

Pyrolysis of Propionitrile and the Resonance Stabilisation Energy of the Cyanomethyl Radical

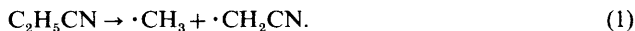
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The pyrolysis of propionitrile has been studied at seven temperatures over the range 789–850 K and pressures between 10 and 100 Torr.† Under these conditions the principal reaction products which are formed by essentially homogeneous processes are hydrogen, hydrogen cyanide, methane, ethane, ethene, acetonitrile and acrylonitrile. For short reaction times (< 3% conversion) the products are formed at rates which do not vary noticeably with reaction time.

A free radical chain mechanism has been proposed which accounts for all the above products. The chain initiating step is the reaction



Measurements of the rate of formation of methane in the subsequent reaction



yield the rate expression

$$\log_{10}(k_1/\text{s}^{-1}) = (15.5 \pm 0.3) - (78\,700 \pm 950)/\theta$$

where $\theta = 2.303RT/\text{cal mol}^{-1}$.‡ The activation energy leads to $D(\text{H}_3\text{C}-\text{CH}_2\text{CN}) = 80.4 \pm 1 \text{ kcal mol}^{-1}$ and a resonance energy of $5.4 \pm 1.4 \text{ kcal mol}^{-1}$ for the cyanomethyl radical.

Propionitrile is an unsaturated molecule with a methyl group attached to a carbon atom in the β -position relative to the multiple bond; thus, as with but-1-ene and its derivatives,¹ the pyrolysis of this compound would be expected to yield methane by a splitting of the terminal C—C bond, followed by hydrogen abstraction by the methyl radical thereby produced. Measurement of the methane formed should therefore yield a value for the heat of formation of the cyanomethyl radical and its resonance stabilisation energy.

Only one detailed investigation of the dissociation of propionitrile has been reported,² and this involved the use of the aniline carrier technique. An activation energy of $72.7 \text{ kcal mol}^{-1}$ was obtained for the dissociation reaction from which $\Delta H_f^\ominus(\cdot\text{CH}_2\text{CN}) = 52.2 \text{ kcal mol}^{-1}$. A higher value of $58.5 \text{ kcal mol}^{-1}$ was obtained more recently³ for the heat of formation of the cyanomethyl radical from the very-low-pressure pyrolysis of *n*-butyronitrile. Other bond dissociation energies obtained by the aniline carrier technique have been found¹ to be on the low side as a result of the pressure dependence of the experimental activation energy at the low pressures of reactant used in this technique. An analogous explanation seems appropriate for the discrepancy in the two values for the heat of formation of the cyanomethyl radical quoted above.

† 1 Torr = 101 325/760 Pa.

‡ 1 cal = 4.18 J.

Information on the overall mechanism of decomposition of propionitrile is limited and conflicting.⁴ On the one hand, evidence has been put forward⁵ to support a molecular elimination reaction yielding hydrogen cyanide and ethene as the only products, and, on the other, a free radical chain mechanism has been proposed^{3, 6} yielding a variety of products.

Although the main objective of the work described herein was to obtain a reliable value for the heat of formation of the cyanomethyl radical and hence its resonance stabilisation energy, the overall decomposition of propionitrile has been studied in more detail than hitherto.

EXPERIMENTAL

MATERIALS

Propionitrile (Aldrich Chemical Co.) of 99% purity was doubly distilled, head and tail fractions being rejected in each distillation. The middle cut of the second distillation, b.p. 97.7 °C at 764 Torr (literature value⁷ 97.35 °C at 760 Torr), was transferred to the vacuum system and outgassed by repeated freezing at 147 K and pumping. After this treatment the only impurities present, detected by gas-chromatographic analysis, were 0.04% acetonitrile and 0.01% propene. Nitric oxide (B.D.H.) of 99% purity and carbon dioxide (B.D.H.) of 99.995% purity were transferred to the vacuum system and, after repeated freezing at 77 K and pumping, were kept in storage bulbs.

