Very Low-Pressure Pyrolysis (VLPP) of Alkyl Cyanides. I. The Thermal Unimolecular Reactions of Isopropyl Cyanide

Keith D. King* and Richard D. Goddard

Contribution from the Department of Chemical Engineering, University of Adelaide, Adelaide, South Australia 5001. *Received October 25, 1974*

Abstract: The unimolecular decomposition of isopropyl cyanide has been studied in the range of 1074–1253°K using the technique of very low-pressure pyrolysis (VLPP). The reaction proceeds via two pathways, C–C bond fission (1) and HCN elimination (2), with (1) being the major reaction by a factor of ca. 10, over the range. The data, analyzed by taking into account the mutual interaction of the two pathways in the fall-off region, are consistent with the high-pressure Arrhenius parameters given by $\log (k_1, \text{sec}^{-1}) = (15.7 \pm 0.3) - (79 \pm 2)/\theta$ and $\log (k_2, \text{sec}^{-1}) = (13.9 \pm 0.3) - (76.2 \pm 2)/\theta$, where $\theta = 2.303RT$ kcal/mol. The bond fission activation energy leads to $DH°[\mathrm{CH_3CH(CN)}\text{–}\mathrm{CH_3}] = 78.8 \pm 2$, $\Delta H_f°(\mathrm{CH_3\dot{C}HCN}, g) = 50.1 \pm 2.3$, and $DH°[\mathrm{CH_3CH(CN)}\text{–}\mathrm{H}] = 89.9 \pm 2.3$, all in kcal/mol at 298°K. The stabilization energy of the α-cyanoethyl radical has been found to be 5.1 ± 2.5 kcal/mol, in good agreement with previous estimates obtained from the pyrolyses of cyclopropyl and cyclobutyl cyanides. The activation energy for HCN elimination is in substantial agreement with an estimate based on the Benson–Haugen semi-ion pair theory. Comparison of the Arrhenius parameters for the two reactions, combined with the observations of other workers on the reaction of hydrogen atoms with alkyl cyanides, leads to the conclusion that free radical chain processes will make a significant contribution to HCN formation in the high-pressure region and this has been confirmed experimentally.

Few observations have been reported on the kinetics and mechanisms of pyrolysis of alkyl cyanides. A brief investigation of the products of pyrolysis of methyl and ethyl cyanides was carried out by Rabinovitch and Winkler in 1942.[1] A more detailed investigation of methyl cyanide pyrolysis has since been carried out by Asmus and Houser.[2] The reaction is complex, involving mixed first- and second-order kinetics. Ethyl and *tert*-butyl cyanides have been investigated by Hunt, Kerr, and Trotman-Dickenson[3] using the aniline carrier technique. In the case of ethyl cyanide, products relating to both HCN elimination and C–C bond fission were observed while for *tert*-butyl cyanide bond fission only was observed. Unfortunately the reported kinetic parameters seem to be subject to a good deal of uncertainty. For example, in the case of ethyl cyanide the Arrhenius A factor (10^{15} sec^{-1}) for HCN elimination is much too high for a reaction of this type[4] and the rate parameters for C–C bond fission, when coupled with the reaction thermochemistry, yield a relatively low value for the recombination rate constant for methyl plus cyanomethyl radicals.[5] Moreover, the bond fission parameters yield a value of ca. 12.5 kcal/mol[5] for the cyano stabilization energy, which differs significantly from recent determinations.[6,7] There were also appreciable yields of hydrogen whose origin could not be determined unambiguously. It has been suggested[5] that the reaction products from both compounds could arise from free radical induced decomposition.

More recently, Dastoor and Emovon[8] have observed HCN elimination from ethyl, isopropyl, and *tert*-butyl cyanides using a conventional flow system over the temperature range 803–943°K. The reactions appeared to be homogeneous and molecular with no indication of C–C bond fission. If the reactions are four-center eliminations with polar transition states similar to HX eliminations from alkyl halides[4] then the reported A factor for ethyl cyanide is reasonable but the values for isopropyl cyanide and *tert*-butyl cyanide are lower than expected (by more than a power of 10). In addition, the activation energies do not show the expected trend with α-methyl substitution (cf. alkyl halides[4,5]).

The overall picture for alkyl cyanide decompositions is far from satisfactory. The modes of decomposition and their relevant Arrhenius parameters are important for several reasons. (i) Activation energies for C–C bond fission will yield heats of formation and stabilization energies of cyanoalkyl radicals. These data should be of fundamental importance in the consideration of bonding and reactivity. (ii) The parameters for HCN elimination should provide an interesting comparison with HX elimination from alkyl halides and hence a further test of the Benson-Haugen semi-ion pair theory.[9] (iii) Fundamental kinetic data for alkyl cyanides should assist in the interpretation of the kinetics and mechanisms of pyrolysis of nitrile polymers.

