\dot{C}HF^* \rightarrow CF_2CHF + Cl$

	active radical	activated complex
ω_i,[a] cm^{-1}		
stretch	650, 1000, 1100(3), 3000	1400, 1100(3), 3000
bending	400, 430, 440(3), 470, 700, 1060 150 (hindered rot.)	280(2), 440(3), 470, 800, 1060 200 (torsion)
E_z,[b] kcal mol^{-1}	17.84	17.31
s	15	14
$E_v^{\dagger}$, kcal mol^{-1}	2, 3, 5	
E_v,[c] kcal mol^{-1}	24.5, 25.5, 27.5	
$10^{-7}k_d(E)$,[d] s^{-1}	1.4, 4.1, 19	

[a] Assigned frequencies for normal and partial bonds. For activated complex the C–Cl stretch is taken as the reaction coordinate. [b] Zero point energy ($E_z = {}^1/_2\Sigma\omega_i$). [c] $E_v = E_v^{\dagger} + E_0$ where E_0 (critical energy) = 22.5 kcal mol^{-1}. [d] $k_d(E) \simeq c(\Pi^{15}\omega_i/\Pi^{14}\omega_i^{\dagger})(Q_1^{\dagger}/Q_1)[(E_v^{\dagger} + aE_z^{\dagger})/(E_v + aE_z)]^{14}$; where $Q_1^{\dagger}/Q_1 \sim 2$ (assumed). For definition of symbols see ref 23.

Effect of Nitric Oxide. The observed relative increase in the olefin quantum yields in the presence of nitric oxide is readily explained by the NO-catalyzed recombination of chlorine atoms. This process reduces the chlorine atom concentration and hence leads to a suppression of the addition reactions R6–R8. With respect to radical reactions, nitric oxide plays a dual role: it reduces haloethyl radical formation reactions R5–R8 by removing chlorine atoms, and it serves as the usual radical scavenger of any residual radicals. The NO-enhanced recombination of chlorine atoms proceeds via nitrosyl chloride as an intermediate:[24]

$$Cl + NO + M \rightarrow ClNO + M \qquad (R12)$$

$$Cl + ClNO \rightarrow Cl_2 + NO \qquad (R13)$$

Since reaction R13 is known to be very fast,[25] the ClNO concentration can be considered to be quasi-stationary and the rate of removal of Cl atoms by recombination is given by $R_{12} = 2k_{12}[M][Cl][NO]$ where $k_{12}[M]$ may be evaluated from the corresponding limiting low and high pressure rate constants: $k_{12}[M] = k_{12}^{\infty}/(1 + k_{12}^{\infty}/k_{12}^{0}[M])$. For helium as diluent, Hippler and Troe[24] reported the values $k_{12}^{\infty} = 4 \times 10^{13}$ cm^3 mol^{-1} s^{-1} and $k_{12}^{0} = 1.4 \times 10^{16}$ cm^6 mol^{-2} s^{-1} at 298 K. At the total pressures used in this study $k_{12}^{\infty}/\lambda' k_{12}^{0}[M] \gg 1$ and hence the recombination rate is given by $R_{12} = 2\lambda' k_{12}^{0}[M][Cl][NO]$ where λ' (= 10 assumed) has been introduced to allow for the higher collisional deactivation efficiency of CF_3CHCl_2 relative to helium.

Equation 7 is easily modified to include the effect of NO on the quantum yield of CF_2CHF:

$$\frac{1}{\phi} = \frac{1}{\phi_0} + \frac{k_6^{\infty}(1 + k_d/\lambda Z P)^{-1}}{k_5 + 2\lambda' k_{12}^{0}[NO]}(It/N) = \frac{1}{\phi_0} + m(P,[NO])It/N \qquad (9)$$

which retains the linear relationship at constant P and [NO]. From eq 7 and 9 the slopes in the absence and presence of NO at the *same* total pressure are related by

$$m(P,[\mathrm{NO}]) = \frac{k_5}{k_5 + 2\lambda' k_{12}{}^0[\mathrm{NO}]} m(P) \qquad (10)$$