APPARATUS AND PROCEDURE

The apparatus was essentially the same as that described earlier⁸ with the exception that for the packed reaction vessel $s/v = 5.3 \text{ cm}^{-1}$ rather than the value of 4.9 cm^{-1} as previously stated. Reaction products were transferred through traps at 147 and 77 K to the Töpler–McLeod gauge. After measuring the total volume of non-condensable products the methane present together with some ethene and ethane were analysed by gas chromatography using a 1 m silica-gel column at 50 °C. Hydrogen, which was shown by mass spectrometry to be present in the non-condensable fraction, was determined by difference. The fraction collected in the traps at 77 K contained the bulk of the ethene and ethane formed together with any propene produced and some hydrogen cyanide. This fraction was also analysed using the 1 m silica-gel column at 50 °C, although under these conditions HCN was irreversibly absorbed on the column. The final fraction held in the trap at 147 K contained unchanged reactant together with acetonitrile and acrylonitrile and some hydrogen cyanide. Gas-chromatographic analysis of this fraction was effected using a 1 m column of Poropak R at 175 °C.

Some estimates of the yields of hydrogen cyanide were made by collecting in a trap at 77 K, into which 1–2 cm³ of water had been placed, all the condensable products from 5 or 6 repeated runs. After allowing the contents of the trap to warm to room temperature, the hydrogen cyanide present in the aqueous solution was estimated by titration with silver nitrate.⁹

RESULTS

Propionitrile decomposes at temperatures in the range 789–850 K to yield hydrogen, methane, ethene, ethane, acrylonitrile, acetonitrile and hydrogen cyanide. For up to 3% decomposition, product against time data were found to lie on straight lines passing through the origin. Acetonitrile was the one exception to this behaviour in that the graphs, which were again linear, invariably had a small intercept with the ordinate due to the trace of this compound present as an impurity in the starting material. Thus all the products listed above may be concluded to be primary products whose initial rates of formation are given by the slopes of the linear graphs. Typical sets of product against time data are shown in fig. 1, which are for the pyrolysis of 50 Torr of propionitrile at 829.5 K.

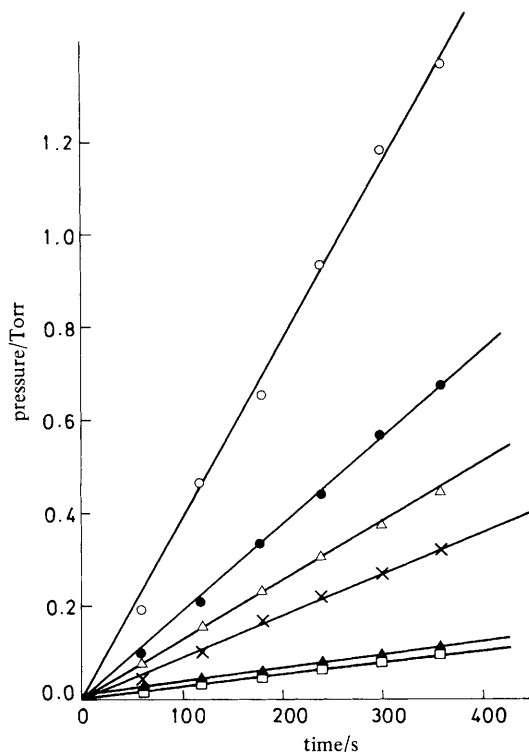


Fig. 1. Products of pyrolysis of 51 Torr propionitrile at 829.5 K: ○, CH₂CHCN; ●, C₂H₆; △, H₂; ×, C₂H₄; ▲, CH₃CN; □, CH₄.

