

Thermal Decomposition of CF_3CN in Shock Waves

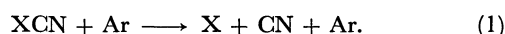
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The thermal decomposition of CF_3CN diluted to 0.2 and 0.5 mol% in argon was studied behind incident shock waves over the temperature range 2450—3610 K. Mass spectrometry of the reaction mixture revealed that the decomposition products are C_2F_6 , C_2N_2 , C_2F_4 , and a trace of FCN. The course of the primary process of decomposition, $\text{CF}_3\text{CN} + \text{Ar} \rightarrow \text{CF}_3 + \text{CN} + \text{Ar}$, was followed by monitoring the $\text{CN}(0-1)$ violet absorption centered at 421.5 nm. It was confirmed that the reaction is still in the low-pressure limit under our experimental conditions. The initial slope of absorption gave the bimolecular rate constant, $k = (7.9 \pm 3.1) \times 10^{15} \exp[-(94.0 \pm 2.8) \text{ kcal mol}^{-1}/RT] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The rate constants obtained are best fitted by the classical collision-theory expression $k = \lambda(Z/n!)(E/RT)^n \exp(-E/RT)$ with $\lambda = 0.44$, $n = 2$, and $E = D_0(\text{CF}_3-\text{CN}) = 102.7 \text{ kcal/mol}$. The mechanism of the overall decomposition was suggested and checked by numerical integrations of the relevant rate equations.

The shock-tube decomposition of simple cyano compounds such as C_2N_2 ,^{1,2)} ClCN ,³⁾ BrCN ,^{4,5)} and HCN ,^{6,7)} in argon has already been a subject of intensive studies by several groups of workers. It is generally agreed that the primary step of the decomposition is the bimolecular process:



The present work is an extension of our previous studies on C_2N_2 ,²⁾ BrCN ,⁵⁾ and HCN ,⁷⁾ to the case of trifluoroacetonitrile CF_3CN . Despite the larger number of atoms involved, the primary decomposition step proved to be still in the low-pressure limit under the shock-wave conditions adopted. The bimolecular rate constants for the primary step (1) were obtained from the initial slopes of the CN absorption records.

Product analysis showed that small amounts of C_2F_4 and FCN were formed in addition to the major decomposition products C_2F_6 and C_2N_2 . The overall decomposition mechanism is thus somewhat more complex than that already established for simpler cyano compounds.^{3-5,7)} Presumably, the sources of these minor products are CF_2 and F which have been generated by a further decomposition of CF_3 . A possible overall mechanism was inferred on this basis. Adequacy of the assumed mechanism was examined by numerical integrations of the overall kinetic equations. The time-concentration profiles calculated for CN radicals showed an excellent agreement with the observed CN absorption traces.

Experimental

Material. Trifluoroacetonitrile was prepared by heating a mixture of trifluoroacetamide and diphosphorus pentaoxide at 145—150 °C for 2 h,⁸⁾ and purified by trap-to-trap distillations. Commercial argon having a purity of 99.999% was used without further purification. Sample gases of 0.2 and 0.5 mol% CF_3CN in Ar were prepared at a total pressure of ca. 600 Torr [1 Torr = (101325/760) Pa].

Kinetic Measurements. Decomposition experiments were conducted in a stainless-steel shock tube having an internal diameter of 10.4 cm. The initial total pressure P_1 of gas samples ranged from 8.3 to 34 Torr. Hydrogen was used as driver gas. The diaphragms used were Mylar sheets of 0.10 and 0.25 mm in thickness, which gave the driver bursting pressures of 3 and 9 atm (1 atm = 101325 Pa), respectively.

The temperatures T calculated for the shock-heated gas samples were in the range from 2450 to 3610 K. No temperature correction was made for the reaction heat, inasmuch as the gas samples used were sufficiently dilute to ignore it.

The course of decomposition was followed by monitoring the $\text{CN } B^2\Sigma^+ - X^2\Sigma^+ (0-1)$ absorption at $421.50 \pm 0.21 \text{ nm}$. To isolate the spectral bandwidth, a Rikotsusho grating monochromator MC-50 was used at the entrance and exit slit width of 0.30 mm. The band selected encompasses the overlapping rotational lines $J = 9-36$ of the ground-state $\text{CN}(X^2\Sigma^+, v = 1)$. The detection devices and procedure used were entirely the same as those described previously.²⁾ The response time of the optics and its associated electronic circuit was no greater than 2 μs .

