may be completely dissimilar to the carbene or it may be that $[C^{11}RH]^*$ is in fact a highly energetic but structurally distorted carbene requiring appreciable atomic motion to allow it to assume a well-defined singlet or triplet carbene structure. Further work is in progress in order to further elucidate this model.

The Rate of Thermal Decomposition of CF₃CN[1,2]

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Abstract In the temperature range above 684° the thermally initiated decomposition of CF₃CN yields C_2F_6 and $(CN)_2$, *i.e.*, $2CF_3CN \rightarrow C_2F_6 + (CN)_2$ (1). The reaction was shown to be second order in CF₃CN following the stoichiometry of eq 1 above. The rate of the decomposition was studied in the temperature range 684–809° with the resulting Arrhenius expression being $k_2 = 10^{11.7} \exp(-64.7 \pm 3.0\, kcal/RT)\, l./(mol\, sec)$.

The thermal stability of trifluoroacetonitrile was first reported by Janz and Stratta[3] in the temperature range 350–550°. Reactions of CF₃CN with mono- and diolefins have also been reported by Janz, *et al.*, in the same temperature range. The ethylene reaction results in the 1:1 adduct, *i.e.*, 4,4,4-trifluorobutyronitrile,[4] while the respective pyridines are formed with conjugated diolefins.[5] Since CF₃CN has only been studied relative to addition reactions, the thermal decomposition was undertaken in the temperature range 684–809°. The present communication reports the results of kinetic measurements for the reaction

$$2CF_3CN \longrightarrow C_2F_6 + (CN)_2 \qquad (1)$$
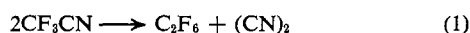
Experimental Section

Kinetic measurements were carried out in a 0.25-l. Vycor stirred-flow reactor with an on-stream sampling system described in detail elsewhere.[6] The rate of decomposition was studied in the temperature range 684–809 ± 2° using contact times between 464 and 2519 sec. Under these conditions, C_2F_6 and $(CN)_2$ were the only products observed. At temperatures above 809°, N_2 and other uncharacterized products were detected. The reaction mixtures were quantitatively analyzed on an Aerograph 204B gas chromatograph, equipped with hydrogen flame detectors, previously calibrated with pure samples of CF₃CN, C_2F_6, and $(CN)_2$.

The materials CF₃CN and C_2F_6 (Peninsular Chemresearch, Inc., 99% minimum) and $(CN)_2$ (Columbia Organic Chemicals Co., Inc., 99% minimum) were degassed under high vacuum and triply distilled at low temperatures prior to use.
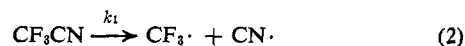
Data and Results

The rate of thermal decomposition of CF₃CN was studied in the previously mentioned temperature range, using constant flow velocities (*i.e.*, contact times) through the reaction zone. The rate of decomposition was not affected by preconditioning the reactor surface

(*i.e.*, CF₃CN pyrolyzed at ∼800° using very long contact times).

The reaction order was determined by assuming both first- and second-order decomposition. The rate derivations are as follows.

A. If CF₃CN decomposes by a Lindeman type mechanism, the result is

$$CF_3CN \xrightarrow{k_1} CF_3\cdot + CN\cdot \qquad (2)$$

$$2CF_3\cdot \xrightarrow{k_2} C_2F_6 \qquad (3)$$

$$2CN\cdot \xrightarrow{k_3} (CN)_2 \qquad (4)$$

$$CF_3\cdot + CN\cdot \xrightarrow{k_4} CF_3CN \qquad (5)$$

Assumption of the stationary state for $CF_3\cdot$ in the reaction zone permits

$$0 = V_r k_1[CF_3CN] - V_r k_2[CF_3\cdot]^2 - V_r k_4[CF_3\cdot][CN\cdot] \qquad (6)$$