We have embarked on a program to study the thermal unimolecular reactions of organic cyanides using mainly the technique of very low-pressure pyrolysis (VLPP).[7,10] An advantage of this technique is that free radical chain reactions can be eliminated. We have already reported on the pyrolysis of cyclobutyl cyanide[7] and the results of a study of isopropyl cyanide (IPCN) are now presented here.

Experimental Section

Materials. IPCN and vinyl cyanide (VCN), both from Koch-Light, were thoroughly degassed and distilled bulb-to-bulb in vacuo and checked for purity by mass spectrometry. Propylene (Matheson, C.P.) was degassed before use. Methane (Matheson, C.P.) and argon (C.I.G., high purity dry) were used directly.

Apparatus and Procedures. The basic principles of the VLPP technique and its application to the study of thermal unimolecular reactions have been well documented.[10] Our particular experimental system has been described in detail previously.[7] Essentially, the experimental method consists of allowing a steady-state flow of reactant (at rates of ca. 10^{14}–10^{17} molecules/sec) to pass through a thermostated quartz reactor under very low-pressure conditions (ca. 10^{-4}–10^{-3} Torr). In such an environment molecules undergo very few gas-phase collisions and energy transfer is predominantly via gas-wall collisions. Secondary reactions are eliminated or minimized and therefore the direct products of primary thermal excitation in unimolecular decomposition can be determined. Reactant and product gases effuse from the reactor into the ionization chamber of a quadrupole mass spectrometer for direct analysis.

Reactant gases are stored in large bulbs and leaked into the reactor via precision-bore capillaries. Flow rates are measured by monitoring the pressure drop per unit time in a calibrated volume.

A complete description of the triple-aperture reactor and its dimensions has been given previously.[7] The collision numbers are Z = 19,550, 2,140, and 246 for exit apertures of 1, 3.3, and 10 mm diameter respectively.

For the reaction

$$A \longrightarrow \text{products}$$

the unimolecular rate constant under VLPP conditions is given by

$$k_{\text{uni}} = k_e[f/(1 - f)] = k_e(I_A{}^0 - I_A)/I_A$$

where k_e is the rate constant for escape through the exit aperture, f is the fraction of reactant molecules decomposed, I_A is the mass spectral peak intensity of the reactant, and $I_A{}^0$ is the intensity in the absence of decomposition. k_e is calculated from the geometry of the reactor and the aperture; details have been given previously.[7,10b]

Results

In principle the primary processes of C–C bond fission

$$CH_3CHCNCH_3 \longrightarrow CH_3\dot{C}HCN + \dot{C}H_3 \qquad (1)$$

and HCN elimination

$$CH_3CHCNCH_3 \longrightarrow C_3H_6 + HCN \qquad (2)$$

must be anticipated for the thermal decomposition of IPCN. The α-cyanoethyl radical should undergo decomposition via H atom loss

$$CH_3\dot{C}HCN \longrightarrow CH_2{=\!=}CHCN + H \qquad (3)$$

with Arrhenius parameters similar to those for the analogous reaction of the isopropyl radical[5] but with E higher by ~6 kcal/mol due to the cyano stabilization energy.[6,7] Thus we estimate

$$\log (k_3, \text{sec}^{-1}) \simeq 14.3 - (47.3/\theta)$$

A limited experimental investigation[11] of reaction 3 has yielded data consistent with this estimate. RRK calculations[12] based on these parameters show that at the temperatures and pressures of the VLPP experiments all of the cyanoethyl radicals will decompose to VCN before leaving the reactor. This was confirmed by a careful interpretation of the product mass spectrum which indicated the presence of species entirely consistent with the occurrence of reactions 1 and 2 followed by reaction 3 going to completion.

Unimolecular rate constants were calculated from the expression

$$k_{\text{uni}} = k_e[\text{product}]/[\text{reactant}]$$

The product to reactant ratio was determined from the mass spectral peak intensities after the system had been calibrated by measuring I_P/I_R for known mixtures of product and reactant. IPCN was monitored at m/e = 68 amu. As a measure of C–C bond fission VCN was monitored at m/e = 53 amu and as a measure of HCN elimination propylene was monitored at m/e = 41 amu. Small corrections were made for contribution of IPCN to 53 and 41 amu. Argon was used as an internal standard for the measurement of total decomposition. It was monitored by the Ar^{2+} peak at m/e = 20 amu rather than the Ar^+ peak at m/e = 40 amu because of contributions of other compounds to the latter mass number.

The results are shown in Tables I and II. Experimental measurement of rate constants was limited to the 1-mm and 3.3-mm apertures (no decomposition was observed with the 10-mm aperture over the temperature range of the experiments). Under VLPP conditions C–C bond fission is clearly the major reaction. The yield of propylene was always small; it accounts for only ca. 10% of the overall decomposition. All of the data have been included in the tables but where the overall decomposition was less than ca. 20% the propylene yield was too small to be used in the calculation of rate constants. It should be kept firmly in mind that even though the percentage decomposition based on propylene is small, it is the directly measured ratio $[C_3H_6]/[IPCN]$, which determines k_{uni}.

