Hydrogen Atom Abstraction by Methyl Radicals in γ-Irradiated Crystalline Methyl Isocyanide at 77–125°K[1]

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Abstract: The elementary reaction $CH_3\cdot + CH_3NC \rightarrow CH_4 + \cdot CH_2NC$ (k_2) has been studied by esr in γ-irradiated crystalline CH_3NC between 77 and 125°K. First-order kinetics apply and good agreement was obtained between the rate constants calculated from $CH_3\cdot$ disappearance and from $\cdot CH_2NC$ appearance, thereby verifying the course of the reaction. The temperature dependence of the reaction rate constant shows an anomalous Arrhenius behavior, the apparent activation energies being 1.4 and 4.5 kcal mol^{-1} at 90 and 120°K, respectively. The corresponding process of deuterium atom abstraction from CD_3NC is too slow to be measured in this temperature range, and $CD_3\cdot$ radicals in CD_3NC disappear above 120°K by other processes. It is estimated from the results that the kinetic isotope effect, k_2^H/k_2^D, at 110°K is at least 1.1×10^3 which is more than the maximum classical effect (1.9×10^2) calculated according to the difference in initial zero point energies. These experimental results provide strong evidence for a large contribution from quantum mechanical tunnelling in this H-atom abstraction reaction at low temperatures.

Chemical reactions involving hydrogen atom abstraction by free radicals have been studied almost exclusively either in the gas phase or in solution above 250°K.[3,4] In solids at low temperatures, the esr technique has been widely used to identify radicals produced in specific reactions[5] but few kinetic measurements have been reported. Recently,[6] the process of hydrogen atom abstraction by methyl radicals from acetonitrile (reaction 1) was established kinetically in the high-temperature crystalline phase of acetonitrile at 77–87°K.

$$CH_3\cdot + CH_3CN \longrightarrow CH_4 + \cdot CH_2CN \qquad (1)$$

In this system, $CH_3\cdot$ radicals were generated by exposing γ-irradiated acetonitrile to visible light; the subsequent decay of $CH_3\cdot$ and the growth of $\cdot CH_2CN$ were followed simultaneously by esr and within experimental error, the two kinetic plots yielded the same rate constant for a first-order reaction.

A striking result of the acetonitrile study[6] is the very low value of 1.4 kcal mol^{-1} for the apparent activation energy of reaction 1 between 77 and 87°K. In contrast, the Arrhenius activation energy for the analogous reaction of $CD_3\cdot$ with CH_3CN in the gas phase[7] between 373 and 573°K was previously found to be 10.0 ± 0.5 kcal mol^{-1} which is not unexpected for this type of reaction. However, these apparently different findings can be reconciled[8] on the basis of the contribution from quantum mechanical tunnelling which becomes largely responsible for the rate at low temperatures. Exact one-dimensional tunnelling calculations show[8] that the two results are accounted for quantitatively in terms of a Gaussian potential energy barrier $V(x) = V_0 \exp(-x^2/a^2)$ with a maximum height V_0 of 10.5 kcal mol^{-1} and a width parameter $a = 0.64$ Å.

All theories of quantum mechanical tunnelling[9] predict a positive curvature in the Arrhenius plot such that the apparent activation energy increases with temperature. Also, a large contribution from tunnelling should be manifested by a considerable primary kinetic isotope effect. Since the maximum value of k^H/k^D in the absence of tunnelling is given by the zero point energy (zpe) expression $\sqrt{2}\exp((h\nu^H - h\nu^D)/2kT)$, a study of the isotope effect at low temperatures is of great interest. Additional work on the acetonitrile system has been concerned with these predictions of tunnelling theories. In this case the $CH_3\cdot$ radicals undergo two parallel first-order processes[6] and in the high-temperature phase above 100°K, the reaction leading to the recovery of the photobleachable center (the dimer radical anion of acetonitrile[10]) predominates over abstraction.[11] By following the recovery of the optical absorption[12] after photobleaching in a variable-temperature cryostat, it has recently been shown[13] that the apparent activation energy for the abstraction reaction increases with temperature, as expected for tunnelling. Accurate measurements of the isotope effect are difficult because the corresponding deuterium abstraction reaction from CD_3CN is extremely slow at the temperatures of interest. However, it was possible to establish[14] that k_1^H/k_1^D is at least 2×10^3 at 87°K in the high-temperature phase, a factor of 3 greater than the maximum zpe isotope effect.

