The Kinetics of the Thermal Decomposition of Hexafluoroazomethane and the Reaction of CF_3 Radicals with Methyl Ethyl Ketone

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The thermal decomposition of hexafluoroazomethane (HFAM) has been investigated in a static system between 327.5 and 377.5° both alone and in the presence of methyl ethyl ketone (MEK). At these temperatures MEK does not undergo thermal decomposition. In both cases, the decomposition of HFAM was found to be first order as determined by the rate of formation of nitrogen. The Arrhenius expression for the HFAM decomposition in the presence of MEK is given by $k_0 = 2.1 \times 10^{15}e^{-52{,}800/RT}$ sec^{-1}, which is in excellent agreement with that reported by other workers for HFAM alone. A reaction mechanism for the HFAM decomposition is presented together with supporting evidence. The reaction of CF_3 radicals with MEK is quite complex. A probable mechanism for the predominant reactions is proposed. Propylene and nitric oxide had no effect on the rate of nitrogen formation from HFAM alone or in the presence of MEK. However, the formation of C_2F_6 and $(CF_3)_2NN(CF_3)_2$ in the first case, and CF_3H in the latter, was reduced to zero by these inhibitors. The mechanism of the inhibition processes is discussed.

Introduction

The kinetics of the decomposition of hexafluoroazomethane (HFAM) have been studied by several investigators. Dacey and Young[2] photolyzed CF_3NNCF_3 using 2537-Å radiation and proposed a mechanism accounting for the observable products: hexafluoroethane, perfluorotetramethyl hydrazine, and perfluorohexamethyl tetrazine. The thermal decomposition was first investigated by Clark and Pritchard[3] in a flow system using toluene as a carrier gas. Leventhal, Simonds, and Steel[4] studied the pyrolysis in a static system between 299 and 361°. It was found to be homogeneous and first order and propylene did not inhibit the reaction.

In the present work, the thermal decomposition of HFAM was reinvestigated as a prelude to employing this compound as a source of CF_3 radicals for reaction with methyl ethyl ketone (MEK).

The kinetics and mechanism of the thermal decomposition of MEK have been investigated by Waring[5,6] and found to be first order and homogeneous. Propylene reduced the rate to a definite, limiting value and the amount of inhibition for a given pressure of propylene was dependent upon the initial pressure of ketone. Nitric oxide, on the other hand, produced a marked catalytic effect. This catalytic effect of nitric oxide appears to be characteristic of all ketones having a methyl-carbonyl group.[6,7]

The current work was undertaken to acquire further information on the mechanism of the MEK decomposition in particular and the effect of CF_3 radicals in inducing the decomposition of ketones in general. Further, it was thought worthwhile to study the effect of nitric oxide and propylene on the free-radical processes induced by trifluoromethyl radicals.

Experimental Section

A. Apparatus. The usual static type system was employed in this investigation. The reaction cell was a cylindrical Pyrex vessel of 250-ml capacity connected to the high-vacuum system with 2.0-mm capillary tubing which was wrapped with heating tape to prevent the condensation of reaction products.

The reaction vessel was heated in an asbestos-packed electric furnace controlled by a Leeds and Northrup Thermocouple Electromax. A 0–2000°F chromel–alumel thermocouple positioned at the furnace wall served as a detector for the Electromax. The reaction temperature was measured by a calibrated chromel–alumel thermocouple positioned in the well of the reaction cell and monitored by a Leeds and Northrup Speedomax H Model S indicating recorder. The temperature of the reaction vessel remained constant to within ±0.05° over several hours.

Changes in total pressure in the reaction cell were measured by a Consolidated Electrodynamics Corporation Type 4-312-002 pressure transducer. The transducer was maintained at a constant temperature of 50° by wrapping with asbestos and heating tape. The

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(1) Presented in partial fulfillment of the requirements for the Ph.D. degree at the University of Connecticut, June 1967.

(2) J. R. Dacey and D. M. Young, *J. Chem. Phys.*, **23**, 1302 (1955).

(3) D. Clark and H. O. Pritchard, *J. Chem. Soc.*, 2136 (1956).

(4) E. Leventhal, C. R. Simonds, and C. Steel, *Can. J. Chem.*, **40**, 930 (1961).

(5) C. E. Waring and W. E. Mutter, *J. Amer. Chem. Soc.*, **70**, 4073 (1948).

(6) C. E. Waring and M. Spector, *ibid.*, **77**, 6453 (1955).

(7) J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.*, **A183**, 33 (1944); C. E. Waring and V. L. Garik, *J. Amer. Chem. Soc.*, **78**, 5198 (1956); P. Lott, Ph.D. Thesis, University of Connecticut, Storrs, Conn., 1956; J. J. Demo, *ibid.*, 1960.

output of the transducer was also recorded on the Leeds and Northrup Speedomax H Model S indicating recorder.

The pressure in the vacuum system was measured by an NRC Type 538-P ionization gauge with an NRC Type 710 thermocouple ionization control.