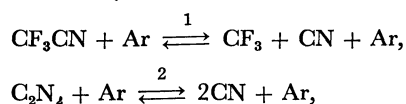
Product Analysis. A gas sample, 4 mol% CF_3CN in Ar, was shock-heated for an unspecified time interval at ca. 3400 K by using helium as driver gas. The gaseous reaction mixture, which was cooled down to room temperature by the rarefaction, was let pass through a trap immersed in liquid nitrogen. After having been degassed in the trap, the liquefied material was allowed to evaporate at room temperature.

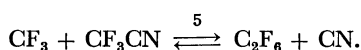
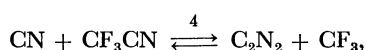
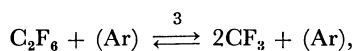
The reactant-product mixture gas thus prepared was subjected to mass-spectrometric analysis. The mass-spectrum obtained had the intensity peaks ascribable to CF_3CN , C_2N_2 , C_2F_6 , C_2F_4 , and FCN. Attempts were made to determine the relative concentrations of these species from the intensity ratios between relevant mass peaks. The standard intensity ratios between such peaks were calibrated beforehand with various equimolar binary mixtures ($\text{CF}_3\text{CN}-\text{C}_2\text{N}_2$, $\text{C}_2\text{F}_6-\text{C}_2\text{N}_2$, $\text{C}_2\text{F}_6-\text{C}_2\text{F}_4$, and $\text{C}_2\text{F}_6-\text{FCN}$) as references. The results of determination (in mol%) were as follows:

$$\begin{aligned} \text{CF}_3\text{CN} : \text{C}_2\text{N}_2 : \text{C}_2\text{F}_6 : \text{C}_2\text{F}_4 : \text{FCN} \\ = 85.15 : 5.16 : 8.01 : 1.50 : 0.16. \end{aligned}$$

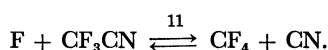
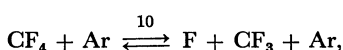
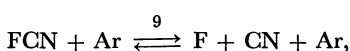
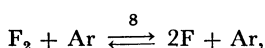
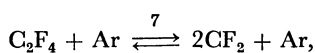
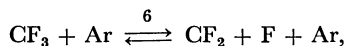
Results

Equilibrium. As has been confirmed by mass-spectrometry, the main products of the CF_3CN decomposition are C_2N_2 and C_2F_6 . By the analogy to the mechanism already established for the decompositions of ClCN ,³⁾ BrCN ,^{4,5)} and HCN ,⁷⁾ the main body of the present decomposition is considered to consist of the following elementary reactions:





The formations of C_2F_4 and FCN as minor products strongly suggest the intermediacies of CF_2 and F . The elementary reactions of importance which involve these transient species are conceivably as follows:



Presumably, both CF_2 and F are generated directly from CF_3 by Reaction 6. Reactions 7 and 8 are the dissociation-homorecombination processes associated with these species. Reactions 9 and 10 concern the associations of F with the primary radicals CN and CF_3 , respectively. Reaction 11 is a bimolecular reaction between F and CF_3CN , which is equivalent in type to Reaction 5.

Oscillographic records of the CN absorption showed, in all cases, an initial rapid rise in intensity, followed by a gradual increase up to a steady level. The constancy in absorbance may be taken as an indication that the overall process, Reactions 1 through 11, is in a complete equilibration.

Of the eleven species (except for Ar) present, only nine can take on independent concentrations at any given instance, since the total numbers of CN and F should be conserved all the time. At complete equilibrium, however, the local equilibria 4 and 5 cannot be independent ones either; $K_4 = K_1/K_2$ and $K_5 = K_1/K_3$. In addition, one may assume complete dissociations of C_2F_6 , C_2F_4 , and F_2 (*i.e.*, $K_3 = K_7 = K_8 = \infty$) in the temperature range studied.⁹ The overall equilibrium

problem could thus be solved for six independent concentrations $[\text{CF}_3\text{CN}]$, $[\text{CF}_3]$, $[\text{CN}]$, $[\text{CF}_2]$, $[\text{F}]$, and $[\text{FCN}]$ by use of the six equilibrium constants for Reactions 1, 2, 6, 9, 10, and 11. The standard free energy changes ΔG_T° for the various elementary reactions have been taken from the JANAF tables¹⁰ and are listed in Table 1.