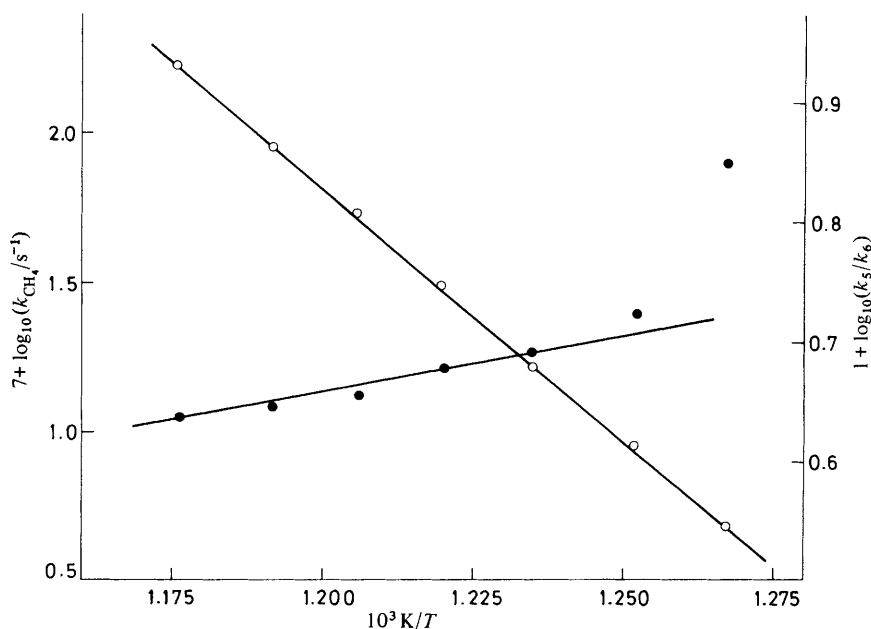
At the highest temperature studied (850 K) a few experiments were performed for longer heating times leading to *ca.* 10% decomposition. Under these conditions there appears to be some slight enhancement of the yields of acrylonitrile, hydrogen and ethene, presumably as a result of secondary reactions. In addition to the products already mentioned, small amounts of propene and also an unidentified C₆ compound were detected among the products obtained from pyrolysis of propionitrile at 850 K. Propene appears to be formed only in secondary reactions since its rate of formation increases with time from a negligible initial value. The C₆ compound could be a chain-terminating product.

Over the temperature range studied, pressure changes in the reaction vessel during the course of any run were negligible for initial pressures of 50 Torr and below, but for initial pressures of 90 Torr there was invariably a noticeable decrease in pressure with reaction time. Thus at all pressures, in addition to decomposition, some polymerisation must be occurring although this is insignificant at pressures < 50 Torr.

Experiments were performed at seven different temperatures over the range 789–850 K and pressures between 10 and 100 Torr. The values which are listed in table 1 for the initial rates of formation of the various products correspond to the mean of yield against time data; standard deviations were never more than ±10% and were generally around ±6%. (Rates of formation of acetonitrile were obtained from least-squares calculations of the slopes of the graphs.)

Table 1. Rates of formation of the products of pyrolysis of propionitrile

| <i>T</i> /K | initial pressure of C_2H_5CN /Torr | rate of formation of products/ 10^{-5} Torr s^{-1} | | | | | | |
|--------------------|--|--|----------|----------|----------|-------|------------|-------|
| | | CH_4 | CH_3CN | C_2H_4 | C_2H_6 | H_2 | CH_2CHCN | HCN |
| 789 | 12.3 | — | — | — | — | — | 6.7 | — |
| 789 | 25.3 | 1.12 | — | 1.26 | 5.60 | 5.0 | 12.3 | — |
| 789 | 51.2 | 2.30 | — | 2.45 | 10.6 | 10.2 | 25.6 | 14.3 |
| 789 | 92.4 | — | — | — | — | — | 40.9 | — |
| 789 | 24.8 + 0.9 NO | 1.08 | — | 0.71 | 3.10 | 2.3 | 7.6 | — |
| 789 | 24.2 + 500 CO_2 | 1.20 | — | — | — | 6.6 | 18.2 | — |
| 799 | 50.5 | 4.56 | — | 6.42 | 22.1 | 14.8 | 60.1 | — |
| 809.5 | 50.5 | 8.18 | 7.43 | 17.0 | 47.2 | 31.5 | 104 | — |
| 819.5 | 12.9 | 3.57 | — | 15.7 | 23.4 | — | — | — |
| 819.5 | 25.9 | 7.86 | — | 27.9 | 51.5 | — | — | — |
| 819.5 | 50.9 | 16.1 | 14.8 | 38.2 | 86.6 | 61.6 | 207 | — |
| 819.5 | 90.6 | 26.6 | — | 47.4 | 142 | — | — | — |
| 819.5 ^a | 51.1 | 17.0 | 16.2 | 31.1 | 77.2 | 86.5 | 190 | — |
| 829.5 | 51.1 | 27.4 | 28.0 | 90.3 | 186 | 125 | 380 | — |
| 839 | 51.5 | 45.7 | 47.6 | 169 | 304 | 207 | 707 | — |
| 850 | 51.1 | 88.1 | 91.5 | 341 | 512 | 375 | 1265 | — |