The reaction system was evacuated by the usual techniques and no experiments were conducted unless the pressure in the reaction system was 10^{-5} Torr or less. The vacuum line was flamed out periodically to eliminate the possibility of oxygen contamination. The unreacted products and reactants were collected in cold fingers connected to the reaction system through standard 12/30 ground-glass joints. Analyses for reactants and products were made on a Perkin-Elmer Model 154 vapor fractometer. These were identified by comparison of retention times with those of known samples; where possible, more than one column was used as a check. In cases where known samples were not readily available, the desired component was separated by preparative gas chromatography and identified on a Consolidated Electrodynamics 21-613 residual-gas analyser. A Perkin-Elmer Infracord and the mass spectrometer were employed to check the purity of starting materials. The analyses for ketenes were performed by dissolving the reaction products in water and titrating with standard sodium hydroxide.[5]

B. Materials. Hexafluoroazomethane was obtained from Merck Sharp and Dohme. Its purity was checked by gas chromatography and mass spectroscopy and found to be 99% or better. It was, therefore, used without further purification.

The methyl ethyl ketone was Matheson Coleman and Bell CP grade. By means of preparative gas chromatography,a sample of 99% purity was obtained. The refractive index of the purified MEK at 15° was 1.3814, which is in good agreement with the literature[8] value of 1.3814.

Nitric oxide was obtained from the Matheson Co. Impurities in the form of NO_2 and N_2O were removed in a cold trap at $-127°$ and the NO was collected and stored in a liquid nitrogen trap. After several such purifications, a mass spectrographic analysis indicated a purity of 99%.

Nitrogen, methane, carbon monoxide, carbon dioxide, and propylene were obtained from Matheson Co. and were used without further purification. Also used directly were CF_3H, C_2F_6, and CF_3NO from the Peninsular Chem Research Co.

The remaining fluorinated products, $CF_3CH_2CH_3$, $CH_2{=}CHCF_3$, $CF_3CH_2CH_2CH_3$, and $(CH_3)_2CHCF_3$, could not be obtained commercially and were synthesized by the method of Hasek, Smith, and Engelhardt[9] by treating SiF_4 with the corresponding carboxylic acids. Mass spectrographic analyses confirmed the fact that the products so obtained were the desired compounds. Gas chromatography indicated that each had a purity of better than 95%. These compounds were then used for calibration purposes.

Results

1. Thermal Decomposition of Hexafluoroazomethane. The thermal decomposition of HFAM was reinvestigated between the temperatures of 327.5 and 377.5°. It was not possible to determine the order of the decomposition by measuring the time required for a particular pressure increase (*i.e.*, $t_{10\%}$, $t_{25\%}$, etc.) at various initial pressures. This was due to the interaction of the CF_3 radicals, produced initially, with the HFAM to form addition compounds. The extent of this addition reaction was measured by determining the ratio of C_2F_6 to N_2 in the reaction products. The results, in Table I, show that the C_2F_6/N_2 ratio decreases with increasing initial pressures, indicating that as the initial pressure increases, the formation of addition compounds over C_2F_6 is greatly favored.

Table I: Variation of C_2F_6/N_2 Ratio with Initial Pressures of HFAM after 14% (5-min) Reaction at 348.5°

$P_{i,\text{HFAM}}$, Torr	Mol % C_2F_6	Mol % N_2	C_2F_6/N_2
30.0	6.7	11.5	0.593
35.0	6.6	12.3	0.537
42.0	6.2	12.5	0.496
50.7	5.9	12.4	0.476
51.4	5.7	12.0	0.475
56.7	5.6	12.8	0.438
67.4	5.2	13.4	0.388
80.4	4.7	13.1	0.359

Accordingly, the decomposition of HFAM was followed by measuring the amount of nitrogen formed at different times, which corresponds directly to the amount of HFAM decomposed. The order of reaction was then determined from the slope of a log $(dp_{N_2}/dt)_0$ *vs.* log $P_{i,\text{HFAM}}$ plot as shown in Figure 1. These data were fitted to a least-squares program on an IBM 1620 computer. The order of the reaction was found to be 1.01 over an initial pressure range of 12–94 Torr of HFAM.

A complete analysis of the products from the decomposition of HFAM was made at 347.5° after 10 min of reaction, which corresponded to 25% decomposition. Table II shows the principal products to be C_2F_6, N_2, and $(CF_3)_2NN(CF_3)_2$.

No evidence could be found, either by gas chromatography or mass spectroscopy, for the presence of $(CF_3)_2NN(CF_3)N(CF_3)N(CF_3)_2$. This compound has been reported previously to be a product of the photol-

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[8] "Handbook of Physics and Chemistry," 46th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1965–1966.

[9] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960).

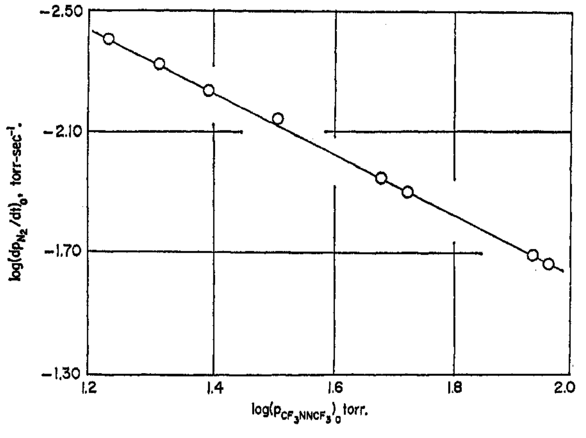

Figure 1. Determination of the order of the decomposition of HFAM at 347.5°.