Table I. VLPP Data for Isopropyl Cyanide (Z = 19,550, flow rate = 9.1×10^{14} molecules/sec)

	% decomposition			k_{uni}, sec^{-1}	
Temp, °K	IPCN decay	VCN formation	C_3H_6 formation	VCN	C_3H_6
1074[a]	5.2	4.3	(0.4)[d]	0.034	
1083[a]	7.9	5.8	(1.9)	0.049	
1094[a]	10.3	7.8	(2.7)	0.067	
1102[b]	9.7	7.0		0.058	
1105[a]	10.8	8.0	(1.0)	0.068	
1107[a]	10.4	9.6	(1.5)	0.084	
1112	12.2	9.4	(0.9)	0.082	
1117[b]	14.1	9.9	(0.4)	0.086	
1123[c]	16.0	11.7	(1.5)	0.105	
1132	19.0	14.9	(1.4)	0.140	
1145[c]	24.0	18.5	2.3	0.185	0.022
1149[a]	24.9	18.9	2.9	0.191	0.029
1156	28.8	22.8	2.8	0.243	0.030
1164[c]	31.9	25.4	2.6	0.28	0.029
1172	36.4	29.3	3.2	0.35	0.038
1186[c]	41.3	33.9	3.2	0.43	0.042
1192	44.8	37.0	3.9	0.50	0.053
1204[c]	50.5	41.3	3.9	0.61	0.058
1211	54.3	45.8	4.4	0.75	0.072
1225[c]	59.2	49.9	4.3	0.89	0.078
1232	63.3	54.4	4.9	1.10	0.099
1243[c]	66.3	56.5	5.1	1.21	0.109
1251	69.4	60.5	5.2	1.46	0.126

[a] Flow rate = 1×10^{15} molecules/sec. [b] Flow rate = 7.5×10^{14} molecules/sec. [c] Flow rate = 5.2×10^{14} molecules/sec. [d] Values in parentheses were not used in the calculation of rate constants.

Table II. VLPP Data for Isopropyl Cyanide (Z = 2140, flow rate = 1.2×10^{15} molecules/sec)

	% decomposition			k_{uni}, sec^{-1}
Temp, °K	IPCN decay	VCN formation	C_3H_6 formation	VCN
1199[a]	10.2	6.3	(0.5)[c]	0.49
1203	10.5	6.6	(0.5)	0.52
1206[b]	9.9	6.7	(0.1)	0.52
1221[a]	13.8	8.9	(1.4)	0.73
1222	13.4	9.4	(1.0)	0.77
1223[b]	14.3	10.2	(0.4)	0.84
1242	18.0	12.9	(1.1)	1.11
1251[b]	19.5	14.3	(0.8)	1.26
1253[a]	22.9	15.2	(4.4)	1.41
1253	20.7	15.1	(1.3)	1.34

[a] Flow rate = 5.4×10^{15} molecules/sec. [b] Flow rate = 7.1×10^{14} molecules/sec. [c] Values in parentheses were not used in the calculation of rate constants.

It can be seen that the formation of VCN and propylene does not quite account for the total disappearance of IPCN. However, the discrepancy is small and it does not show any significant trend. Visual inspection of the reactor revealed the formation of a light carbonaceous coating. This is probably the end result of the IPCN not accounted for and it raises the question of heterogeneous decomposition. We have checked the results by also monitoring the reactant and products at mass numbers different from those quoted above. When IPCN was monitored at 42 amu, VCN at 26 amu, and propylene at 39 amu, the results agreed, within experimental error, with those shown in Tables I and II. Moreover, the formation of VCN and propylene showed good reproducibility over a period of several months and the rate constants are independent of flow rate and reactor collision number. Also, during the course of the experiments air was admitted to the reactor on several occasions as a result of enforced maintenance to some of the apparatus and

Table III. Thermochemical Data

Species	ΔH_f° (298°K) kcal/mol	S°_{298}, cal °K^{-1} mol^{-1}	C_p°, cal °K^{-1} mol^{-1} 300	500	800	1000
i-C_3H_7CN[a]	5.4[b]	76.2	23.4	32.9	43.3	48.1
$\dot{C}H_3$[c]	34.1[d]	46.4	8.3	10.1	12.6	14.0
$CH_3\dot{C}HCN$	e	68.8	15.3	22.2	29.0	31.9
C_3H_6[a]	4.9	63.8	15.3	22.6	30.7	34.5
HCN[f]	32.3	48.2	8.6	10.0	11.3	12.2

[a] Reference 15. [b] Reference 16. [c] H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, 1, 221 (1969). [d] Reference 17. [e] See discussion. [f] JANAF Thermochemical Tables, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1970).

this was found to have no effect on the rate constants. Results obtained with a "fresh" reactor were the same as those obtained with an "aged" reactor. We conclude that reactions 1-3 are entirely homogeneous and any processes contributing to the formation of carbon must occur independently of these reactions.