Equation 10 indicates that the slope decreases with the addition of NO and should approach zero at sufficiently high NO concentration (since $m(P) \rightarrow k_6{}^\infty/k_5$ with increasing P). Comparison with the data in Figure 1 shows some qualitative agreement: as expected, the addition of NO decreases the slope drastically, and a linear relation is obeyed. However, within the experimental scatter, the data at all NO and reactant pressures are represented by the same straight line and, moreover, this line has a positive slope. The first observation can be explained, as shown below, by the predominance of reactions R12 and R13 with respect to chlorine atom removal even at the lowest NO pressure used in this study (i.e., $k_5 \ll 2\lambda' k_{12}{}^0 \cdot [\mathrm{NO}]$), but this explanation alone would also require the slope to be nearly zero. The fact that the slope is nonzero suggests that there is some other minor olefin removal reaction which is not affected by nitric oxide. We can only speculate here as to the nature of such a reaction. Haszeldine and co-workers[26] have found that difluoromethylfluorocarbene, $CHF_2\ddot{C}F$, produced in the thermal decomposition of $CHF_2CF_2SiF_3$, not only isomerizes to trifluoroethylene, but, in the presence of olefins, or in the later stages of the reaction, it also undergoes addition reactions to give the corresponding cyclopropane derivatives. It is therefore possible that the trifluoromethylcarbene produced in the primary process R2a may react in an analogous manner which would be reflected in the olefin quantum yield with increasing conversion. Thus, if the Cl-atom concentration in the presence of NO is reduced to a level such that reactions R5–R8 are negligible, and we consider the detailed scheme of the isomerization and addition reactions of the $CF_3\ddot{C}H$ radical produced in reaction R2a

$$CF_3\ddot{C}H^* \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} CF_2CHF^* \xrightarrow{k_s'[\mathrm{M}]} CF_2CHF$$

$$CF_3\ddot{C}H^* + CF_2CHF \xrightarrow{k_r} \text{product}$$

where the asterisk denotes some excess energy derived in the photochemical process, it can be easily shown that

$$\phi^{-1} = \phi_0{}^{-1} + (k_{-i} + k_s'[\mathrm{M}])(k_r/k_i k_s')It/N \qquad (11)$$

If one now makes the further assumption $k_{-i} \gg k_s'[\mathrm{M}]$, which corresponds to a quasi-equilibrium, eq 11 reduces to

$$\phi^{-1} = \phi_0{}^{-1} + (k_r/Kk_s')It/N \qquad (12)$$

which is independent of nitric oxide and total pressure, yet shows a residual decrease in the olefin quantum yield with conversion.

In our recent study of the 147-nm photolysis of $CF_2ClCHCl_2$ the nitric oxide experiments were confined to only one set of pressures [$P(CF_2ClCHCl_2) \simeq 10$ torr, $P(\mathrm{NO}) \simeq 1$ torr]. The residual slope in the plot of ϕ^{-1} vs. It/N in the presence of NO was there interpreted to indicate that the amount of nitric oxide was insufficient to remove all Cl atoms. From the experimental slope ratio in the absence and presence of NO we obtained an estimate of the rate constant for the abstraction reaction: $Cl + CF_2ClCHCl_2 \rightarrow HCl + CF_2Cl\dot{C}Cl_2$, $k_{abs} \simeq 1.3 \times 10^{10}$ cm^3 mol^{-1} s^{-1} at 298 K. By assuming a "normal" preexponential factor of $A \simeq 10^{13}$ cm^3 mol^{-1} s^{-1} we obtained an activation energy of ~3.9 kcal mol^{-1}. In light of the present work and interpretation this rate constant would appear to be too high and the activation energy too low. For Cl–hydrogen abstraction from CF_3CH_3 Cadman et al.[16] report approximate Arrhenius parameters of $\log (A/\mathrm{cm^3\ mol^{-1}\ s^{-1}}) \sim 12.3$ and $E = 5.9$ kcal mol^{-1}. Using these figures for an estimate of k_5 we obtain the rate ratio $R_5/R_{12} = k_5/2\lambda' k_{12}{}^0[\mathrm{NO}] \sim 0.05$ at our lowest NO pressure of 0.1 torr. Although the uncertainties in k_5 and λ' are large, this calculation supports the conclusion that, at the pressures of NO used in this study, reactions R12 and R13 provide the principal sink for chlorine atom removal.

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