Table II: Partial Pressures and Mole Per Cent of Gaseous Products from the Decomposition of 51.2 Torr of HFAM at 347.5°

Product	p, Torr	Mol %
N_2	11.9	21.7
C_2F_6	5.9	10.7
$(CF_3)_2NN(CF_3)_2$	5.7–8.6[a]	10.4–15.7
CF_3NNCF_3	31.4	57.2

[a] No pure sample of this compound was available for an accurate quantitative determination. A reasonable estimate was made, however, from the area under the chromatographic curve.

ysis of HFAM.[2] Neither was any perfluoromethane, CF_4, detected in the reaction products.

2. Reaction of CF_3 Radicals with Methyl Ethyl Ketone. HFAM was also decomposed in the presence of MEK vapor to provide a source of CF_3 radicals for reaction with the ketone. Over the temperature range investigated, 327.5–377.5°, the ketone does not undergo pyrolysis.

The order of the HFAM decomposition was again investigated to determine whether or not the presence of MEK had any effect on the decomposition. Mixtures of 33% HFAM and 67% MEK were used in these and subsequent experiments. The order, as determined from the slope of the plot of log $(dp_{N_2}/dt)_0$ *vs.* log $P_{i,\text{HFAM}}$ in Figure 2, was found to be 0.99 over an initial pressure range of 10 to 29 Torr of HFAM.

The energy of activation for the decomposition of HFAM was determined in the presence of MEK. The rate constants were calculated from the initial rates of formation of nitrogen at various initial pressures of HFAM. Figure 3 presents a plot of the log of the initial rate constants, k_0, against the reciprocal of the absolute temperatures. A least-squares analysis of these data, expressed in terms of the Arrhenius equation, gave

$$k_0 = 2.1 \times 10^{15}e^{-52,800/RT} \text{ sec}^{-1} \qquad (1)$$

This is in very satisfactory agreement with the expression

$$k = 3.2 \times 10^{15}e^{-52,700/RT} \text{ sec}^{-1} \qquad (2)$$

obtained by Leventhal, Simonds, and Steel.[4]

Table III presents the analyses of the gaseous products and remaining reactants resulting from the interaction of CF_3 radicals with MEK at 347.5°.

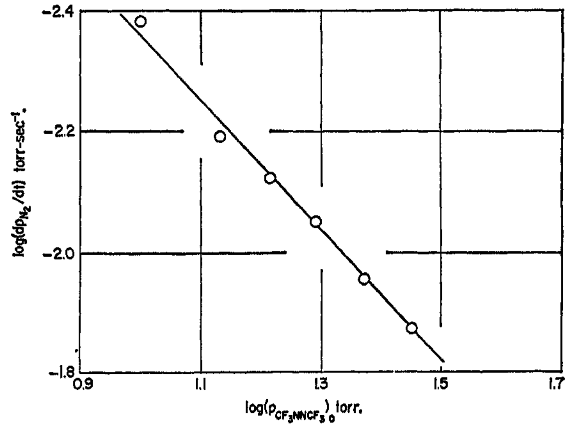

Figure 2. Determination of the order of the decomposition of HFAM in the presence of MEK at 347.5°.

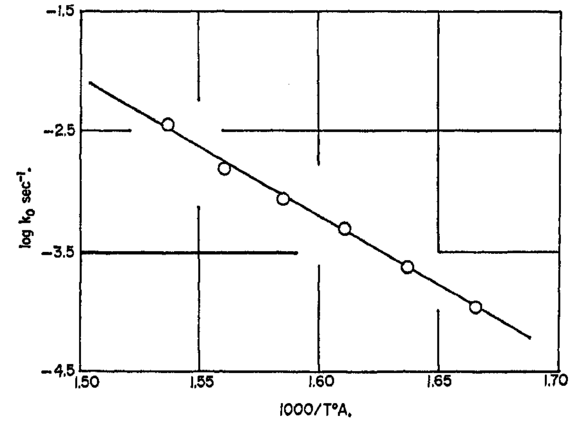

Figure 3. Variation of log k_0 with the reciprocal of the absolute temperature for the decomposition of CF_3NNCF_3 in the presence of MEK.

It is seen that CF_3H and ketenes, along with N_2, were the predominant products of reaction. In contrast to the decomposition of HFAM alone, neither C_2F_6 nor $(CF_3)_2NN(CF_3)_2$ was formed in the presence of MEK. Significant also by their absence were such expected products as C_2H_6, C_2H_4, CH_3CF_3, CH_2CF_2, CHFCHF, CH_3COCF_3, and $CF_3COCH_2CH_3$.

In the reaction between HFAM and MEK, a solid residue, possibly polymeric material, was observed to condense in the tubing around the collection bulb. No such solid was observed in the decompositions of HFAM

Table III: Partial Pressures (Torr) of Gaseous Products and Remaining Reactants from the Decomposition of 18.8 Torr of HFAM in the Presence of 38.8 Torr of MEK at 347.5°

	% HFAM decomposition					
	3.7	9.6	14.4	24.0	45.8	81.4
N_2	0.7	1.8	2.7	4.5	8.6	15.3
CO	0.2	0.6	1.1	1.6	3.5	8.2
CO_2	Trace	0.1	0.1	0.3	0.7	3.0
CH_4	Trace	0.1	0.1	0.3	0.6	2.2
CF_3H	0.9	2.7	3.9	7.6	10.8	19.0
CH_2CHCF_3	Trace	Trace	Trace	0.1	0.1	0.1
$C_2H_5CF_3$	Trace	Trace	0.1	0.3	0.7	1.7
Ketenes	0.8	1.7	2.5	5.0	6.9	16.3
CF_3NNCF_3	19.0	17.7	16.0	13.3	8.8	0.6
$CH_3COC_2H_5$	36.0	35.4	34.6	32.8	29.0	24.0

alone. Infrared analysis of the residue dissolved in CCl_4 and an elemental analysis could not positively identify any individual product. Both nitrogen and fluorine, as well as hydrogen and carbon, were reported in the elemental analysis. The residue is most probably a polymer formed by the addition of radicals to the double bond of the HFAM molecule. Thus, it appears likely that a considerable portion of the hydrocarbon material unaccounted for in the analyses of the gaseous products may be present in this polymeric substance.