The equilibrium concentrations $[\text{CN}]_e$ calculated in the above-described manner should be related to the observed absorbance at equilibrium through^{1,2,5)}

$$\ln(I_0/I)_e = \beta_{01} l F_{ab}(T) [\text{CN}]_e \quad (2)$$

Here, β_{01} is the effective absorption coefficient for the CN radicals in the absorbing levels, l is the optical path length ($l=10.4$ cm), and $F_{ab}(T)$ is the fractional population of the absorbing $\text{CN}(\text{X}^2\Sigma^+)$ radicals ($v=1$, $J=9-36$). The $F_{ab}(T)$ for the present case is given by

$$F_{ab}(T) = \frac{\sum_{J=9}^{36} (2J+1) \exp\left(-\frac{J(J+1)\varepsilon_r + \varepsilon_v}{kT}\right)}{Q_r Q_v}, \quad (3)$$

where ε_r and ε_v respectively denote the rotational and vibrational quanta of CN radicals and where Q_r and Q_v are the corresponding partition functions.

The β_{01} values to be obtained for different runs should be least temperature-dependent.^{2,5)} This was

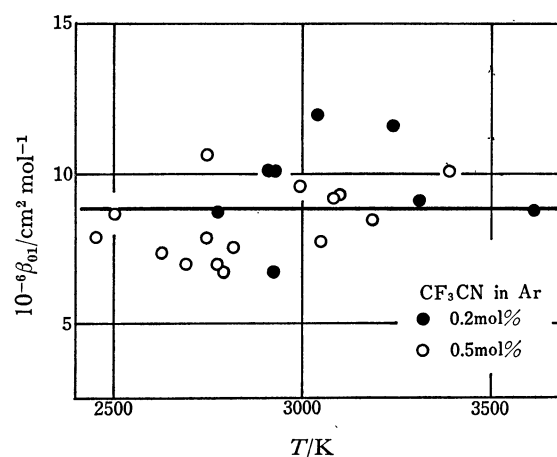


Fig. 1. Constancy of the CN absorption coefficient β_{01} over the temperature range studied.

TABLE 1. ELEMENTARY REACTIONS

	$H_0^{\text{a)}$ kcal mol ⁻¹	$G_T^{\text{a)}$ kcal mol ⁻¹	Rate constant $k_i/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Reference
1	102.7	$-0.03522T + 98.3$	$k_1 = 7.9 \times 10^{15} \exp(-94.0 \text{ kcal mol}^{-1}/RT)$	This work
2	125.6	$-0.03547T + 122.2$	$k_2 = 6.66 \times 10^{16} \exp(-98.6 \text{ kcal mol}^{-1}/RT)$	2
3	91.2	$-0.0383 T + 92.6$	$k_3 = (1/[\text{Ar}]_0) 3.2 \times 10^{16} \exp(-88.0 \text{ kcal mol}^{-1}/RT)^{\text{b)}$	—
4	-22.9	$0.00040T - 24.8$	$k_4 = 1.2 \times 10^{12} \exp(-8.7 \text{ kcal mol}^{-1}/RT)$	Adjusted ^{c)}
5	11.5	$0.00340T + 12.5$	$k_5 = 1.2 \times 10^{12} \exp(-11.5 \text{ kcal mol}^{-1}/RT)^{\text{b)}$	—
6	89.1	$-0.0338 T + 89.8$	$k_6 = 1.57 \times 10^{49} T^{-9} \exp(-92.25 \text{ kcal mol}^{-1}/RT)$	11
7	72.0	$-0.0373 T + 65.2$	$k_7 = 5.2 \times 10^{29} T^{-3.5} \exp(-72.0 \text{ kcal mol}^{-1}/RT)^{\text{b)}$	—
8	36.8	$-0.0310 T + 40.6$	$k_8 = 3.1 \times 10^{12} \exp(-27.3 \text{ kcal mol}^{-1}/RT)^{\text{b)}$	12
9	111.4	$-0.0331 T + 112.8$	$k_9 = 1.3 \times 10^{22} T^{-1.5} \exp(-111.0 \text{ kcal mol}^{-1}/RT)$	Estimated
10	125.7	$-0.0386 T + 126.8$	$k_{10} = 6.15 \times 10^{34} T^{-4.64} \exp(-122.4 \text{ kcal mol}^{-1}/RT)$	11
11	-23.0	$0.0030 T - 27.4$	$k_{11} = 2.1 \times 10^{13} \exp(-26.5 \text{ kcal mol}^{-1}/RT)$	Adjusted ^{c)}