Since under VLPP conditions unimolecular reactions are in the fall-off region the experimental rate constants must be treated according to RRK(M) theory[13] in order to determine A_∞ and E_∞. In this treatment a previous knowledge of either A_∞ or E_∞ is required; they cannot be determined independently. In general, A_∞ for unimolecular reactions can be estimated with considerable accuracy if the process is unambiguous[4,5] and the usual procedure in VLPP studies is to determine E_∞ from a fit of k_{uni} vs. T to a RRK(M) computed curve using an estimated A_∞. An appropriate transition-state model is postulated but the exact details are not important in determining the degree of fall-off.[13]

We have estimated $A_\infty(1100°\text{K}) = 10^{15.7}$ sec^{-1} for C-C bond fission in IPCN by considering the reverse reaction, the reaction thermochemistry, and A factors for analogous reactions as outlined below.

Benson and O'Neal[5] have analyzed a large number of unimolecular bond fission reactions and from this they recommend ranges of values for rate constants for the combination of various types of radicals. For the combination stabilized radical + radical they recommend log (k_r, M^{-1} sec^{-1}) = 8.4 ± 0.5. This should be a reasonable estimate for the combination $CH_3\dot{C}HCN + \dot{C}H_3$. Calculation of A_1 from k_{-1} and thermochemistry requires a knowledge of E_{-1}. Radical recombination rates and their temperature dependence are subject to some uncertainty and controversy, and there is currently a good deal of experimental activity in this area.[14] However, whatever the outcome of these investigations it does seem fairly conclusive that most radical combinations have activation energies close to zero at 300°K if not at higher temperatures. Thus if we take log $k_{-1} = 8.4 = A_{-1}$ at 300°K and combine it with log $[A_1(\text{sec}^{-1})/A_{-1}(M^{-1}\text{sec}^{-1})] = 6.96$ from thermochemical data (Table III) then log (A_1, sec^{-1}) = 15.4, which seems reasonable. Extrapolation to higher temperatures depends on the transition-state heat capacity which in turn depends on the chosen model.

Bond fission reactions resulting in the formation of resonance-stabilized radicals such as benzyl and allyl have lower A factors than their saturated counterparts.[5,18] This difference may be attributed to resonance stiffening of hindered rotations. In the case of alkyl cyanides and alkynes there are no rotational constraints because of the cylindrical symmetry of the triple bond. However, resonance should cause upward changes in low-frequency $C{-}C{\equiv}N$[7] or $C{-}C{\equiv}CH$ bends with resultant lower A factors than for alkanes. The alkyne analog of IPCN is 3-methyl-1-butyne but the only detailed experimental study of C-C bond fission in an alkyne is the shock tube work of Tsang on 4-methyl-1-pentyne.[19] The A factor is $10^{15.56}$ sec^{-1} at 1100°K which is $\sim 10^{0.6}$ sec^{-1} per path lower than for alkanes. The usual transition-state model for C-C bond fission is as follows:[20] the assignment of the C-C stretch in the breaking bond as the reaction coordinate, the lengthening of that bond with the barrier to internal rotation about it being reduced to zero, and the weakening of the four bending modes which are destined to become external rotations of the product radicals. If this sort of model is applied to alkanes ($A_\infty(1100°\text{K}) = 10^{16.2}$ sec^{-1} per reaction path[18b]), then we find that the appropriate four bending frequencies have to be lowered to ca. 30% of their molecular values. Extension of these calculations to 4-methyl-1-pentyne shows that the two $C{-}C{\equiv}CH$ bending frequencies have to be increased to ca. 140% of their molecular values in order to achieve agreement with the experimental A_∞. This result seems to be a reasonable consequence of the development of resonance in the transition state. If exactly the same model is now applied to IPCN, the calculated $A_\infty(1100°\text{K})$ is $10^{15.4}$ sec^{-1} per path or $10^{15.7}$ sec^{-1} overall. This model gives $A_\infty(300°\text{K}) = 10^{15.3}$ sec^{-1} which agrees very well with our estimate based on the reverse reaction and thermochemistry.

A four-center transition-state model was assumed for HCN elimination and the A factor was estimated according to the method of O'Neal and Benson.[4,17] The value obtained is (including reaction path degeneracy) $10^{13.9}$ sec^{-1} at 1100°K or $10^{13.7}$ sec^{-1} at 600°K which is about the same as experimental and theoretical values for HX elimination from isopropyl-X where X is halogen.[4]

Details of the frequency assignments for the molecule and the activated complexes are given in the Appendix.