^a Packed reaction vessel.**Fig. 2.** Graphs of $\log_{10}(k_{CH_4}/s^{-1})$ against $1/T$ (○) and of $\log_{10}(k_5/k_6)$ against $1/T$ (●).

A double logarithmic plot of rate of formation of methane against pressure yielded a straight line of slope 1.04 ± 0.04 . The observation that addition of a twenty-fold excess of the inert gas carbon dioxide to 25 Torr propionitrile led to an increase of only 7% in the rate of formation of methane at 789 K supports the view that methane formation is by a process which is close to first order. From the appropriate Arrhenius plot shown in fig. 2 the first-order rate coefficient for methane formation was found to be given by the expression

$$\log_{10}(k_{\text{CH}_4}/\text{s}^{-1}) = (15.5 \pm 0.3) - (78700 \pm 1000)/\theta$$

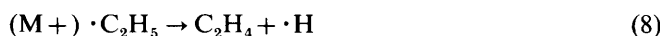
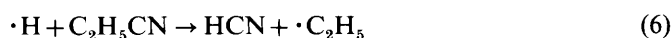
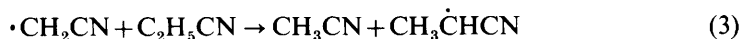
where $\theta = 2.303 RT/\text{cal K}^{-1} \text{mol}^{-1}$.

The effect of a change of the s/v ratio on reaction rates was investigated by pyrolysis of 50 Torr propionitrile in the packed reaction vessel at 819.5 K. The results, which are included in table 1, indicate that a seven-fold increase in s/v leads to an increase in the rate of formation of hydrogen (*ca.* 40%) and at the same time rates of formation of ethane, ethene and acrylonitrile decrease slightly (*ca.* 10%), whilst rates of formation of other products are virtually unchanged.

Finally, the pyrolysis at 789 K of 25 Torr propionitrile with 0.9 Torr nitric oxide was investigated. The results show a small decrease (*ca.* 4%) in the rate of formation of methane as compared with that from propionitrile alone. With hydrogen, ethane, ethene and acrylonitrile, on the other hand, more significant decreases (*ca.* 40%) in rates of formation were observed.

DISCUSSION

The variety of primary products of pyrolysis of propionitrile strongly supports the view proposed earlier^{3, 6} that the thermal decomposition of this compound occurs by a free radical chain mechanism. Although the inhibiting effect of nitric oxide does not provide conclusive evidence for a free radical chain mechanism, it does show that such a process is probable. The following reaction scheme is proposed since it accounts for all observed primary products and provides a rationale for the various changes in rate of formation with pressure:



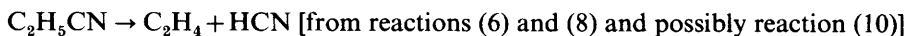
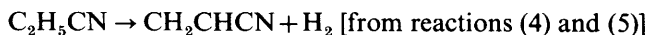
The above reaction mechanism is an extension of that already proposed,³ reactions (3), (5) and (7) being added to account for the products acetonitrile, hydrogen and ethane, respectively, and reaction (9) is considered to be the most likely chain-

terminating step although others are clearly possible. The four-centred molecular elimination process