3. Effect of Inhibitors. The effect of inhibitors on the reaction between CF_3 radicals and MEK was investigated to determine the possible occurrence of chain processes in the reaction.

(*a*) *Propylene.* The effect of propylene was studied by determining the initial rates of formation of N_2 and CF_3H. The rate of nitrogen formation at several different partial pressures of inhibitor was the same as in the uninhibited reaction, indicating that propylene had no effect on the rate of decomposition of HFAM. There was, however, a marked effect on the rate of formation of CF_3H. In Figure 4, the ratio of the initial rates of formation of the inhibited to the initial rates of formation of the uninhibited reactions are plotted as a function of the partial pressure of propylene for two different HFAM/MEK ratios. It is seen that the rate of formation of CF_3H is reduced almost to zero at maximum inhibition.

(*b*) *Nitric Oxide.* The effect of nitric oxide as an inhibitor was also investigated by determining the initial rates of formation of CF_3H and N_2. As in the study with propylene, nitric oxide had no effect on the rate of decomposition of HFAM as measured by the rate of production of N_2. The rate of formation of CF_3H, however, was markedly decreased in a manner analogous to the propylene inhibition. Figure 5 shows the effect of nitric oxide on two different HFAM-MEK mixtures. It is of interest to note that for the same concentration of inhibitor, propylene, beyond any question, is the more effective in removing CF_3 radicals. This is just the opposite of what one usually observes when the efficiencies of these two inhibitors are compared in systems involving hydrocarbon free radicals.

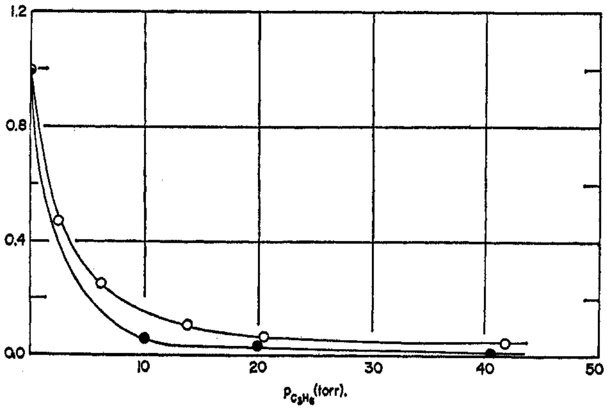

Figure 4. Effect of propylene on the rate of formation of CF_3H in HFAM-MEK mixtures at 347.5°: ○ = 16.4 HFAM:33.6 MEK (Torr); ● = 28.1 HFAM:21.9 MEK (Torr).

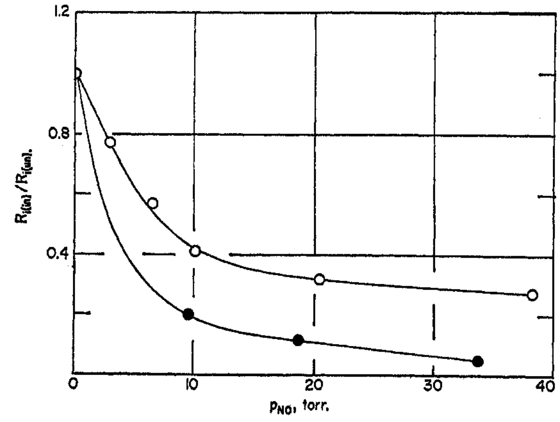

Figure 5. Effect of nitric oxide on the rate of formation of CF_3H in HFAM-MEK mixtures at 347.5°: ○ = 16.4 HFAM:33.6 MEK (Torr); ● = 28.1 HFAM:21.9 MEK (Torr).

(*c*) *Products of the Inhibited Reactions.* The products of the propylene and nitric oxide inhibited reactions were determined and are presented in Table IV.

Table IV: Product Analysis for the Propylene- and Nitric Oxide-Inhibited Decomposition of 16.4 Torr of HFAM in the Presence of 33.6 Torr of MEK at 347.5° ($P_{C_3H_6}$ = 22.6 Torr; P_{NO} = 20.4 Torr)

% Decomp. HFAM	Products, Torr											
	C_3H_6	NO	N_2	CO	CO_2	CH_4	CF_3H	CH_2-$CHCF_3$	$C_2H_5CF_3$	$(CH_3)_2$-$CHCF_3$	CH_3-$(CH_2)_2CF_3$	C_2F_6
24	16.1	...	4.0	0.4	0.3	0.1	0.4	0.1	Trace	0.1	2.4	Trace
22	...	14.6	3.6	0.2	0.3	0.1	1.7	0.1	Trace	...	...	Trace

Table V: Product Analysis for the Propylene- and Nitric Oxide Inhibited Decomposition of 50.0 Torr of HFAM at 347.5° ($P_{C_3H_6}$ = 24.0 Torr; P_{NO} = 24.2 Torr)