When a reactant decomposes by competing unimolecular paths in the fall-off region, energized molecules are depleted by all reaction paths and each path feels the effect of the drain on energized molecules of other paths. The usual unimolecular rate theory expression for k_{uni} has to be modified to take into account this interaction among reaction paths. This has been done previously for the system of two competitive reaction paths and full details are given in ref 10b. The modification was applied to RRK theory and the procedure is called the RRK/2 method. (It has been shown that RRK (using $s \equiv C_{\text{vib}}(T)/R$) and RRKM theory give substantially the same result for fall-off calculations for thermally activated systems.[10b,21])

We have treated the data for IPCN pyrolysis according to the RRK/2 method and the results are shown in Figure 1. Also shown are the lines computed using RRK and RRKM theory.

Using initial estimates for $E_\infty(1)$ and $E_\infty(2)$ we found that the minor reaction path, HCN elimination, had little effect on the major process of C-C bond fission. Reasonable variations in $E_\infty(2)$ did not alter the RRK/2 computed curve for reaction 1. It can be seen from Figure 1 that for this reaction, RRK and RRK/2 calculations give identical results and, as expected, RRKM calculations are little different. Thus we were able to use RRK(M) theory on reaction 1 alone to determine $E_\infty(1)$ and then use the RRK/2 method to determine $E_\infty(2)$. The effect of C-C bond fission on HCN elimination is quite dramatic. Interaction of the competitive paths causes the rate constants for the latter to be depressed by a factor of ~ 3 below the values predicted on the basis of no interaction.

The estimated A factors used herein are probably accurate to ca. $10^{\pm 0.3}$ sec^{-1}. Changes in A_∞ of this amount require changes in E_∞ of ca. ±1 kcal/mol for both reactions. The scatter of the measured rate constants with fixed A factors allows for further errors of ca. ±1 kcal/mol. Thus the data are in accord with high-pressure rate constants given by log $k_1(1100°K) = (15.7 \pm 0.3) - (79 \pm 2)/\theta$ and log $k_2(1100°K) = (13.9 \pm 0.3) - (76.2 \pm 2)/\theta$, where k is in sec^{-1}.

Discussion

The reaction scheme of concurrent C-C bond fission and HCN elimination has been established for VLPP conditions. Over the temperature range 1074-1253°K bond fission is the major reaction by a factor of ca. 10, caused in part by the interaction of the competitive paths in the energy-dependent region.

C-C Bond Fission. The chosen transition-state model produces little change in Arrhenius parameters with temperature ($E_\infty(298°K) = 78.2$ kcal/mol)[22] and if it is assumed that the activation energy of the reverse radical combination reaction is zero at 298°K, when the rate constant is measured in molar concentration units, then

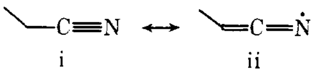
$$\Delta H^\circ_{298} = E_\infty(298\,°K) + RT = 78.8 \pm 2 \text{ kcal/mol}$$

which is equivalent to the C-C bond dissociation energy. Combining this value with the known values (including error limits) of the heats of formation of IPCN and $\dot{C}H_3$ (see Table III) yields $\Delta H_f°(CH_3\dot{C}HCN, g) = 50.1 \pm 2.3$ kcal/mol. Since the heats of formation of H (52.1 kcal/mol)[17] and ethyl cyanide (12.3 ± 0.13 kcal/mol)[16] are known, we can thus compute

$$DH^\circ_{298}[CH_3CH(CN){-}H] = 89.9 \pm 2.3 \text{ kcal/mol}$$

Comparison of this value with the secondary C-H bond strength in propane (95 ± 1 kcal/mol)[23] yields a value of 5.1 ± 2.5 kcal/mol for the stabilization energy of the α-cyanoethyl radical. This result agrees very well with our previous determination of 6 ± 1 kcal/mol based on the VLPP of cyclobutyl cyanide and the value of 7.2 kcal/mol obtained by Luckraft and Robinson[6a] from the pyrolysis of cyclopropyl cyanide.

In terms of valence-bond theory, resonance stabilization in radicals is due to simple delocalization of the unpaired electron and experimental evidence for its occurrence in α-cyano radicals was first noted by Talât-Erben and Bywater[24] who observed the formation of the keteneimine dimer from the recombination of 2-cyanoisopropyl radicals. The two contributing canonical forms of the α-cyanoethyl radical are



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The relative thermodynamic stabilities of these structures may be determined from a comparison of the C=C π-bond energy in the keteneimine with the C≡N π-bond energy in the cyanide. The lack of thermochemical and bond energy data for imines prevents calculation of these π-bond energies but rough estimates[25] indicate that ii is considerably less stable than i. Thus it is not surprising that the stabilization energy of the α-cyanoethyl radical is ~7.4 kcal/mol less than that of the methylallyl radical[23] since the contributing canonical forms of the latter are structurally similar and therefore of very similar energies.

