# THE PHOTOLYSIS OF TRIFLUOROMETHYL CYANIDE<sup>1</sup>

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ABSTRACT

The photolysis of CF<sub>3</sub>CN at 1849 Å has been studied. The major products are hexafluoroethane, cyanogen, and perfluoro-3-methyl-2-aza-2-butene. The experimental value for  $k_3/k_2^{\frac{1}{2}}$  is:

 $10^{-9.08\pm.13} e^{-5.00\pm.21} \text{ kcal mole}^{-1/RT} \text{ molecule}^{-\frac{1}{2}} \text{ cc}^{\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$ 

where:

#### $CF_3 + CF_3 \rightarrow C_2F_6$ [2]

$$CF_3 + CF_3CN \rightarrow (CF_3)_2CN.$$
 [3]

Another product was isolated in smaller amounts and has been tentatively identified as perfluorotrimethyl-aza-2-pentene.

# INTRODUCTION

Earlier work on the photolysis of  $CH_3CN$  (1) showed the mechanism to be so complex that a unique interpretation was difficult. It was felt that the vulnerability of the C-H bond, both to break in the primary step and to subsequent abstraction, led to the wide variety of reaction paths and products. It was thus hoped that a study of the photolysis of CF<sub>3</sub>CN would give information for the interpretation of the CH<sub>3</sub>CN studies. In particular the importance of reaction [8]:

$$CN + CF_3CN \rightarrow C_2N_2 + CF_3$$
 [8]

was sought.

# EXPERIMENTAL

Photolyses were carried out in a cylindrical guartz reaction vessel 4.8 cm long and 4.7 cm in diameter, which was connected to a mercury-free system with a Hoke No. 413 high-vacuum stainless-steel valve. The windows of the cell were 1.00-mm-thick quartz, each of which transmitted about 75% of the 1849 Å radiation used in this work. The initial pressure in the reaction cell was measured with a quartz spiral Bourdon gauge nulled with a mercury manometer. When a mixture of gases was desired in the reaction cell, the appropriate amounts of the gases were premixed in a 125-cc bulb with a magnetically driven stirrer and then expanded into the reaction cell. The techniques described by McElcheran et al. (1) were used; the reaction products were transferred to the analytical system through a silicone oil diffusion pump, a stopcock, and two liquid nitrogen traps to keep the mercury vapor in the analytical system out of the reaction cell.

The cell was placed inside a cylindrical furnace which was mounted on an optical bench. The quartz spiral low-pressure mercury lamp and the platinum photocell were also mounted on the optical bench as part of an airtight system with the furnace tube. This permitted nitrogen to flow through the light path and yet allowed the lamp and photocell to be easily moved for heating the windows of the reaction cell with a torch.

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The nitrogen was passed through the system at approximately 200 cc min<sup>-1</sup> by means of a small heater in a Dewar of fresh liquid nitrogen. Provision was also made to introduce glass plates between the lamp and the reaction cell. A Vycor plate (Corning No. 7910) was inserted when only 2537 Å radiation was desired and several 3-mm-thick quartz plates were inserted to reduce the 1849 Å intensity to about 20% of the usual value.

Because of polymer formation during the photolysis it was necessary at the end of each run to fill the cell with an atmosphere of oxygen and flame both windows to red heat. This removed the polymer from the windows and ends of the cylindrical walls, but after a number of runs some polymer was built up on the walls of the central section of the cell. The relative amount of polymer was determined for each run by the drop in transmitted 1849 Å radiation during the photolysis and this intensity decrease was as high as 50% for some of the higher-pressure experiments.

The photocell consisted of a semicylindrical cathode of platinum (2) mounted in a quartz envelope that had been thinned slightly in front of the cathode to decrease the light absorption by the envelope. Before the photocell was sealed off, it was evacuated overnight at  $10^{-6}$  mm of Hg with the envelope heated to  $500^{\circ}$  C, and then the cathode was heated with an induction heater (two thin strips of platinum had been spot-welded to the top and bottom of the cathode to complete the loop and give more effective coupling) until the cathode was no longer sensitive to 2537 Å light. This was determined by measuring the photocurrent produced by a low-pressure Hg lamp with a Vycor plate in front of the photocell. The effective area of the photocell was about 4 cm<sup>2</sup> and the operating anode potential was 135 v. Photocurrents of the order of  $10^{-9}$  amp were obtained in this work and were measured with a Keithley electrometer and decade resistance attachment. After more than a year of use, the photocell remained completely insensitive to the 2537 Å radiation of the mercury lamp.