% Decomp. HFAM	Products and remaining HFAM, Torr							
	N_2	C_2F_6	$(CF_3)_2N$-$N(CF_3)_2$	$(CH_3)_2CHCF_3$	$CH_3(CH_2)_2CF_3$	C_3H_6	NO	HFAM
25	12.7	Trace	Trace	0.3	3.0	1.2	...	33.4
25	12.6	Trace	Trace	...	...	...	10.6	30.6

The data in Table IV reveal that the products are essentially the same in the propylene- and nitric oxide-inhibited reactions. It is noted, however, that in the propylene-inhibited reaction two fluorinated compounds, $(CH_3)_2CHCF_3$ and $CH_3(CH_2)_2CF_3$, were detected, and, as seen in Figures 4 and 5, propylene is more effective in reducing the formation of CF_3H.

The possibility of CF_3NO being formed in the NO-inhibited reaction was investigated. A sample of trifluoronitrosomethane, however, was found to decompose readily at 347.5°. The principal product that could be identified from this decomposition was nitric oxide. Only a trace of C_2F_6 was observed. This leads to the conclusion that the CF_3 radicals must be combining with CF_3NO molecules to form species such as $(CF_3)_2NOCF_3$. The latter, among more complex products, has been reported in a pyrolysis study of CF_3NO at 250 to 300°.[10] Gas chromatography did not indicate the presence of CF_3NO in the nitric oxide inhibited reactions even at very low per cent decompositions.

In order to obtain an insight as to whether the source of the products in the inhibited processes originated from the HFAM or from the interaction of HFAM and MEK, HFAM alone was decomposed in the presence of both propylene and nitric oxide, and the resulting products analyzed. These are presented in Table V.

It is evident from these data that $(CH_3)_2CHCF_3$ and $CH_3(CH_2)_2CF_3$ are produced from the interaction of propylene and CF_3 radicals. Also significant is the fact that the concentrations of C_2F_6 and $(CF_3)_2NNCF_3)_2$ are reduced to virtually zero, indicating that the inhibitors are, indeed, effective in removing CF_3 radicals.

Discussion

1. *Mechanism of the Hexafluoroazomethane Decomposition.* A mechanism that adequately accounts for all the major products of the HFAM decomposition may be written as

$$CF_3NNCF_3 \xrightarrow{k_3} N_2 + 2CF_3 \tag{3}$$

$$CF_3 + CF_3NNCF_3 \xrightarrow{k_4} (CF_3)_2NNCF_3 \tag{4}$$

$$CF_3 + (CF_3)_2NNCF_3 \xrightarrow{k_5} (CF_3)_2NN(CF_3)_2 \tag{5}$$

$$CF_3 + CF_3 \xrightarrow{k_6} C_2F_6 \tag{6}$$

Steps 4 and 5 are analogous to those previously proposed.[2,4] If step 6 required a third body (*e.g.*, HFAM) for the chain termination process, then, under steady-state conditions it can be shown that

$$k_6[CF_3]^2 + 2k_4[CF_3] - k_3 = 0 \tag{7}$$

This implies that the rate of formation of $(CF_3)_2NN(CF_3)_2$ and C_2F_6 would be first order. However, the formation of C_2F_6 by a two-body rather than a three-body radical recombination process in the pressure range investigated is fairly well supported by the present experimental data. In Figure 6, plots of log $(d[C_2F_6]/dt)_0$ and log $(d[(CF_3)_2NN(CF_3)_2/dt)_0$ *vs.* log P_{HFAM} yield straight lines with respective slopes, n, of 0.67 and 1.50. This is compelling argument that the formation of these compounds—and the overall order of the reaction—occurs by an order other than first.

From eq 3, the rate of nitrogen formation is seen to be first order in accordance with experimental observations

$$d[N_2]/dt = k_3[HFAM] \tag{8}$$

Further, it can be shown that

$$\frac{d[(CF_3)_2N_2(CF_3)_2]/dt}{(d[C_2F_6]/dt)^{1/2}} = \frac{k_4[HFAM]}{k_6^{1/2}} \tag{9}$$

A plot of this rate ratio against the initial pressures of HFAM is shown in Figure 7. From the slope, $k_4/k_6^{1/2} = 2 \times 10^{-1}$ ml$^{1/2}$ mol$^{-1/2}$ sec$^{-1/2}$. In the photolysis

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[10] A. Y. Yakubovich, S. P. Makarov, V. A. Ginsburg, N. F. Privezentseva, and L. L. Martynova, *Dokl. Akad. Nauk SSSR*, **141**, 125 (1961).

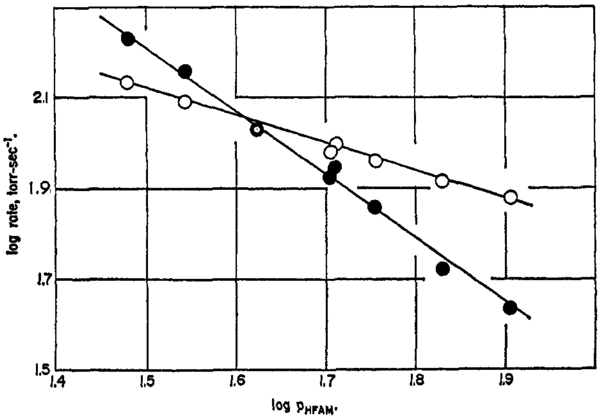

Figure 6. Determination of the order of formation of C_2F_6 (O) and $(CF_3)_2NN(CF_3)_2$ (●)at 347.5°. $n_{C_2F_6}$ = 0.67; $n_{(CF_3)_2NN(CF_3)_2}$ = 1.50.