a) 1 kcal=4.184 kJ. b) Not used for the computation of the overall kinetics. c) Adjusted by fitting the calculated CN concentration profiles to the observed CN absorption curves.

TABLE 2. RATE DATA

m mol%	P_1 Torr	$U_s^{a)}$ mm/ μ s	$\rho_{21}^{b)}$	T K	$[Ar]_0$ 10^{-6} mol/cm ³	$[CN]_e$ 10^{-9} mol/cm ³	$x_e - y_e^{c)}$	k_1 cm ³ mol ⁻¹ s ⁻¹
0.200	18.9	1.67	3.60	2775	3.66	4.35	0.593	2.47×10^8
0.207	16.8	1.72	3.62	2920	3.29	5.81	0.851	7.03×10^8
0.206	13.5	1.82	3.66	3235	2.66	5.28	0.960	3.21×10^8
0.206	10.1	1.93	3.69	3610	2.02	4.16	0.998	1.44×10^{10}
0.498	30.1	1.56	3.55	2455	5.78	2.93	0.101	2.89×10^7
0.502	29.5	1.62	3.58	2625	5.73	7.69	0.266	8.84×10^7
0.501	12.0	1.69	3.61	2815	2.35	7.18	0.608	3.65×10^8
0.501	9.79	1.78	3.64	3100	1.92	8.92	0.921	1.78×10^9
0.498	9.05	1.80	3.65	3180	1.79	8.57	0.958	3.60×10^9
0.498	8.32	1.86	3.67	3385	1.65	8.12	0.981	5.44×10^9

a) Shock velocity. b) Density ratio across the shock front. c) $[CN]_e/[CF_3CN]_0$, Ref. 5.

substantiated as is shown in Fig. 1. The average value of β_{01} was found to be $(8.85 \pm 0.95) \times 10^6$ cm² mol⁻¹, in good agreement with the value $(9.16 \pm 0.76) \times 10^6$ cm² mol⁻¹ observed previously in the study of the dissociation equilibrium: $C_2N_2 \rightleftharpoons 2CN$.²⁾

Dissociation Rates of CF₃CN. With the β_{01} value at hand, we have determined the bimolecular rate constants k_1 from the initial slope of absorbance

$$r_0 = \{d \ln (I_0/I)/dt\}_0, \quad (4)$$

where t is the particle time. k_1 is obtained as

$$k_1 = r_0/\beta_{01} I_{ab}(T) [CF_3CN]_0 [Ar]_0, \quad (5)$$

where $[CF_3CN]_0$ and $[Ar]_0$ are the concentrations at zero time, *i.e.*, immediately behind the shock front. The values of k_1 obtained for some representative runs are given in Table 2, together with pertinent experimental data.

Figure 2 shows the Arrhenius plots of k_1 obtained for a total of 25 runs. A single straight line is seen to fit the plots, irrespective of the $[CF_3CN]_0/[Ar]_0$ ratio. Although the total gas pressure was not changed independently

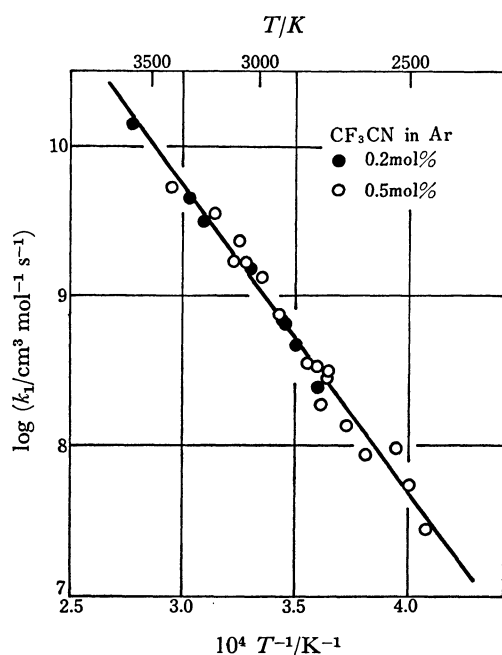


Fig. 2. Arrhenius plots of k_1 .