The volatile products were condensed at  $-195^{\circ}$  C and then separated by distillation from a Ward-Leroy still (3). The  $C_2F_6$  and the bulk of the CF<sub>3</sub>CN were removed at  $-150^{\circ}$  C and condensed in a liquid nitrogen trap until the distillation pressure had dropped to approximately half the value of the equilibrium pressure during the bulk of the distillation. This procedure removed at least 95% of the CF<sub>3</sub>CN, but none of the higher-boiling products. The  $CF_3CN-C_2F_6$  mixture was then reacted in a microhydrogenation tube with about 500 mm of hydrogen over a nickel-kieselguhr catalyst (4) at 85° C for 1 to 2 hours. This converted about 95% of the CF<sub>3</sub>CN, principally to higher-boiling amines. The excess hydrogen was pumped off at liquid nitrogen temperature, and the products of the hydrogenation were distilled from  $-140^{\circ}$  C to a liquid nitrogen trap. The quantity of this fraction (cut No. 4) was measured in a gas burette and sealed off in a sample tube for mass spectrometric analysis. This cut consisted mainly of the unreacted  $CF_3CN$ , the  $C_2F_6$  (from the photolysis only; none was found in a blank hydrogenation), and some ammonia. This procedure thus served to concentrate the  $C_2F_6$  from about 1% of the original fraction to an appreciable component that could readily be measured by mass spectrometry.

Other fractions of the photolysis reaction products were taken at  $-130^{\circ}$  C (cut No. 1),  $-115^{\circ}$  C (cut No. 2), and the residual higher boiling compounds that remained condensed at  $-115^{\circ}$  C were collected as cut No. 3. The total quantity of each of the samples was measured on a gas burette and then the sample was sealed in a tube for mass spectrometric analysis. The total volume of the inlet system of the mass spectrometer was calibrated by expanding samples of known quantities of pure nitrogen (similar sample size to the unknown samples) into the spectrometer, measuring the

1738

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m/e 28 peak height, and comparing with the nitrogen sensitivity. Calculation of analyses for two component samples where standards were not available is described in the Appendix.

The CF<sub>3</sub>CN was obtained from Peninsular Chemresearch Inc., practical grade, and was purified by several fractionations from  $-80^{\circ}$  C to  $-195^{\circ}$  C. The hexafluoroacetone was obtained by reacting the hydrate (Merck Chemical) with phosphorus pentoxide, followed by several vacuum fractionations. This gas was stored in a blackened bulb until used.

### RESULTS

Mass spectrometric analyses indicated that cut No. 1 contained the remaining CF<sub>3</sub>CN (pattern given in Table I) and some of the  $C_2N_2$ , while cut No. 2 contained the remainder of the  $C_2N_2$  and a fluorinated product. The pattern for this product is listed in Table I and is consistent with the pattern to be expected for perfluoro-3-methyl-2-aza-2-butene  $((CF_3)_2C=NCF_3)$ , hereafter called MAB). This type of compound gives mass spectral patterns with a small parent peak (m/e 233), medium-sized peaks corresponding to loss of one or two fluorine atoms (m/e 214 and 195), a large peak for loss of a CF<sub>3</sub> group (m/e 164), and a large m/e 69 peak. All other peaks are also consistent with the structure of MAB. Further evidence of consistency with the proposed structure is indicated by the metastable transitions observed which are also listed in Table I. In every case they correspond to transitions of the important ions in the spectrum by typical reaction paths found in mass spectral fragmentation patterns, e.g. references 5 and 6.