and

$$U_T[C_2F_6] = V_r k_2[CF_3\cdot]^2 \qquad (7)$$

where U_T is the total volumetric flow rate of the reactor effluent, *i.e.*, $U_{CF_3CN} + U_{C_2F_6} + U_{(CN)_2}$, and V_r is the volume of the reaction zone. If the assumption is made that $[CF_3\cdot] \simeq [CN\cdot]$, and $k_2 \simeq \frac{1}{2}k_4$, then

$$k_1 = \frac{3U_T[C_2F_6]}{V_r[CF_3CN]} \qquad (8)$$

which, upon rearranging gives

$$\frac{U_T}{V_r} = k_1 \frac{[CF_3CN]}{3[C_2F_6]} \qquad (9)$$

A plot of U/V vs. $[CF_3CN]/[C_2F_6]$ should result in a straight line with a slope of $\frac{1}{3}k_1$ if the order and mechanism are correct.[7] Figure 1 depicts such a curve. It appears that the plot is not a "good" straight line; thus, first-order kinetics are assumed to be invalid.

(1) Based in part on a thesis submitted by D. J. P. in partial fulfillment of the requirements of the Ph.D. degree, Rensselaer Polytechnic Institute, June 1968.

(2) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(3) G. J. Janz and J. J. Stratta, *J. Org. Chem.*, **26**, 2169 (1961).

(4) J. B. Flannery and G. J. Janz, *J. Amer. Chem. Soc.*, **88**, 5097 (1966).

(5) G. J. Janz and A. R. Monahan, *J. Org. Chem.*, **29**, 569 (1964); and A. R. Monahan and G. J. Janz, *J. Phys. Chem.*, **69**, 1070 (1965).

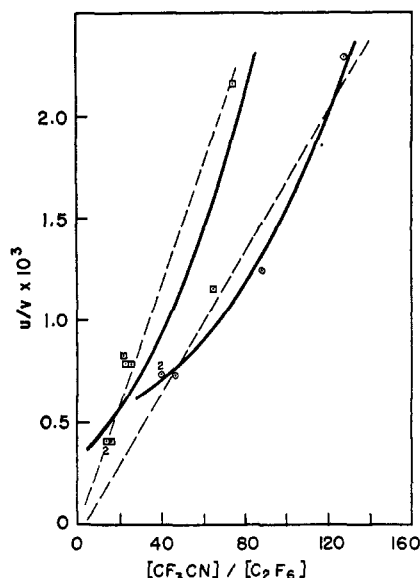(6) D. J. Perettie, R. J. Tofte, and G. J. Janz, *Chem. Instr.*, **1**, 221 (1968).

(7) W. C. Herndon, *J. Chem. Educ.*, **41**, 42 (1964).

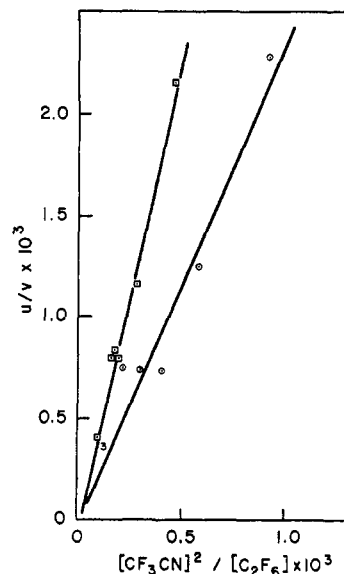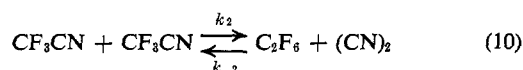Figure 1. The first-order plot for the decomposition of CF_3CN: ⊙, 990°K; ▣, 1013°K.

Figure 2. The second-order plot for the decomposition of CF_3CN: ⊙, 990°K; ▣, 1013°K.