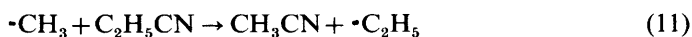
should perhaps be added, although available evidence suggests that amounts of ethene and hydrogen cyanide formed by this route must be comparatively small. Thus it is seen from table 1 that in the presence of nitric oxide the yields of ethene and of ethane are both *ca.* 55% of those for the uninhibited reaction, a situation which would not pertain if an appreciable proportion of the ethene formed came from reaction (10). From the proposed chain mechanism alone we have $d[\text{C}_2\text{H}_6]/d[\text{C}_2\text{H}_4] = k_7[\text{C}_2\text{H}_5\text{CN}]/k_8$. A rough estimate of this ratio may be obtained by assuming first that the Arrhenius parameters for k_7 are the same as those reported for the analogous reaction with methyl radicals,¹⁰ *i.e.* $\log_{10}(k_7/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 8.6 - 8600/\theta$, the limiting high-pressure rate constant for reaction (8) is given by¹¹ $\log_{10}(k_8/\text{s}^{-1}) = 14.4 - 40900/\theta$, and assuming secondly that in this reaction ethane and propionitrile have similar third-body efficiencies [the data of Loucks and Laidler¹¹ yield for a pressure of 50 Torr propionitrile $k_8/(k_8)_\infty = 0.2$]. Thus we obtain an estimate of $d[\text{C}_2\text{H}_6]/d[\text{C}_2\text{H}_4] = 6.4$ which compares reasonably with the experimental value of 4.3 at 789 K, the difference being well within the error limits of the calculation. The slightly lower experimental value does not, however, rule out the possibility that *ca.* 25% of the ethene formed could result from the molecular process (10).

The alternative modes of reaction of atomic hydrogen with propionitrile, *i.e.* reactions (5) and (6), and the alternative fates of the ethyl radical through reactions (7) and (8) means that the chain process involving reactions (4)–(8) cannot satisfactorily be represented by a single equation and that the overall process involves the sum of three separate steps, *viz.*



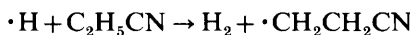
Thus $-d[\text{C}_2\text{H}_5\text{CN}]/dt = 2d[\text{C}_2\text{H}_6]/dt + d[\text{C}_2\text{H}_4]/dt + d[\text{H}_2]/dt$. The results obtained from experiments at 850 K yield $-d[\text{C}_2\text{H}_5\text{CN}]/dt = 1652 \times 10^{-5} \text{ Torr s}^{-1}$, in satisfactory agreement with the figure of $1740 \times 10^{-5} \text{ Torr s}^{-1}$ obtained from the sum of the three quantities on the right-hand side of the equation. Further, we have from the three overall steps $d[\text{HCN}]/dt = d[\text{C}_2\text{H}_4]/dt + d[\text{C}_2\text{H}_6]/dt$, and assuming that acrylonitrile formation by disproportionation in reaction (9) is negligible compared with that obtained from reaction (4) we have $d[\text{CH}_2\text{CHCN}]/dt + d[\text{C}_2\text{H}_4]/dt = d[\text{H}_2]/dt + d[\text{HCN}]/dt$. From the rates of product formation at 789 K we have $14.3 \times 10^{-5} \text{ Torr s}^{-1}$ and $13.1 \times 10^{-5} \text{ Torr s}^{-1}$ for the right- and left-hand sides of the first of these equalities, with $27.0 \times 10^{-5} \text{ Torr s}^{-1}$ and $24.5 \times 10^{-5} \text{ Torr s}^{-1}$ for the two sides of the second equality. Thus the experimental results are consistent with both of the above equations, agreement being within the limit of experimental error. A further equality necessitated by the proposed reaction mechanism is $d[\text{CH}_4]/dt = d[\text{CH}_3\text{CN}]/dt$, and the data shown in table 1 indicate that this is indeed the case at the temperatures where rates of formation of both of these products were measured; differences in rate never exceed 9% of the methane rate and are generally much less than this.