TABLE I Mass spectral patterns for CF<sub>3</sub>CN and MAB

m/e	CF <sub>3</sub> CN	MAB	m/e	CF3CN	MAB	
12	5.3				0.2	
24	0.5		145		5.2	
$\overline{26}$	11 6		164		(100)	
$\frac{20}{27}$	1 7		165		3 7	
31	25.8	9.8	169		0.3	
38	4.2	0.0	171		0.2	
50	50.2	12.8	176		21	
51	0.6	12.0	195		4 3	
57	0.0		211		25.7	
	210	949	214		0.1	
09	311. 2 =	2°±2. 0 0	2.00	Matastable ion	o observed o	nd avagaated
10	3.0	4.0		metastable for	is observed a	na suggestea
10	(100.)	11.8		N7	transition	Turnet
( (	2.5	0.7		ivone	m/e	Transition
81		0.7		observed	20	1.0.1 0.0
93		1.1			29.	$104 \rightarrow 09$
95	5.1	1.2			32.8	$76 \rightarrow 50$
100		1.8			60.9	$214 \rightarrow 114$
114		16.7			79.	$164 \rightarrow 114$
119		1.3			115.5	$233 \rightarrow 164$
126 + n	1 <sup>÷</sup>	<b>2.6</b>			125.9	$214 \rightarrow 164$

Because of lack of mass spectral standards for MAB and because of troubles in obtaining a reproducible cyanogen standard (apparently due to absorption problems), the effective sensitivities of the cyanogen m/e 52 peak and the MAB m/e 164 peak were determined by the method described in the Appendix. A typical plot of equation [A-3] for a set of analyses performed on the same day is shown in Fig. 1 with the sensitivities of C<sub>2</sub>N<sub>2</sub> and MAB being determined from the slope and the intercept, respectively, of the straight



FIG. 1. Plot of equation [A-3] for a typical group of cut No. 2 analyses. Open circles used to determine linear plot and closed circles are for points above the line that indicate an additional component present.

line. These sensitivities were used to calculate the absolute amounts of  $C_2N_2$  and MAB in the samples of cut No. 2 as well as samples of cut No. 1 that were analyzed at the same time.

Cut No. 4 was analyzed for  $C_2F_6$  by using the m/e 119 peak. Because of absorption of the ammonia and amines in the sample, a complete analysis of the sample was not undertaken. Rather, by expanding the total sample into the calibrated volume on the inlet system of the mass spectrometer, one could relate the partial pressure of  $C_2F_6$ (from the m/e 119 peak height) directly to the absolute amount of  $C_2F_6$  in the sample.

The small amount of high-boiling products (cut No. 3) was analyzed on the mass spectrometer and found to contain two major components. One component was distinguished by peaks at m/e 96 and 97 (as well as 77, 76, 69, etc.) and is tentatively identified as 2,2,2-trifluoroethylideneimine (CF<sub>3</sub>CH==NH) or a similar partially hydrogenated compound. This compound must arise from reaction of photolytic species or photolysis products with adsorbed water on the walls or with the silicone oil in the diffusion pump, because this compound was not found after a similar fractionation procedure on a sample of CF<sub>3</sub>CN that had not been photolysed.

The pattern assigned to the major component of cut No. 3 is shown in Table II. Because of the small quantity of this product in any of the samples, the smaller-sized peaks are subject to considerable scatter and only the major peaks are listed. Many of the lower mass peaks are also omitted because of interference from the other component. The higher mass peaks are consistent with a molecular weight of 383 (loss of one fluorine atom gives m/e 364; loss of CF<sub>3</sub> gives m/e 314, which is a major peak, etc.). This would indicate a formula of C<sub>7</sub>F<sub>15</sub>N and would probably be either perfluoro-3,4,4trimethyl-2-aza-2-pentene (CF<sub>3</sub>C(CF<sub>3</sub>)<sub>2</sub>C(CF<sub>3</sub>)=NCF<sub>3</sub>) or perfluoro-2,4,4-trimethyl-3aza-2-pentene (CF<sub>3</sub>C(CF<sub>3</sub>)<sub>2</sub>N=C(CF<sub>3</sub>)<sub>2</sub>), hereafter called TAP. A plot of equation [A-3] for cut No. 3 (Fig. 2) indicates that the amounts of the two major components present are proportional to the m/e 314 and 96 peak heights and that there are no other compounds consistently present in significant quantity in these samples (see Appendix).