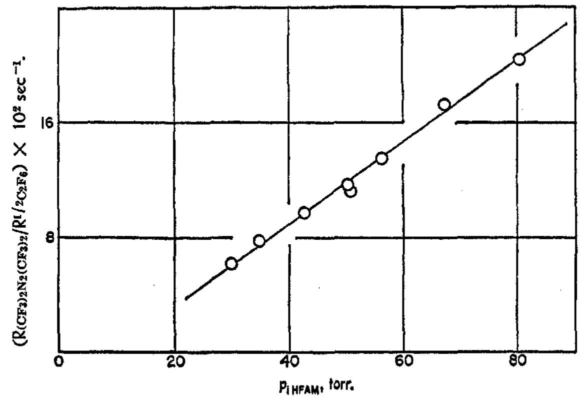

Figure 7. Ratio of rate of formation of $(CF_3)_2NN(CF_3)_2$ to square root of rate of formation of C_2F_6 *vs.* initial pressure of HFAM at 347.5°.

of HFAM, Pritchard, *et al.*,[11] found $A_4/A_6^{1/2} = 10^3$ ml$^{1/2}$ mol$^{-1/2}$ sec$^{-1/2}$. Combining their frequency factor ratio with the preceding rate constant ratio in the Arrhenius equation, a value of 4.8 kcal/mol is obtained for $E_4 - E_6/2$. If $E_6 = 0$,[12,13] then $E_4 = 4.8$ kcal/mol. This compares not unfavorably with the value of 3.5 kcal/mol reported by Pritchard and coworkers.[11] Further, if one employs the value of 10^{12} ml mol^{-1} sec^{-1} given[14] as the frequency factor for the combination of two trifluoromethyl radicals in eq 6, then $A_4 = 10^9$ ml mol^{-1} sec^{-1}. While this is somewhat lower than the theoretical bimolecular collision frequency, it is nevertheless the same order of magnitude as that of many bimolecular association reactions.[14,15]

The mechanism, eq 3–6, also has the advantage that it is in agreement with the results of the inhibition studies. If nitric oxide and propylene effectively remove CF_3 and $(CF_3)_2NNCF_3$ radicals, the mechanism predicts that the concentration of perfluoroethane and perfluorotetramethyl hydrazine should fall to zero. Table V shows that this is what is observed experimentally.

2. Reaction of CF_3 Radicals with Methyl Ethyl Ketone. While the presence of MEK does not affect either the rate or the order of the HFAM decomposition, the trifluoromethyl radicals so produced undergo quite different reactions than when in the presence of HFAM alone. Most startling, perhaps, is the complete absence of C_2F_6 and $(CF_3)_2NN(CF_3)_2$, as seen in Table III. Further, the large amount of CF_3H as compared to CH_4 is also somewhat unexpected. Based upon the analyses, it appears that a hydrogen abstraction process is now occurring at the expense of certain of the addition and combination reactions in steps 4 to 6. Thus, one of the predominant reactions following the initial break-up of the HFAM molecule in the presence of MEK now is

$$CF_3 + CH_3COCH_2CH_3 \longrightarrow CF_3H + R_1 \quad (10)$$

where $R_1 = CH_3COCH_2CH_2$, $CH_2COCH_2CH_3$, or $CH_3COCHCH_3$. By analogy to the abstraction of hydrogen atoms from MEK by methyl radicals at 550°,[5] one would expect R_1 to decompose into a smaller radical and stable molecules, giving such products as ketene, methyl ketene, ethylene, and ethane as major products of reaction according to

$$CH_3COCH_2CH_2 \longrightarrow CO + C_2H_4 + CH_3 \quad (11)$$

$$CH_2COCH_2CH_3 \longrightarrow CH_2CO + C_2H_5 \quad (12)$$

$$CH_3COCHCH_3 \longrightarrow CH_3CHCO + CH_3 \quad (13)$$

Of the three possibilities, it is probably safe to conclude that reaction 11 does not occur to any appreciable extent due to the absence of ethylene. Although no ethane was observed, reaction 12 cannot be eliminated since there is a strong possibility that the ethyl radicals may undergo addition reactions with HFAM rather than hydrogen abstraction from MEK. The presence of ketene in the products of reaction could be due to reaction 12 or 13 or both.

Neither all of the CF_3 nor all of the CH_3 and/or C_2H_5 radicals formed in the reaction could be accounted for. Although no perfluorotetramethyl hydrazine was observed in the reactions involving MEK, there is evidence for the formation of other more complex addition compounds. Since the amount of HFAM that actually reacted was consistently greater than the amount of nitrogen produced, it is logical to assume that addition compounds involving certain of the radicals produced in the reaction are the components of the solid polymeric residue previously mentioned.

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(11) G. O. Pritchard, H. O. Pritchard, H. I. Schiff, and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **52**, 849 (1956).

(12) G. O. Pritchard and J. R. Dacey, *Can. J. Chem.*, **38**, 182 (1960).

(13) R. D. Giles and E. Whittles, *Trans. Faraday Soc.*, **61**, 1425 (1965).

(14) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 302.