In view of the potential importance of these low-temperature studies as a means of providing unambiguous evidence for tunnelling, we have sought additional ex-

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amples of hydrogen atom abstraction processes. This paper describes the results obtained in an esr study of the reaction of methyl radicals in γ-irradiated crystalline methyl isocyanide between 77 and 125°K. The experimental observations are particularly clear in this system and the kinetic data appear to provide definitive evidence for a large degree of tunnelling.

Experimental Section

Materials. Methyl isocyanide and methyl-d_3 isocyanide were prepared and purified essentially according to the directions given by Mottern and Fletcher,[15] except for the fact that we carried out the initial reaction between methyl iodide and silver cyanide at 40–45° instead of 70–75°. This change resulted in better and more reproducible yields of final product.

Sample Preparation and γ-Irradiation Techniques. Samples were prepared by standard high-vacuum techniques in Suprasil tubes of 2–4 mm i.d. Irradiations were carried out at 77°K in a Gammacell-200 source of cobalt-60 at a dose rate of *ca.* 0.15 Mrad/hr. Irradiations of less than 30-min duration usually sufficed to give radical concentrations that were ample for the subsequent esr measurements.

Esr Measurements. The basic spectrometer and the ancillary instrumentation have been described.[16] Sample temperatures of 77.3 and 87.4°K were obtained by using a conventional esr dewar filled with liquid nitrogen and liquid argon, respectively. These liquid gases were obtained from commercial suppliers. Studies at other temperatures were carried out using the dewar arrangement and temperature controller provided by the Varian V-4557 variable-temperature accessory; the actual temperature was monitored inside the cavity during the experiment by means of a copper–constantan thermocouple positioned close to the sample tube. The thermocouple wires were connected to the bridge network of a digital thermometer (United Systems Corp. Digitec thermocouple thermometer, Model 564) which had been previously calibrated. Temperature fluctuations were usually not more than ±1° over a period of several hours provided the flow of cold nitrogen gas was uninterrupted.

Kinetic Analysis. The data for $CH_3\cdot$ decay and $\cdot CH_2NC$ growth were obtained from the esr spectra and were found to obey first-order kinetics (see Results). Rate constants were obtained by a least-squares analysis using computer programs written for both the standard and Guggenheim forms of the integrated rate expression.[17] Only the Guggenheim method could be used for the analysis of $\cdot CH_2NC$ growth when the reaction time was long, but otherwise both methods were employed for each set of data, and the rate constants so derived were always in satisfactory agreement.

Results

Radical Formation and Assignments. As revealed by the esr spectrum in Figure 1, methyl radicals were generated during γ irradiation of crystalline methyl isocyanide in the dark at 77°K. There was no observable change in the spectrum on subsequent exposure of the γ-irradiated sample to a high-intensity beam of visible light. It may be noted that the direct radiation-induced formation of $CH_3\cdot$ radicals in very good yield from CH_3NC contrasts with the findings for CH_3CN where the $CH_3\cdot$ radicals were produced on photobleaching.[6]

In addition to the characteristic quartet spectrum of $CH_3\cdot$ radicals with $A_{iso}(H) = 22.5$ G, there is a weaker but reasonably well-resolved 1:1:1 triplet structure in the center of the spectrum shown in Figure 1. As indicated by the stick diagram, these three inner hyperfine components are attributed to the center lines ($m_I^H = 0$) of $\cdot CH_2NC$, the nitrogen hyperfine splitting being 6.5 G. It is well known[18] that in the esr powder spectrum of a monosubstituted methyl radical in which the two hydrogen atoms become equivalent through the rapid rotation of the methylene group, the central $m_I^H = 0$ component is much narrower than the outer lines belonging to $m_I^H = +1$ and $m_I^H = -1$ which are broadened by the anisotropic hydrogen hyperfine tensor. For $\cdot CH_2NC$, the features corresponding to these latter components are further split by the nitrogen hyperfine interaction and as expected, the center of gravity of each group appears to be located about 20–25 G from the center of the spectrum; these features are overlapped and largely obscured by the more intense outer lines of the $CH_3\cdot$ radical in the spectrum of Figure 1 but they are clearly evident in the spectra of Figure 2 which will be considered below. As far as we know, the esr spectrum of $\cdot CH_2NC$ has not been described before. The near equivalence in the heights of the three center lines of $\cdot CH_2NC$ in a powder (polycrystalline) spectrum strongly suggests that the observed nitrogen coupling (6.5 G) is mainly isotropic. A similar observation was made in the case of $\cdot CH_2NCO$,[19] for which $A_{iso}(N)$ is 4.5 G.