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IADLE II										
Mass spectrum of TAP										
m/e	Relative peak height	m/e	Relative peak height							
$\begin{array}{c} 31\\ 50\\ 69\\ 76\\ 112\\ 114\\ 131\\ 138\\ 145\\ 146\\ 150\\ 159\\ 164\\ 169\\ 176\\ \end{array}$	$\begin{array}{c} 5.0\\ 4.5\\ 270.\\ 4.7\\ 3.5\\ 2.\\ 4.0\\ 1.5\\ 2.\\ 1.\\ 2.1\\ 3.\\ 9.\\ 4.3\\ 3.6\end{array}$	196 214 221 226 245 and 246 259 264 271 295 303 310 314 314 322 328 342	$\begin{array}{c} 2.1\\ 9.\\ 2.3\\ 11.7\\ 12.\\ 11.2\\ 22.6\\ 2.3\\ 1.4\\ 0.8\\ 3.9\\ (100.)\\ 1.\\ 3.\\ 4.6\end{array}$							
$\begin{array}{c} 192 \\ 195 \end{array}$	$\begin{array}{c} 2.6\\ 1.6 \end{array}$	$\begin{array}{c} 354 \\ 364 \end{array}$	1.5.5							

The sensitivities for these two components were determined from the graph and were used to calculate the absolute amount of TAP formed.



FIG. 2. Plot of equation [A-3] for a group of cut No. 3 analyses. Open circles used to determine linear plot and closed circles are for points above the line that indicate an additional component present.

On the basis of the reaction mechanism one might expect perfluorodiisopropylidene hydrazine  $((CF_3)_2C=N-N=C(CF_3)_2(PDH))$ , or its isomer perfluoro-3,4-dimethyl-2,5-diaza-2,4-hexadiene  $(CF_3N=C(CF_3)C(CF_3)=NCF_3)$ , as a product. This compound would have a parent peak at m/e 328 and significant peaks at m/e 309, 290, and 259. Peaks are observed at m/e 328, 310, and 259, but the ratio of these peak heights to the m/e 314 peak height is reasonably constant (although with more scatter than some of the other peaks in the spectrum of TAP), indicating that traces of PDH may be present, but that the major contribution to these peaks comes from the same compound that gives the m/e 314 peak. (A coincidental proportionality between the yields of two different products for all runs under the variety of conditions studied is very unlikely.) The polymer formation (measured as the decrease in the logarithm of the 1849Å light transmitted) as a function of irradiation time was found to be linear after an initial induction period. The slope of the linear region was found to be proportional to the square root of the CF<sub>3</sub>CN pressure at constant light input (uncorrected for the change in optical density of the CF<sub>3</sub>CN) and approximately proportional to the incident intensity at constant pressure. One photolysis was carried out on a mixture of CF<sub>3</sub>CN and CF<sub>3</sub>COCF<sub>3</sub> with 2537 Å light so that only CF<sub>3</sub>COCF<sub>3</sub> would undergo photolysis. No polymer formation was detected with 1849Å light after the run, although a 20–30% decrease in intensity was observed for runs on CF<sub>3</sub>CN alone at 1849Å at the same pressure and temperature. This indicated that the formation of polymer required reactants in addition to the CF<sub>3</sub>· radical and CF<sub>3</sub>CN. This fact, and the induction period observed, indicate that the polymer must arise from polymerization of the cyanogen formed during the photolysis.

A blank photolysis of CF<sub>3</sub>COCF<sub>3</sub> at 2537 Å in the reaction cell that was partially coated with paracyanogen gave a  $C_2F_6/CO$  ratio of about 0.6, indicating an appreciable loss of CF<sub>3</sub>· radicals by addition to the unsaturated paracyanogen. This is also confirmed by the observation of the evolution of  $C_2F_6$  on heating the polymer formed in the photolysis of CF<sub>3</sub>CN. Because of loss of some of the  $C_2N_2$  product by polymerization and some of the CF<sub>3</sub>· radicals by reaction with the polymer, attempts at absolute quantum measurements in order to test the existence of reaction [8] are useless.