(15) A. F. Trotman-Dickenson and G. S. Milne, "Tables of Bimolecular Gas Reactions," NSRDS-NBS 9, 1967.

The following mechanism for the interaction of CF_3 radicals with MEK is proposed as being the most predominant.

$$CF_3N_2CF_3 \xrightarrow{k_{14}} 2CF_3 + N_2 \qquad (14)$$

$$CF_3 + CH_3COCH_2CH_3 \xrightarrow{k_{15}} CF_3H + CH_2CO + C_2H_5 \qquad (15)$$

$$CF_3 + CH_3COCH_2CH_3 \xrightarrow{k_{16}} C_2H_5CF_3 + CO + CH_3 \qquad (16)$$

$$CH_3 + CH_3COCH_2CH_3 \xrightarrow{k_{17}} CH_4 + R_1 \qquad (17)$$

$$C_2H_5 + CF_3N_2CF_3 \xrightarrow{k_{18}} R_2 \qquad (18)$$

$$R_1 + R_2 \xrightarrow{k_{19}} \text{polymer} \qquad (19)$$

This mechanism, which is consistent with the experimental data, has the following support. It is seen in Table III that the rates of formation of CH_4 and $C_2H_5CF_3$ are the same throughout the course of the decomposition. It can be further observed that, at about 80% decomposition, the rate of formation of CF_3H is approximately 10 times faster than that of CH_4 and $C_2H_5CF_3$. Assuming steady-state conditions, it can be readily shown that

$$[CF_3] = \frac{2k_{14}[\text{HFAM}]}{(k_{15} + k_{16})[\text{MEK}]} \qquad (20)$$

and

$$[CH_3] = \frac{2k_{14}k_{16}[\text{HFAM}]}{k_{17}(k_{15} + k_{16})[\text{MEK}]} \qquad (21)$$

By making the appropriate substitutions, it can be further demonstrated that

$$\frac{d[C_2H_5CF_3]/dt}{d[CH_4]/dt} = \frac{k_{16}[CF_3]}{k_{17}[CH_3]} = 1.0 \qquad (22)$$

and

$$\frac{d[CF_3H]/dt}{d[CH_4]/dt} = \frac{k_{15}[CF_3]}{k_{17}[CH_3]} = \frac{k_{15}}{k_{16}} \qquad (23)$$

and

$$\frac{d[CF_3H]/dt}{d[C_2H_5CF_3]/dt} = \frac{k_{15}}{k_{16}} \qquad (24)$$

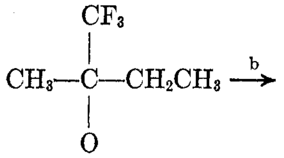
Equation 22 predicts that the rates of formation of $C_2H_5CF_3$ and CH_4 should be the same. The data in Table III show that this is, indeed, the case. Equations 23 and 24, on the other hand, indicate that the ratios of the rates of formation of CF_3H to CH_4 and to $C_2H_5CF_3$ should be identical. Again, in Table III, it is seen that these two ratios are essentially the same throughout the course of the decomposition. Further, at 347.5° and 80% decomposition, the average ratio of $(d[CF_3H]/dt)/(d[CH_4]/dt)$ and $(d[CF_3H]/dt)/(d[C_2H_5CF_3]/dt)$ is 19/2 or 9.5. It follows, therefore, that

$$\frac{d[CF_3H]/dt}{d[C_2H_5CF_3]/dt} = \frac{k_{15}}{k_{16}} = \frac{A_{15}e^{-E_{15}/RT}}{A_{16}e^{-E_{16}/RT}} = 9.5 \qquad (25)$$

If one makes the not unreasonable assumption that the values of the frequency factors, A_{15} and A_{16}, are equal, then $E_{16} - E_{15}$ is found to be 2.8 kcal/mol. This represents the difference in the activation energy required for the abstraction of an ethyl radical by a trifluoromethyl radical over that required for hydrogen abstraction. It is of interest to note that this value is essentially the same as that found by Sieger and Calvert[16] for the difference in activation energy for hydrogen abstraction by a methyl radical as opposed to the corresponding trifluoromethyl abstraction process, namely, $E_{17} - E_{15} = 2.3$ kcal/mol. Employing this value and setting $E_{17} = 7.4$ kcal/mol,[17] $E_{15} = 5.1$ kcal/mol. From $E_{16} - E_{15} = 2.8$ kcal/mol, it is seen that $E_{16} = 7.9$ kcal/mol.

Reaction 16 is, of course, speculative and perhaps oversimplified. There is evidence, however, from current studies[18] that trifluoromethyl radicals do, in fact, abstract methyl groups from ketones. On this basis, it would be expected that ethyl groups could be similarly removed. There is also the possibility that $C_2H_5CF_3$ may be formed through an addition process in a manner analogous to that described by Alcock and Whittle.[19]

$$CF_3 + CH_3COC_2H_5 \xrightarrow{a}$$



$$CH_3-\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle O}{|}}{C}}-CH_2CH_3 \xrightarrow{b}$$

$$C_2H_5CF_3 + CO + CH_3 \qquad (26)$$

In this case, most of the energetics of the reaction would be confined to (26a) since (26b) would probably occur with little or no activation energy.