The heat of formation of the α-cyanoethyl radical enables us to calculate $\Delta H_3°$, the enthalpy of its decomposition to VCN. Using $\Delta H_f°(VCN) = 43$ kcal/mol[16] yields $\Delta H_3° = 45$ kcal/mol. This value is also the difference between $DH°[\beta\ C{-}H]$ and the C=C π-bond energy in VCN. Assuming $DH°[\beta\ C{-}H] = DH°(C_2H_5{-}H) = 98$ kcal/mol, then $DH_\pi°(CH_2{=}CHCN) = 53$ kcal/mol which is 6.3 kcal/mol less than $DH_\pi°(CH_2{=}CH_2)$.[26] Thus the CN group reduces $DH_\pi°(C{=}C)$ by about the same amount as its effect on the monoradical. This result agrees with the calculations of Egger and Cocks[26] on the effect of substituents on $DH_\pi°(C{=}C)$.

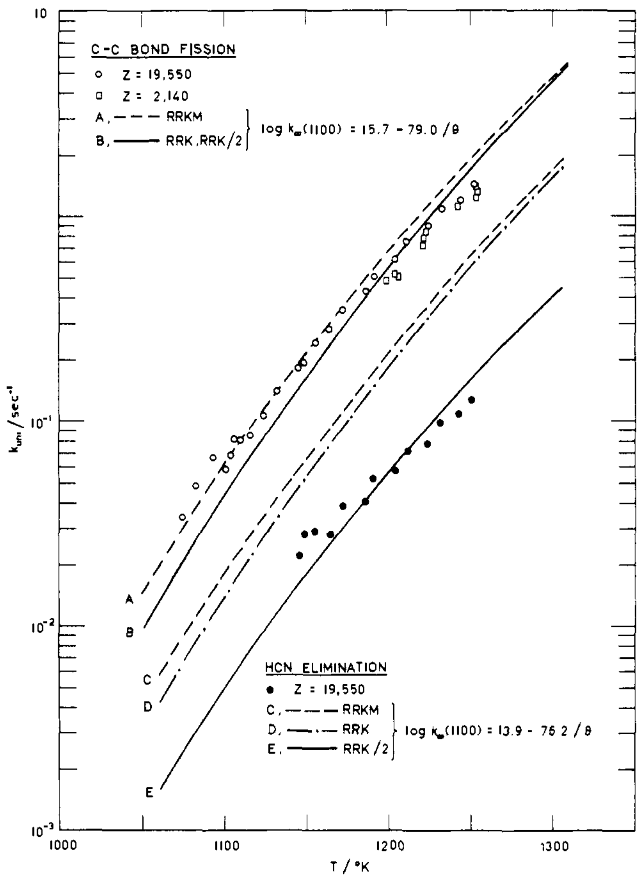

Figure 1. k_{uni} as a function of T for the decomposition of isopropyl cyanide.

The Arrhenius expression for C-C bond fission may be used in conjunction with the thermochemical data in Table III to compute log $(k_{-1}, M^{-1}\ sec^{-1}) = 9.2$ for the cross combination of methyl and cyanoethyl radicals which, in turn, yields log $(k_r, M^{-1}\ sec^{-1}) = 7.4$ for the recombination of cyanoethyl radicals (assuming the geometric mean rule and taking log $(k, M^{-1}\ sec^{-1}) = 10.4$ for the recombination of methyl radicals[27]); both results seem reasonable.

HCN Elimination. The Arrhenius parameters derived from VLPP data may be compared with log $(k, sec^{-1}) = 12.2 - (64.14/\theta)$ determined by Dastoor and Emovon (DE).[8] As mentioned previously, DE's A factor is clearly too low for a four-center molecular elimination. (It is worth noting that in a similar study of the pyrolysis of alkyl fluorides[28] DE again obtained low A factors.) If the reported rate constant at the mid-temperature of their study is combined with our predicted A factor, then $E = 70.9$ kcal/mol which is closer to our VLPP estimate than their original value.

The data of DE are shown plotted in Figure 2 along with the line corresponding to the parameters from our work ($A = 10^{13.9}$ sec^{-1}, $E = 76.2$ kcal/mol). Also shown is the line corresponding to $A = 10^{15.7}$ sec^{-1}, $E = 79$ kcal/mol, the parameters for C-C bond fission. It can be seen that our parameters indicate HCN elimination cannot compete with C-C bond fission over the temperature range of DE's study. Free radical chain processes then should be considered seriously in the interpretation of their experimental data.

DE argued that HCN is formed by a molecular mechanism because $DH°(C{-}CN)$ is too large to allow participation of the CN radical in the reaction scheme. We would suggest that HCN may be formed by the reaction of H atoms with IPCN. Several workers[29] have shown that H atoms react rapidly with CH_3CN and C_2H_5CN to form mainly HCN with very little accompanying H abstraction.