The absorption coefficient of  $CF_3CN$  at 1849 Å was found to vary with temperature and a statistical analysis of the data taken during the course of this work yielded:

 $\epsilon = 10^{1.483 \pm .045} e^{-1620 \pm 70 \text{ cal mole}^{-1/RT}} \text{ mole}^{-1} \text{ l. cm}^{-1}.$ 

This rather significant dependence on temperature would seem to indicate that the 1849 Å line coincides with the edge of an absorption band. The same situation occurs for CH<sub>3</sub>CN (7), and thus it would appear that the substitution of fluorine atoms on the methyl group of CH<sub>3</sub>CN does not shift the absorption band edge very much.

#### DISCUSSION

The experimental data are summarized in Table III. On the basis of these data and the other results discussed above, the following mechanism is proposed:

 $CF_3CN + h\nu \rightarrow CF_3 + CN,$  [1]

$$CF_3 + CF_3 \rightarrow C_2F_6, \qquad [2]$$

 $CF_3 + CF_3CN \rightarrow (CF_3)_2C = N \cdot,$  [3]

 $CF_3 + (CF_3)_2 CN \cdot \rightarrow (CF_3)_2 C = NCF_3 (MAB),$  [4]

$$CF_3 + MAB \rightarrow \rightarrow TAP,$$
 [5]

$$CN + CN + M \rightarrow C_2 N_2 + M, \qquad [6]$$

wall?  

$$C_2N_2 + R(CN^2) \rightarrow paracvanogen,$$
[7]

The formation of MAB proceeds through reactions [3] and [4] with reaction [3] the rate-determining step. An Arrhenius plot of  $R_{MAB}/R_{C_2F_6}^{\frac{1}{2}}[CF_3CN]$  is shown in Fig. 3 and gives

 $k_3/k_2^{\frac{1}{2}} = 10^{-9.09 \pm \cdot 11} e^{-5.05 \pm \cdot 17 \operatorname{kcal mole}^{-1/RT}} \operatorname{molecule}^{-\frac{1}{2}} \operatorname{cc}^{\frac{1}{2}} \operatorname{sec}^{-\frac{1}{2}}.$ 

The mechanism for the formation of TAP is subject to some doubt, but the best kinetic agreement has been found for  $R_{TAP}/R_{MAB}R_{C2F6}^{\frac{1}{2}t}$  (where t is the reaction time),

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FIG. 3. Arrhenius plot of  $k_3/k_2^{\frac{1}{2}}$ . Circles (lower plot) represent  $R_{(CF_3)_2CN} = R_{MAB}$ . Squares (upper plot) represent  $R_{(CF_3)_2CN} = R_{MAB} + 2R_{TAP}$ . Solid circles and squares indicate low-intensity runs.



FIG. 4. Arrhenius plot of  $k_3/k_2^{\frac{1}{2}}$ . Solid circles indicate low-intensity runs.

indicating the rate-determining step for the formation of TAP is the addition of  $CF_3$ . to MAB. An Arrhenius plot of this function is shown in Fig. 4 and the lack of effect of intensity on the plot indicates this function represents the rate-determining step for the formation of TAP. From Fig. 4 and assuming the average concentration of MAB is  $\frac{1}{2}R_{MAB}t$ , one obtains:

 $k_5/k_2^{\frac{1}{2}} = 10^{-8.81 \pm .22} e^{-3.87 \pm .33 \text{ kcal mole}^{-1}/RT} \text{ molecule}^{-\frac{1}{2}} \text{ cc}^{\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}.$ 

It is difficult to decide what additional reaction steps following reaction [5] must be involved to explain the formation of TAP. The difficult part is the origin of the perfluoro-

1743

Note: \*n.d., not determined. Outside 2.5 X standard deviation.