B. If the system obeys second-order kinetics and assuming a simple bimolecular reaction, the result is

$$CF_3CN + CF_3CN \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_2F_6 + (CN)_2 \tag{10}$$

If we again assume a stationary state in the reaction zone

$$U_T[C_2F_6] = k_2V_r[CF_3CN]^2 - k_{-2}V_r[C_2F_6][(CN)_2] \tag{11}$$

which can again be rearranged to read

$$\frac{U_T}{V_r} = k_2\frac{[CF_3CN]^2}{[C_2F_6]} - k_{-2}[(CN)_2] \tag{12}$$

where U_T and V_r have the previous definition. The experimental data plotted in the form of the above equation, for experiments at different temperatures, are illustrated in Figure 2. Since the data plotted in this form result in a straight line, the reaction is substantiated as second order. From eq 12, it follows that an intercept of $\sim$0 results in k_{-2} being negligible. As can be seen from Figure 2, the y intercept is very close to zero resulting in $k_{-2}[(CN)_2] \simeq 0$ or k_{-2} being insignificant. If the reverse reaction is neglected, eq 11 reduces to

$$U_T[C_2F_6] = k_2V_r[CF_3CN]^2 \tag{13}$$

which rearranges to

$$k_2 = \frac{U_T}{V_r}\frac{[C_2F_6]}{[CF_3CN]^2} \tag{14}$$

Direct solution of eq 14 results in the rate constants summarized in Table I. A plot of the temperature dependence of these rate constants is illustrated in Figure 3. The resulting Arrhenius expression is $k_2 = 10^{11.7}$ exp(-64.7 ± 3.0 kcal/RT) l./(mol sec)

An approximate value of k_{-2} can be gained from k_2 and an extrapolated value for the equilibrium constant for the reaction

$$2CF_3CN \rightleftharpoons C_2F_6 + (CN)_2 \tag{15}$$
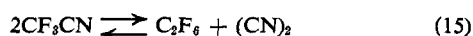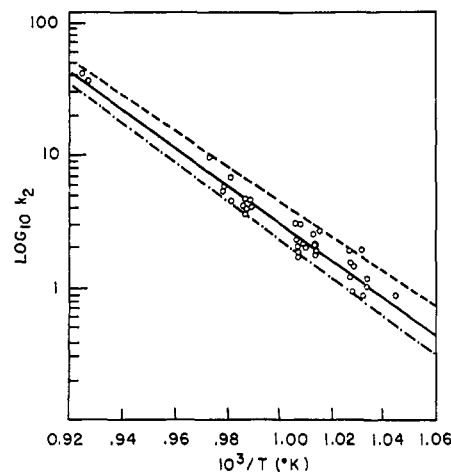
The high-temperature equilibrium reaction, eq 15, has

Figure 3. The temperature dependence of the rate of decomposition of CF_3CN. $k_2 = 10^{11.7}$ exp(-64.7 ± 3.0 kcal/RT) l./(mol sec).

recently been studied in the temperature range 592–652°.[8] The equilibrium studies result in $K_{eq} = 17.4$ (extrapolated to 1000°K) and $\Delta H_{r°,295} = -10.5$ kcal/mol. With $E_2 = 64.7$ kcal/mol, and k_2 (1000°K) = 3.0×10^{-3} l./(mol sec), the resulting Arrhenius expression for the reverse reaction is estimated to be

$$k_{-2} = 10^{12.5} \exp(-75.2 \text{ kcal}/RT) \text{ l./(mol sec)}$$

Discussion

The actual mechanism or transition state for the reaction is difficult to postulate. Since CF_3CN and HCN may both be classified as "cyanogen-like" compounds,[9] one could expect the decomposition mechanism for CF_3CN to be analogous to that reported for HCN,[10] i.e., a Bodenstein–Lind mechanism. Since the decomposition of CF_3CN obeys second-order kinetics, it is not

(8) D. J. Perettie, G. C. Sinke, L. C. Walker, A. N. Syverud, and G. J. Janz, submitted for publication.

(9) G. J. Janz, "Cyclo-Addition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1966, Chapter 4.