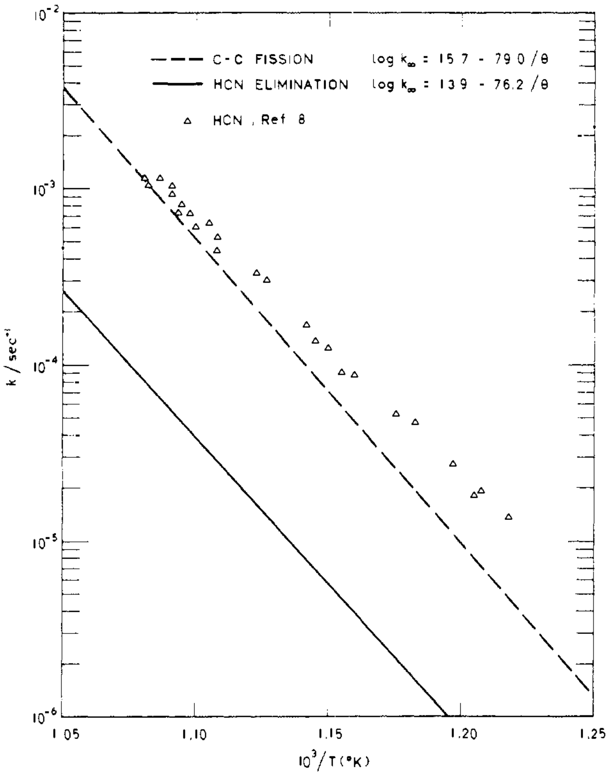

Figure 2. Arrhenius plot for the decomposition of isopropyl cyanide: — and - - - parameters from this work; the data points are from ref 8.

Thus HCN and propylene may be formed in equimolar quantities from IPCN via the chain propagation steps

$$\mathrm{H + CH_3CHCNCH_3 \longrightarrow HCN + CH_3\dot{C}HCH_3} \quad (4)$$

$$\mathrm{CH_3\dot{C}HCH_3 \longrightarrow C_3H_6 + H} \quad (5)$$

DE found that the rate of formation of HCN was not affected by the presence of toluene and this result was used as support for their arguments in favor of a molecular reaction. In order to check these observations and to test our suggestion of a substantial contribution from H-atom chains we have also carried out some experiments on the pyrolysis of IPCN both in the absence and presence of toluene using a conventional stirred flow system. A detailed product analysis was not carried out but VCN, EtCN, CH_4, C_3H_6, and HCN were observed to be the major reaction products over the temperature range 873-973°K. Both VCN and EtCN were formed always in greater quantities than C_3H_6 and the VCN/EtCN ratio was found to be a function of both the relative concentration of toluene and the temperature, probably as a result of competition between the reactions

$$\mathrm{CH_3\dot{C}HCN + PhCH_3 \longrightarrow CH_3CH_2CN + Ph\dot{C}H_2}$$

$$\mathrm{CH_3\dot{C}HCN \longrightarrow C_2H_3CN + H}$$

The yield of C_3H_6 was affected quite markedly by the presence of toluene. In two series of experiments carried out at 903 and 927°K the rate of formation of C_3H_6 was determined for $[PhCH_3]_0/[IPCN]_0$ ratios up to ~15. Over this range of inhibitor the rate declined by a factor of ca. 50 and it was not clear that a limiting value had been reached. (In any case, the maximally inhibited reaction is not necessarily molecular, especially at these temperatures.[5]) In view of the above observations and the parameters illustrated in Figure 2, we find it difficult to understand why DE did not observe products relating to C-C bond fission.

It becomes legitimate to raise the question of the possibility of reaction 4 occurring under VLPP conditions as well.

Table IV. Molecular Parameters for Isopropyl Cyanide Pyrolysis

	Molecule	Complex (C–C)	Complex (–HCN)
Frequencies (cm⁻¹) and degeneracies	2950 (7)	2950 (7)	2950 (6)
	2255 (1)	2255 (1)	2230 (2)
	1440 (6)	1440 (6)	1440 (6)
	1310 (2)	1310 (2)	1310 (2)
	1110 (3)	1140 (2)	1140 (2)
	925 (2)	932 (1)	933 (2)
	754 (2)	738 (1)	770 (1)
	500 (2)	490 (1)	660 (1)
	355 (1)	300 (3)	510 (1)
	220 (3)	243 (1)	369 (3)
	175 (1)	220 (1)	220 (1)
		153 (1)	158 (1)
		107 (1)	126 (1)
$I_AI_BI_C$, (g cm²)³ × 10¹¹⁴	6.23	15.6	15.9
I_r, g cm² × 10⁴⁰		5.34[a]	
Sigma[b]	1.0	0.5	1.0
Collision diameter, Å	5.5[c]		
$S°_{300}$, cal °K⁻¹ mol⁻¹	76.2	85.6	77.8

[a] Using symmetry ≡ "foldness" of barrier = 3. [b] Sigma = σ/n, where σ is the symmetry number for external rotation and n is the number of optical isomers. [c] Assumed equal to that for n-propyl cyanide: S. C. Chan, J. T. Bryant, L. D. Spicer, and B. S. Rabinovitch, *J. Phys. Chem.*, 74, 2058 (1970).