$$k_1 = 7.9 \times 10^{15} \exp(-94.0 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

of the reaction temperature, it is evident that the dissociation rate is proportional to $[Ar]_0$. Thus the reaction is indeed bimolecular under the experimental conditions adopted in this work. Least-squares treatment of the linearity has led to the Arrhenius expression

$$k_1 = (7.9 \pm 3.1) \times 10^{15} \times \exp[-(94.0 \pm 2.8) \text{ kcal mol}^{-1}/RT] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}. \quad (6)$$

Overall Decomposition Kinetics. The rate equations for the entire mechanism comprising Reactions 1–11 were subjected to numerical (Runge-Kutta-Gill) integration on a computer. The rate constants used for computation are listed in Table 1. The forward rate constants for Reactions 1, 2, 6, 8, and 10 were those determined experimentally.^{2,11,12)} The constant k_3 , when multiplied by $[Ar]_0$, was assumed to be equal to the first-order rate constant for the ethane decomposition in the high-pressure limit.¹³⁾ The preexponential factors for k_7 and k_9 were estimated from those observed for the dissociations of N_2F_4 ¹⁴⁾ and $BrCN$.⁵⁾ Entirely indeterminate at this stage are k_4 , k_5 , and k_{11} . Most likely, the preexponential factor for k_5 would be about the same as that for k_4 , and the activation parameter in k_5 would be nearly equal to the endothermicity of Reaction 5. It was decided to estimate k_4 and k_{11} by requiring the best overall fit of the calculated time-concentration profiles of CN radicals to the observed absorption curves. The rate constants for the reverse reactions were all calculated from those for the forward reactions and the equilibrium constants. The time step used for integration was 0.5 μ s.

Preliminary calculations showed that the rate constants k_3 , k_5 , k_7 , and k_8 exert virtually no effect on the CN concentration profiles. In what follows, therefore, we will ignore Reactions 3, 5, 7, and 8 throughout. The simplification is in line with the assumption of complete dissociations of C_2F_6 , C_2F_4 , and F_2 which has been invoked in the equilibrium considerations.

The time histories of the CN radical concentrations calculated for the cases of $T=3385$ and 2920 K are shown in Fig. 3. The full lines indicate the CN concentrations calculated for the entire mechanism (excluding Reactions 3, 5, 7, and 8), while the dashed lines show the concentrations which CN radicals would have if Reaction 1 were the only reaction to be considered.

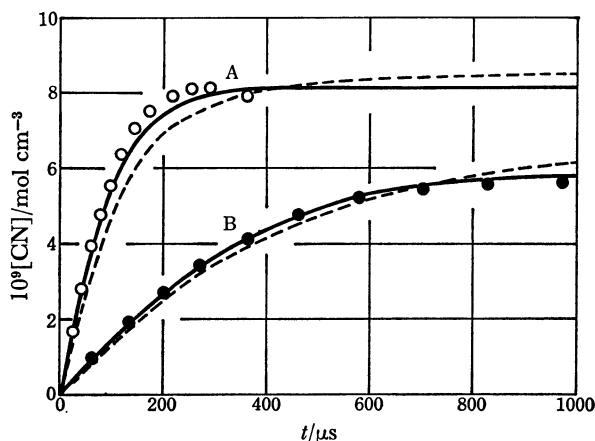


Fig. 3. Comparisons of the computed CN concentration profiles with the observed.

A: $T=3385$ K, $m=0.5$ mol%, $[\text{Ar}]_0=1.65 \times 10^{-6}$ mol/cm³;

B: $T=2920$ K, $m=0.2$ mol%, $[\text{Ar}]_0=3.29 \times 10^{-6}$ mol/cm³.

—: Computed with the rate constants given in Table 1;
 ---: Reaction 1 alone; ○, ●: experimental; t : particle time.

The experimental values of $[\text{CN}]$ read from the absorbance records are indicated with circles.