By analogy with reactions (5) and (6) it would at first sight seem reasonable to propose the reaction

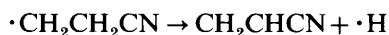


as an alternative to reaction (2). The fact that the rates of formation of methane and acetonitrile are in good agreement, however, effectively rules reaction (11) out as a source of acetonitrile since it would lead to a rate of formation of this product which must exceed that of methane. The removal of cyanomethyl radicals by recombination with themselves or other radicals present would also seem to be a possibility. Again, this alternative to reaction (3) as a fate for cyanomethyl must be unlikely because of the similar rates of formation of methane and acetonitrile, as well as the observation that at all temperatures studied no succinonitrile could be found among the reaction products. In the first reported investigation of the pyrolysis of propionitrile¹² a small amount of succinonitrile was found to be formed (*ca.* 16% of the methane produced at 948 K), but this was after 65% of the starting material had reacted so that the succinonitrile could have resulted here from a secondary process.

Thus the proposed reaction scheme, although perhaps slightly oversimplified, accounts for all the observed products and yields equations for the overall reactions which are consistent with their measured rates of formation. In addition to reactions (5) and (6) the reaction



should, for completeness, also be included and is probably not significantly slower than either of the alternatives. The most probable mode of decomposition of the cyano radical so formed is the reaction



which is *ca.* 26 kcal mol⁻¹ less endothermic than the alternative loss of a cyanide radical, so that the overall result of these two reactions is the same as that from reactions (4) and (5). The results obtained using the packed reaction vessel indicate that an increase in the ratio *s/v* leads to an enhancement of the yield of hydrogen, probably as a result of the surface reaction



which must occur much more rapidly in the packed reactor. This in turn must lead to a decrease in the steady-state concentration of hydrogen atoms and hence to the observed decrease in the rates of formation of acrylonitrile, ethene and ethane. From the measured rates of formation of hydrogen in the packed and unpacked reaction vessels it is likely that at 819.5 K no more than *ca.* 7% of the hydrogen formed in the latter vessel results from the surface reaction (12). The negligible variation in yields of methane and acetonitrile formed in the packed and unpacked vessels indicates that reactions leading to the formation of these products in chain-initiating steps are entirely homogeneous.

On the basis of the proposed reaction mechanism, the measured rate constant k_{CH_4} must correspond to k_1 , this being the rate-determining step for methane formation. Since the measured order for the formation of this product is close to unity, the reported Arrhenius parameters should be close to the limiting high-pressure value for this reaction. On applying the reported values to the R.R.K. expression for k/k_∞ and taking $s = 12$, the ratio k/k_∞ is found to be *ca.* 0.9 for a pressure of 50 Torr and at a temperature in the middle of the experimental range. Hence any difference between the limiting high-pressure Arrhenius parameters for reaction (1) and those reported here must be small, and in particular the measured activation energy cannot be more than 1.5 kcal mol⁻¹ below the limiting value.

From the measured activation energy we have for reaction (1) $\Delta H_{298}^{\ominus} = 80.4 \pm 1 \text{ kcal mol}^{-1}$, assuming the reverse reaction to have an activation energy of zero. [Specific heat data were taken from ref. (13) and (14).] Taking values of $12.4 \text{ kcal mol}^{-1}$ and $34.8 \text{ kcal mol}^{-1}$ for ΔH_f^{\ominus} of propionitrile¹³ and methyl,¹⁵ respectively, yields $\Delta H_f^{\ominus}(\cdot\text{CH}_2\text{CN}) = 58.0 \text{ kcal mol}^{-1}$, in excellent agreement with the value of $58.5 \text{ kcal mol}^{-1}$ reported by King and Goddard.³ In view of the known uncertainty in the value for $\Delta H_f^{\ominus}(\text{CH}_3\text{CN})$, the resonance stabilisation energy has been estimated by the same procedure as that adopted by King and Goddard, *i.e.* $\text{R.E.} = D_{298}(\text{CH}_3\text{—CH}_2\text{CH}_3) - D_{298}(\text{CH}_3\text{—CH}_2\text{CN})$. Taking for the C—C bond dissociation energy in propane¹⁶ a value of $85.8 \pm 1 \text{ kcal mol}^{-1}$ we obtain a resonance stabilisation energy of $5.4 \pm 1.4 \text{ kcal mol}^{-1}$ for the cyanomethyl radical. This is significantly lower than that for the allyl radical¹⁷ ($12.6 \text{ kcal mol}^{-1}$), a difference which can be ascribed to the very different stabilities of the two canonical forms for this radical, *i.e.*