However, this second-order reaction has to compete with two first-order loss processes for H atoms, namely escape through the reactor aperture and recombination at the walls which is a very rapid process, particularly on quartz.[30] Because of the nature of VLPP the latter is likely to be the dominant path for removal of H atoms. The observations that the decomposition of IPCN is independent of aperture size and flow rate confirms the unimolecularity of the reactions studied.

E_2 may be calculated theoretically by using the Benson-Haugen semi-ion pair theory[9] to calculate the activation energy for the four-center addition of HCN to the propylene double bond and adding the endothermicity of the elimination reaction. The activation energy calculated in this way (see Appendix) is 74.0 kcal/mol at 298°K which is fairly close to our experimental value (75.3 kcal/mol at 300°K). However, there are some problems involved with this calculation. We have treated the HCN molecule as a pseudo-diatomic, which may be an oversimplification. Treatment of HCN as a triatomic, however, raises the question of its configuration in the transition state; it may not be linear. In the smooth transition from reactant to products the "extra" reorganizational energy involved, either about the C—C≡N angle (HCN linear) or the H—C≡N angle (HCN bent), may require some modification to the Benson-Haugen calculation.

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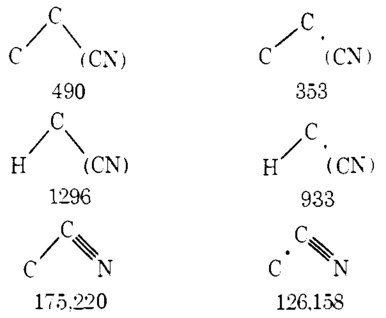
Appendix

Molecular and Activated Complex Models. Table IV shows the molecular parameters used to make the RRK(M) calculations. The frequencies listed are averaged and rounded.

Frequency assignments for the molecule were based on the results of Klaboe[31] and Durig et al.[32] The moments of inertia, which were calculated using normal bond lengths and angles, agree with the results of Durig and Li.[33] The calculated molecular entropy at 300°K agrees with that predicted from group additivity.[15]

For C-C bond fission the C-C stretch at 769 cm^{-1} was taken as the reaction coordinate, the rotational barrier about this bond was reduced to zero, and the frequencies of two methyl rocks (1068, 916 cm^{-1}), one C-C-C bend (510 cm^{-1}) and one C-C-(CN) bend (355 cm^{-1}), were lowered to 30% of their molecular values. In addition, two C—C≡N bends (175, 220 cm^{-1}) were increased to 140% of their molecular values. The moments of inertia were calculated using the same distances and angles in the molecule except that the breaking C-C bond was lengthened by 1 to 2.54 Å.

A four-center transition-state model was assumed for HCN elimination and the distances and angles were determined according to the method of Benson and Haugen.[9] The frequency assignment for the transition state was made by following the procedure of Benson and O'Neal.[4,17] Frequencies (cm^{-1}) not listed by Benson and O'Neal are as follows:



The transition-state frequencies are ~72% of their molecular values, in line with other estimates.[4,17]

The Activation Energy for HCN Elimination. The activation energy for the four-center Markovnikov addition of HCN to propylene was calculated using the Benson-Haugen semi-ion pair theory[9] by treating the HCN molecule as a pseudo-diatomic with bond length equal to the H-N distance in the molecule (2.226 Å).[34] The polarizabilities of HCN ($\alpha^0_{\text{mean}} = 2.50$ Å^3, $\alpha_l = 3.92$ Å^3) were taken from Landolt-Bornstein[35] and the dipole moment ($\mu = 3.00$ D) was obtained from the tables of Bhattacharya and Gordy.[36] Other data for the calculation were taken from Benson and Haugen's papers.

The equilibrium distance between the dipole centers in the reacting bonds was calculated to be 2.193 Å and, using $\alpha_{\text{mean}}(CN^-)/\alpha_{\text{mean}}(HCN) = 1.29$, the average value between the ground and transition states of the longitudinal polarizability of HCN, $\alpha_l^{\ddagger}(HCN)$, was calculated to be 4.20 Å^3 by following the method outlined in ref 9b. These results lead to values of 68.1 kcal/mol for the energy necessary to polarize the HCN molecule and 21.7 kcal/mol for the equilibrium electrostatic interaction energy of the dipoles. These values, when combined with 9.9 kcal/mol for the polarization energy of the propylene double bond[9] and 16.4 kcal/mol for the ground state polarization energy of HCN (obtained from μ and α^0_{mean}), lead to $E_{\text{act}}(0°\text{K}) =$ 39.9 kcal/mol. Inclusion of the change in thermal energy content of the reactants upon activation leads to $E_{\text{act}}(298°\text{K}) = 42.2$ kcal/mol. The endothermicity of the reaction is 31.8 kcal/mol (Table III); thus $E_2(298°\text{K}) =$ 74.0 kcal/mol for HCN elimination.

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