As a whole, the assumed mechanism with the rate constants given in Table 1 seems to be detailed enough to account for the observed time-concentration profiles of CN radicals. It has also been verified that the various reactions following the primary step 1 exert little influence on the initial slope. These results corroborate not only the adequacy of the assumed overall mechanism but also the legitimacy of the initial slope technique used to determine the k_1 values.

Discussion

In the computer tracing of the CN concentration profiles, the rate constants for the abstraction Reactions 4 and 11 were treated as the only adjustable parameters. The values for the Arrhenius A factors obtained for k_4 and k_{11} both appear to be reasonable; the A factors for abstractions by a radical are generally of the order of 10^{12} cm³ mol⁻¹ s⁻¹ while those for similar reactions of an atom are usually *ca.* 10^{14} cm³ mol⁻¹ s⁻¹.¹⁵⁾ Not much can be said, however, about the activation energies obtained.

The experimental activation energy $E_a=94.0$ kcal/mol found for the CF_3CN dissociation is apparently smaller than the bond dissociation energy $D_0=102.7$ kcal/mol. This can readily be accounted for in terms of the participation of the internal energy of CF_3CN to its dissociation.

The classical collision theory due to Fowler and Guggenheim¹⁶⁾ provides a semi-quantitative clue for understanding the above-stated situation. According to the theory, the rate constant for a bimolecular reaction is expressed as

$$k_1 = \lambda(Z/n!)(D_0/RT)^n \exp(-D_0/RT), \quad (7)$$

where n is the effective number of the internal degrees of freedom contributing to the activation process and where λ is a correction factor termed the "steric" factor. The temperature variation of the present experimental results, Eq. 6, is best fitted to that of Eq. 7, when n is assigned a value of 2. The least-squares fit of Eq. 7 with $n=2$ to the experimental k_1 values has led to the expression

$$k_1 = [4.30 \times 10^{12}/2] T^{1/2} (D_0/RT)^2 \exp(-D_0/RT) \quad \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \quad (8)$$

Assuming the CF_3CN -Ar collision diameter to be 0.42 nm, we get $\lambda=0.44$, a value which does not appear unreasonable.

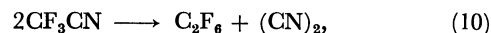
The Fowler-Guggenheim expression, Eq. 7 is formally equivalent to the low-pressure-limit form of the RRK theory for unimolecular reactions.¹⁷⁾ The theory permits a rough estimation of the "fall-off pressure"

$$P_{1/2} \approx \frac{\bar{\nu}}{\lambda Z} \left\{ 1 + \frac{D_0}{(n+1)RT} \right\}^{-n} RT, \quad (9)$$

where $\bar{\nu}$ is a mean frequency of the vibrations participating in the activation process. Taking $\bar{\nu}=10^{13}$ s⁻¹, $P_{1/2}$ for the CF_3CN dissociation was calculated to be 210 and 140 atm at 3000 and 2500 K, respectively. The dissociation in question is thus considered to be in the low-pressure limit under our experimental conditions.

It was not *a priori* obvious that the thermal dissociation of CF_3CN , a six-atom molecule, would exhibit the bimolecular behavior. Perhaps, the C-F bondings are rigid enough for the CF_3 group to be regarded as a pseudoatom. The value $n=2$ agrees closely with $n=1.5$ found for the case of BrCN ,⁵⁾ a triatomic molecule.

The conclusion that the CF_3CN dissociation is bimolecular in the ordinary pressure region is interesting in connection with the results reported by Perettie and Janz.¹⁸⁾ They investigated the thermal decomposition of pure CF_3CN by the flow method in the temperature range 684–809 K. The reaction obeyed a kinetics of second order in CF_3CN



with the bimolecular rate constant

$$k = 10^{14.7} \exp[-(64.7 \pm 3.0) \text{ kcal mol}^{-1}/RT] \quad \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \quad (11)$$

Although the conclusion that Reaction 10 is a concerted (one-step) process involving a four-centered cyclic activated complex may perhaps be still debatable, the observed kinetics certainly negates a dominance of the unimolecular decomposition of CF_3CN . Even if the concerted Process 10 is involved in our shock-wave kinetics, it is least significant in our reaction system in which CF_3CN was used in an extremely high dilution in argon as environment gas. At 2455 K, the lowest temperature studied, the rate of Reaction 10 should be only one-sixth that of Reaction 1.

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