(10) N. C. Robertson and R. M. Pease, J. Amer. Chem. Soc., 64, 1880 (1942).

Table I. Bimolecular Rate Constants Calculated for
the Thermal Decomposition of CF$_3$CN

| Expt	$10^3/T$	Time, sec	k_2, cc/ (mol sec)
1	1.043	484.5	0.879
2	1.043	2403.8	0.371
3	1.032	895.3	2.094
4	1.032	2518.9	0.876
5	1.032	2445.0	1.068
6	1.032	2475.2	1.230
7	1.027	2481.5	0.970
8	1.027	2506.3	1.223
9	1.027	1140.2	2.023
10	1.027	1213.6	1.569
11	1.027	1201.9	1.457
12	1.014	2369.7	1.849
13	1.014	2331.0	2.149
14	1.014	2197.8	2.185
15	1.014	1265.8	2.651
16	1.014	1322.8	2.778
17	1.014	1368.0	1.954
18	1.007	439.0	3.055
19	1.007	798.1	2.125
20	1.007	1373.6	1.805
21	1.007	1356.9	2.462
22	1.007	1345.9	3.403
23	0.987	2445.0	4.139
24	0.987	2457.0	4.757
25	0.987	2457.0	3.699
26	0.987	1207.7	4.672
27	0.987	1254.7	4.080
28	0.987	1262.6	4.999
29	0.987	464.0	4.550
30	0.987	864.3	3.970
31	0.978	1297.0	5.613
32	0.978	1424.5	5.854
33	0.978	554.0	9.885
34	0.925	1422.5	36.908
35	0.925	570.1	40.425

in accord with the HCN reaction mentioned above. It would appear that the CF$_3$CN decomposition proceeds *via* a transition state quite analogous to that postulated by Bodenstein[11] for the HI decomposition.

The entropy of activation for the decomposition of CF$_3$CN ($\Delta S_2^{\ddagger}$) is -16 eu while that for the reverse reaction ($\Delta S_{-2}^{\ddagger}$) is -12 eu. Both these values are consistent with a charge-transfer complex similar to that

(11) M. Bodenstein, *Z. Phys. Chem.*, **29**, 295 (1899); also, G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **50**, 2315 (1928).

advanced elsewhere for some 1,4-cycloaddition reactions for which the $\Delta S^{\ddagger}$ values fall in the range from -11.8 to -19.4 eu.[12] A cyclic complex between two CF$_3$CN molecules resulting in the formation of C$_2$F$_6$ and (CN)$_2$ should obey second-order kinetics, and also have an entropy of activation comparable with those calculated from the Arrhenius equation.

A simple approximation method may be employed to estimate the entropy of activation. This method has been described by Benson[13] and leads to an approximate value of $\Delta S_2^{\ddagger} = -17$ eu assuming the four-centered complex
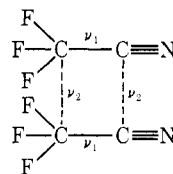
where $\nu_1 \simeq 500$ cm^{-1}, $\nu_2 \simeq 250$ cm^{-1}, and the ring deformations are about 300 cm^{-1}. The entropy of activation for the reverse reaction can be estimated to be ≥ 15.6 eu. The difference between these two values for the reverse process, 1.4 eu, is understood as due to the symmetry involved (in the reverse process, there are two possible orientations of the reacting molecules, so that a factor of $R \ln 2$ must be taken into account in the entropy calculations). Calculations for the reverse reaction are more approximate owing to the larger number of bending modes that must be taken into account in the transition state configuration.

From these estimates for the entropy of activation, and the values gained from the rate data and transition state theory, a four-centered cyclic complex for the transition state appears not improbably in the mechanism of the thermal decomposition of CF$_3$CN.

(12) G. J. Janz and J. M. S. Jarvie, *J. Phys. Chem.*, **60**, 1430 (1956).
(13) S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968.