From available entropy and specific heat data^{13, 14} we have for reaction (1), $\Delta S_{298}^{\ominus} = 27.6 \text{ cal K}^{-1} \text{ mol}^{-1}$ at 800 K for a standard state of 1 mol dm^{-3} . Assuming the recombination rate constant for cyanomethyl radicals to be the same as for allyl radicals,¹⁸ *i.e.* $\log_{10}(k_r/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 9.9$, and taking for methyl radicals¹⁹ $\log_{10}(k_r/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 10.4$, we have for reaction (-1), using the geometric mean rule, $\log_{10}(k_{(-1)}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 10.45$ and hence for reaction (-1) $\Delta S_{298}^{\ddagger} = -16.66 \text{ cal K}^{-1} \text{ mol}^{-1}$. Thus for reaction (1) $\Delta S_{298}^{\ddagger} = 10.94$ and $\log_{10}(A/\text{s}^{-1}) = 16.0$. The agreement between this value and that obtained experimentally is reasonable in view of the approximations necessary to deduce the former.

As with reaction (1), the unimolecular reactions (4) and (8) would, under the experimental conditions employed here, be expected to be in their pressure-dependent regions. Thus the rate of reaction (4), again assuming acrylonitrile formation from reaction (9) to be negligible, is given by

$$d[\text{CH}_2\text{CHCN}]/dt = k_4[\text{CH}_3\dot{\text{C}}\text{HCN}][\text{C}_2\text{H}_5\text{CN}]^x$$

and the rate of reaction (8) by

$$d[\text{C}_2\text{H}_4]/dt = k_8[\text{C}_2\text{H}_5][\text{C}_2\text{H}_5\text{CN}]^y.$$

Making the usual steady-state assumption that the rates of the chain-initiating reaction (1) and the chain-terminating reaction (9) are the same, we have

$$[\text{CH}_3\dot{\text{C}}\text{HCN}] = \left(\frac{k_1[\text{C}_2\text{H}_5\text{CN}]}{k_9} \right)^{\frac{1}{2}}.$$

Thus we have for reaction (4)

$$d[\text{CH}_2\text{CHCN}]/dt = \frac{k_1^{\frac{1}{2}}k_4}{k_9^{\frac{1}{2}}}[\text{C}_2\text{H}_5\text{CN}]^{\frac{1}{2}+x}.$$

Using the data obtained from pyrolysis at 789 K, a double logarithmic plot of $d[\text{CH}_2\text{CHCN}]/dt$ against pressure of reactant gave a straight line of slope 0.91 ± 0.02 . Hence in the above equation $x = 0.41 \pm 0.02$ and over the pressure-range studied, the overall order of reaction (4) is 1.41 ± 0.02 . From reactions (7) and (8) we have

$$d[\text{C}_2\text{H}_6]/d[\text{C}_2\text{H}_4] = (k_7/k_8)[\text{C}_2\text{H}_5\text{CN}]^{(1-y)}.$$

Using the ethane and ethene yields obtained from the pyrolysis of various initial pressures of propionitrile at 819.5 K, a double logarithmic plot of $d[\text{C}_2\text{H}_6]/d[\text{C}_2\text{H}_4]$ against pressure of reactant yielded a straight line of slope 0.35 ± 0.03 , so that $y = 0.65 \pm 0.03$ and the overall order of reaction (8) over the pressure range 10–100 Torr is 1.65 ± 0.03 .