Since trifluoromethane was one of the principal products from the interaction of CF_3 radicals with MEK, its initial rates of formation were determined by least-squares analyses of plots of P_{CF_3H} *vs.* time. The rate constants were then calculated at several temperatures by dividing $(dp_{CF_3H}/dt)_0$ by various initial HFAM concentrations. From the data in Table VI, the Arrhenius expression for the rate of formation of CF_3H in terms of the rate of disappearance of HFAM is given by

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[16] R. A. Sieger and J. G. Calvert, *J. Amer. Chem. Soc.*, **76**, 5197 (1954).

[17] P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1062 (1955).

[18] C. E. Waring and A. Fekete, unpublished results.

[19] W. G. Alcock and E. Whittle, *Trans. Faraday Soc.*, **61**, 244 (1965).

$$k_0 = 3.1 \times 10^{15} e^{-53,100/RT} \text{ sec}^{-1} \tag{27}$$

The close agreement between the terms of eq 1 and 27 is not wholly unexpected. It indicates that steps 15 and 16 are dependent primarily upon the decomposition process of reaction 14.

Table VI

$1/T$°K × 10^3	$R_{\mathrm{CF_3H}}$ × 10^2, Torr/sec	$R_{\mathrm{CF_3H}}$/[HFAM] × 10^4 sec^{-1}	log ($R_{\mathrm{CF_3H}}$/[HFAM]), sec^{-1}
1.665	0.274	1.67	−3.7773
1.637	0.441	2.68	−3.5719
1.611	1.01	6.14	−3.2118
1.585	2.10	12.5	−2.9031
1.561	3.82	23.4	−2.6308
1.537	7.53	47.2	−2.3261

In view of the fact that the activation energies, E_4 and E_{15}, are essentially the same, the question arises as to why, in the presence of MEK, reaction 4 is apparently eliminated by the overwhelming predominance of reaction 15. The most logical explanation lies in the difference in the frequency factors, A_4 and A_{15}. A_4 has been shown to be of the order of 10^9 ml mol^{-1} sec^{-1}. The frequency factor for trifluoromethyl radicals reacting with acetone is given[15] as 3×10^{11} ml mol^{-1} sec^{-1} and that for the normal bimolecular collision frequency is generally taken to be in the order of 10^{12} ml mol^{-1} sec^{-1}.[14] The frequency factor value for reaction 15 would not be expected to differ greatly from the CF_3 + acetone value so that to assume that $A_{15} = 10^{11}$ to 10^{12} would not be unreasonable. This would indicate, then, that reaction 15 is occurring at a rate 100 to 1000 times faster than reaction 4. It is obvious that under these conditions reaction 4 would become negligible. That it does is evidenced by the absence of perfluorotetramethyl hydrazine in the products of the HFAM–MEK reaction.

Reactions 18 and 19 are proposed to account for the observed experimental facts: (1) that the amount of HFAM reacting was always greater than the amount of nitrogen formed; and (2) that a solid polymeric residue was formed. Batt and Pearson[20] reported that the addition reaction

$$CH_3 + CF_3NNCF_3 \longrightarrow CF_3(CH_3)N\dot{N}CF_3 \tag{28}$$

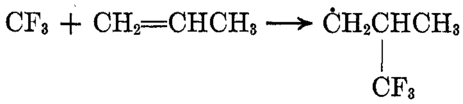
is about 20 kcal/mol exothermic. By analogy, the probability of ethyl radical addition to HFAM would be expected to be about as high.

The question may also be raised as to why the mechanism 14–19 does not account for the carbon monoxide and carbon dioxide reported in Table III. Since CO has been shown to be produced primarily from the decomposition[5–7] and/or interaction of ketenes, for simplicity these secondary steps were omitted. The presence of CO_2 in the pyrolysis of ketones has been attributed to the equilibrium reaction $2CO = CO_2 + C$ which goes about 24% to the right at 580°. The small amount of CO_2 observed in the present study is probably the product of this process.

3. Inhibition by Propylene and Nitric Oxide. From a comparison of the amounts of CF_3H, CH_4, and C_2H_5-CF_3 formed in the uninhibited CF_3–MEK reaction (Table III) with those formed in the inhibited process (Table IV), it is apparent that propylene and nitric oxide are both effective in removing CF_3 radicals.

In the case of propylene, the product analysis give a rather clear explanation of this inhibition. The hydrogen abstraction reaction must now be in competition with two possible addition reactions

$$CF_3 + CH_2{=}CHCH_3 \longrightarrow CF_3CH_2\dot{C}HCH_3 \tag{29}$$



$$CF_3 + CH_2{=}CHCH_3 \longrightarrow \dot{C}H_2CH(CF_3)CH_3 \tag{30}$$

the first involving the formation of a secondary free radical and the second a primary. Either of these radicals can then add a hydrogen to form a saturated butane. The secondary radical should be the more stable of the two and hence more 1,1,1-trifluorobutane than 2-trifluoromethyl propane should be formed. That this is the case is seen in Tables IV and V. These reactions alone, however, do not account for all the CF_3 radicals formed nor all the propylene consumed. It appears probable, therefore, that the butyl radicals formed in (29) and (30) are either involved in addition to the HFAM molecules or are combining with themselves to produce fluorinated octanes.

The mechanism of the nitric oxide inhibition is presently not so self-evident. The data indicate a reaction involving both CF_3 radicals and NO, since both are consumed in the reaction. Although CF_3NO was not detected in the reaction products, it is possible that it existed as a transitory intermediate. As such, it could either decompose or, by addition, form $(CF_3)_2NOCF_3$.

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[20] L. Batt and J. M. Pearson, *Chem. Commun.*, **22**, 575 (1965).