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2.103	9 083	1.007	1.045	2.74	2.15	1.610	0.482	2.97	2.36	1.717	1.130	0.599	3.124	1.597	2.40	1.826	$cc^{-1} \times 10^{-18}$	Concn. of CF <sub>3</sub> CN	
374.7	373.0	371.6	360.2	350.8	351.2	351.8	351.8	333.8	332.6	332.4	333.8	332.0	312.2	312.8	313.4	314.2	(° K)	T	AMUG -
0.320	2.10 2.10	2.32	0.382	2.40	2.04	1.87	1.96	2.44	2.38	1.86	1.88	1.84	0.418	0.400	2.40	2.38	intensity	Rel.	
23.8	6.20 6.46	$\tilde{2.01}$	32.76	6.82	7.60	6.65	6.20	6.18	6.42	6.64	6.32	6.13	24.55	30.40	6.48	6.06	$(\sec \times 10^{-4})$	T::::>	
0.0404	0.731	0.737	0.049	1.170	1.065	0.850	0.294	1.71	1.548	1.188	0.977	0.783	0.193	0.113	2.34	1.24	$R_{\mathrm{C}_{2}\mathrm{F}_{6}}$		
1.030	4.49 6.00	2.35	0.469	5.31	4.23	2.80	0.482	5.16	4.13	2.25	1.33	0.564	0.987	0.411	3.29	0.687	RMAB	Molecule cc <sup>−1</sup> se	
0.957	4.47 5.79	. 3. 43	0.049	9.80	4.07	4.29	1.95	5.02	3.75	5.59	3.73	2.23	0.978	0.514	5.18	2.01	$R_{C_2N_2}$	2C <sup>-1</sup> ×10 <sup>-11</sup> 0	
0.0800	0.283	0.165	0.0305	0.443	n.d.*	n.d.*	0.010	n.d.*	0.289	0.112	0.080	0.018	0.0480	0.0200	0.144	0.037	$R_{\mathrm{TAP}}$	f:	
7.70	10.60	8.58	6.41	5.68	6.00	5.98	5.85	4.21	4.45	3.81	3.78	3,36	2.27	2.42	2.83	2.50	×10 <sup>13</sup>	$R_{C_2 F_6} $ $(molecule^{-\frac{1}{3}})$	Rмлв
4.95	3.71	3.68	2.84	3.56	1	1	$(1.94)^{\dagger}$	ł	2.76	2.16	3.04	1.86	1.39	1.51	1.39	$(2.52)^{\dagger}$	×10 <sup>12</sup>	$\begin{bmatrix} R_{\text{MAB}} \\ R_{\text{C}_2 F_6} & \\ \text{(molecule}^{-\frac{1}{4}} \\ \text{(molecule}^{-\frac{1}{4}} \end{bmatrix}$	$R_{\mathrm{TAP}}$
8.90	11.99	9.79	7.26	6.60	l	1	6.10		5.09	4.19	4.24	3.58	2.49	2.68	3.08	2.78	×10 <sup>13</sup>	$\begin{bmatrix} R_{C_2} F_6 \\ CF_3 CN \end{bmatrix}$ (molecule <sup>-1</sup> )	$R_{MAB} + 2R_{TA}$

Summary of experimental results TABLE III

t-butyl group. This may have required breaking a C-N bond, possibly by addition of two CF<sub>3</sub> radicals to MAB and then breaking of the C-N bond due to steric repulsion. If the t-butyl radical is an intermediate, one would expect perfluoroneopentane as a detectable product. From the boiling point of this compound (8), one would expect it to appear in cut No. 2 and to give a large m/e 219 peak, but none is observed.

Another possibility is that the C-N bond does not break until after 2 molecules of the original  $CF_3CN$  are associated in some intermediate compound that contains a number of additional  $CF_3$  groups. This would not require the *t*-butyl radical as an intermediate, but again the absence of any other obvious intermediate is difficult to explain. Still another possibility is that TAP is not the actual product, but rather none of the higher mass peaks (above m/e 364) in the pattern of the actual product is stable. Thus the C—N bond has been broken on electron impact of the compound in the mass spectrometer to give a pattern resembling TAP. (It should be emphasized that the kinetic dependence for the formation of the compound giving the m/e 314 peak is much better understood from the data available than the structure of the compound.)