As would be anticipated, therefore, the rate of reaction (4) which involves the decomposition of a radical with 18 vibrational degrees of freedom is, under the experimental conditions, closer to the limiting high-pressure value than is the similar reaction (8), where the radical involved has only 15 vibrational degrees of freedom. The order of 1.65 obtained for reaction (8) compares well with the estimate, from the data of Loucks and Laidler,¹¹ of an order of 1.55 for the same reaction under the same conditions with ethane as the chaperon rather than propionitrile. The pressure dependences of reactions (4) and (8) provide a ready explanation for the enhanced rates of formation of both hydrogen and acrylonitrile in the presence of an added excess of carbon dioxide.

The ethyl radical produced in reaction (6) reacts subsequently to form either ethene or ethane. Thus from reactions (5) and (6) we have

$$\frac{d[\text{H}_2]}{d([\text{C}_2\text{H}_4] + [\text{C}_2\text{H}_6])} = \frac{k_5}{k_6}$$

Using rate measurements obtained over the temperature range 809.5–850 K, a plot of the logarithm of the left-hand side of the above equation against $1/T$, which is shown in fig. 2, yielded the expression

$$\log_{10}(k_5/k_6) = (-1.4 \pm 0.2) + (4000 \pm 800)/\theta.$$

Thus, as might be anticipated, reaction (6) has a slightly higher activation energy than reaction (5). Both the difference in the activation energies and the ratio of the A factors are very close to those for the analogous reactions of hydrogen atoms with acetonitrile,²⁰ *i.e.* $4.8 \text{ kcal mol}^{-1}$ and $10^{-1.3}$, respectively. Unfortunately information on metathetical reactions of hydrogen atoms is limited and it is not possible to deduce from the above reliable Arrhenius parameters for either k_5 or k_6 . It will be seen from fig. 2 that the data obtained at the lower temperatures deviate significantly from the best straight line plot through the remaining points. This may be due to the fact that in this temperature region a significant proportion of the hydrogen produced results from the low-activation-energy reaction (12). For this reason the data for only the top five temperatures were used in the least-squares calculation of slope and intercept.

Finally, the slope of a plot of $\log_{10}(d[\text{C}_2\text{H}_6]/d[\text{C}_2\text{H}_4])$ against $1/T$ yielded $E_8 - E_7 = 22.5 \pm 0.5 \text{ kcal mol}^{-1}$. The value for E_8 must be roughly half-way between the limiting high- and low-pressure values for this reaction,²¹ *i.e.* in the region of 35 kcal mol^{-1} . This leads to an activation energy of $12.5 \text{ kcal mol}^{-1}$ for reaction (7). Although slightly higher than the value reported for the analogous reaction involving methyl radicals,¹⁰ the difference is not unreasonable since a number of metathetical reactions involving ethyl radicals appear to have activation energies which are a few kcal mol^{-1} higher than those for analogous reactions involving methyl radicals.²²

To summarise, the experimental evidence indicates that propionitrile decomposes predominantly by a homogeneous free radical chain mechanism initiated by the dissociation of the reactant into methyl and cyanomethyl radicals, a process which, under the experimental conditions employed, is close to first order. Alternative modes of reaction of hydrogen atoms with propionitrile lead to minor complications in the chain mechanism, as do the two alternative fates of the ethyl radical. The cyanoethyl

radical is an important intermediate in the chain mechanism and as a result of the resonance stabilisation of this radical the chains are necessarily short, involving no more than 5 or 6 units. Even so, there is a marked difference between the stability of the cyanoethyl radical formed in this system and the 3-methylallyl radical which must be formed in the pyrolysis of but-1-ene. The ratio $d[\text{H}_2]/d[\text{CH}_4]$ for each system gives a measure of the stability of the respective resonance-stabilised free radicals and this is close to 4 for propionitrile whilst with but-1-ene it is *ca.* 0.1 under similar experimental conditions. Thus in the decomposition of but-1-ene, dissociation of the methylallyl radical into atomic hydrogen and butadiene is unimportant compared with radical recombination and any possible chain process can be disregarded. This is in accord with the considerably higher resonance stabilisation energy found for the allyl and methylallyl radicals¹ (*ca.* 13 kcal mol⁻¹) as compared with that found here (5.4 kcal mol⁻¹) for the cyanomethyl, a figure which must be close to that for the cyanoethyl radical.

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