If TAP is formed by the reaction of MAB, then  $k_3/k_2^{\frac{1}{2}}$  should be corrected for the number of  $(CF_3)_2CN$  radicals or MAB molecules that are consumed in the formation of TAP. If two  $(CF_3)_2CN$  radicals are assumed to be precursors for each molecule of TAP,  $k_3/k_2^{\frac{1}{2}}$  would be determined from  $(R_{MAB}+2R_{TAP})/R_{C_2F_6}^{\frac{1}{2}}$  [CF<sub>3</sub>CN]. A plot of this function (also shown in Fig. 3) results in a value for  $(k_3/k_2^{\frac{1}{2}})_{corr}$  of:

 $10^{-9.08\pm.13} e^{-5.00\pm.21 \text{ kcal mole}^{-1/RT}}$  molecule  $-\frac{1}{2} \text{ cc}^{\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$ 

It is seen that the uncertainty in the number of precursor  $(CF_3)_2CN \cdot$  radicals in the formation of TAP will have only a small effect on the experimental value of  $k_3$ .

Using the latter value of  $k_3/k_2^{\frac{1}{2}}$ , assuming  $E_2 = 0$ , collision diameters for CF<sub>3</sub>, CF<sub>3</sub>CN, and MAB as 4.0, 7.0, and 8.0 Å, respectively, and a temperature of 343° K, one calculates  $E_3 = 5.0 \pm .2$  kcal mole<sup>-1</sup>,  $E_5 = 3.9 \pm .3$  kcal mole<sup>-1</sup>,  $p_3/p_2^{\frac{1}{2}} = 2.2 \times 10^{-5}$ ,  $p_5/p_2^{\frac{1}{2}} = 2.2 \times 10^{-5}$  $3.4 \times 10^{-5}$ . If  $p_2$  is taken to be unity, then  $p_3$  and  $p_5$  are about  $2 \times 10^{-5}$  and  $3 \times 10^{-5}$ , respectively.

Reactions [3] and [5] are similar to the addition of  $CH_3$  radicals to simple olefins where the activation energies are about 5–7 kcal mole<sup>-1</sup> and the steric factors are about  $4 \times 10^{-4}$  (9). The activation energies observed here are about the same, but the steric factors are lower by about a factor of 20. This decrease from the hydrocarbon case is presumably due to the increased size of the fluorinated groups.

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### CANADIAN JOURNAL OF CHEMISTRY. VOL. 37, 1959

# APPENDIX

Consider the case of a mass spectral analysis on a two-component mixture where each of two peaks in the spectrum can be attributed solely to each component. The total pressure  $(p_t)$  is equal to the sum of the partial pressures of the two components and thus:

$$p_{t} = (h_{1}/S_{1}) + (h_{2}/S_{2}), \qquad [A-1]$$

where h refers to the peak height and S the sensitivity of the particular component.

If the total quantity of the sample  $(q_t)$  is known and the entire sample is expanded into a volume (V), then:

$$q_{\rm t}/V = (h_1/S_1) + (h_2/S_2),$$
 [A-2]

and rearranging,

$$q_{\rm t}/h_2 = (h_1/h_2)(V/S_1) + (V/S_2).$$
 [A-3]

A plot of  $q_t/h_2$  vs.  $h_1/h_2$  for a series of samples of varying relative composition will give the constants  $V/S_1$  and  $V/S_2$  from the slope and intercept, respectively. Since the absolute quantity of each component is:

$$q_1 = h_1(V/S_1),$$
 [A-4]

the absolute quantity can be calculated from the peak height in the individual samples and the constant determined from the plot of equation [A-3] for a set of analyses. No standards are therefore required and the volume (V) need not be known, merely that it is the same for all of the samples. If different volumes have to be used for different sample sizes, only the ratio of volumes needs to be known.

The presence of a third component in all of the samples will cause a scatter of the plot, but an occasional impurity in only a few samples will show up as a few points above the line with the remainder of the analyses giving a good linear plot. Figures 1 and 2 show this latter type of deviation, indicating that there are no significant additional components present in cuts No. 2 and No. 3.

This technique has the added advantage that if one of the components shows preferential absorption on the walls of the inlet system of the mass spectrometer, no effect on the linearity of equation [A-3] will be observed if the fraction of the component absorbed is independent of the total quantity of that component present. The  $V/S_1$ thus obtained is an effective reciprocal sensitivity and the correct absolute quantities will still be obtained when the effective reciprocal sensitivity is used in equation [A-4].