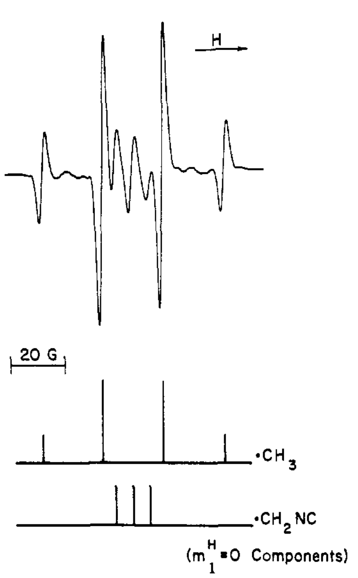

Figure 1. Esr spectrum of γ-irradiated CH_3NC at 77°K recorded *ca.* 10 min after γ irradiation at 77°K for 20 min (dose, 0.05 Mrad).

Reaction Path. It is vitally important to establish the reaction path in studies of solid-state reactions because a number of possible processes can usually be advanced to explain the disappearance of an intermediate species. Unfortunately, serious experimental problems are often encountered because the product species may elude detection by the available analytical techniques. This observation applies particularly to esr studies where the powder spectrum of the product radical consists entirely of broad unresolved features. In such cases, the problem of radical identification is compounded by the fact that whenever there is a change involving the replacement of an almost isotropic spectrum (as for the $CH_3\cdot$ radical) by one that is highly anisotropic, this is accompanied by a considerable reduction in spectral sensitivity. Consequently, in certain circumstances it may even be hard to detect any significant

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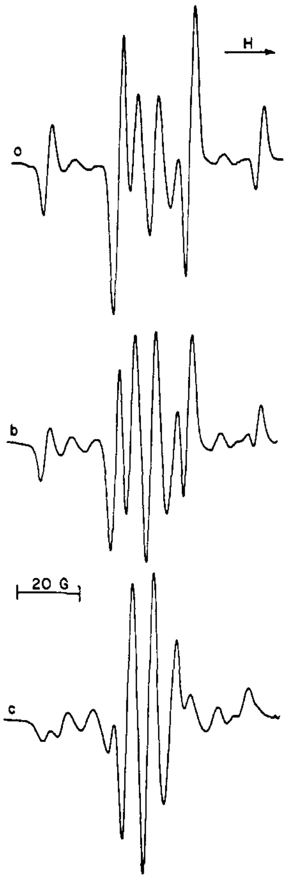

Figure 2. Esr spectra of γ-irradiated CH_3NC recorded under identical conditions after (a) 10 min, (b) 70 min, and (c) 270 min at 87°K.

change in the broad underlying spectrum. Therefore, the fact that the solid-state esr spectra of both $CH_3\cdot$ and $\cdot CH_2NC$ have sharp isotropic components makes the methyl isocyanide system extremely suitable for a study of hydrogen atom abstraction, as represented by reaction 2.

$$CH_3\cdot + CH_3NC \longrightarrow CH_4 + \cdot CH_2NC \qquad (2)$$

The series of spectra presented in Figure 2 demonstrate clearly that postirradiation decay of the $CH_3\cdot$ radical is accompanied by the simultaneous growth of the $\cdot CH_2NC$ radical. The reaction proceeds slowly at 77°K ($t_{1/2} \approx 210$ min) so very little thermal decay of $CH_3\cdot$ occurred during typical irradiation times of 15–30 min, and the sample could be brought to the desired temperature for isothermal kinetic studies without a large interim conversion.

At each temperature the reaction was followed by scanning the spectrum repeatedly at suitable intervals. The outer line of the $CH_3\cdot$ quartet at low field was selected to construct plots of $CH_3\cdot$ decay while the center line ($m_I^H = 0$, $m_I^N = 0$) of $\cdot CH_2NC$ served to measure $\cdot CH_2NC$ growth, the concentration being taken as proportional to the height of the line. Neither of these two representative lines overlaps with the isotropic lines from the spectrum of the other radical so they should be subject to the least distortion in the composite spectrum. Typical first-order plots as shown in Figure 3 resulted in good agreement between the rate constant calculated from $CH_3\cdot$ decay and that obtained from $\cdot CH_2NC$ growth. Similar agreement was found at several other temperatures, and the two sets of rate constants are plotted as data points in Figure 4. This demonstration of kinetic coincidence proves that reaction 2 accounts for the observations over the entire temperature range from 77 to 125°K.

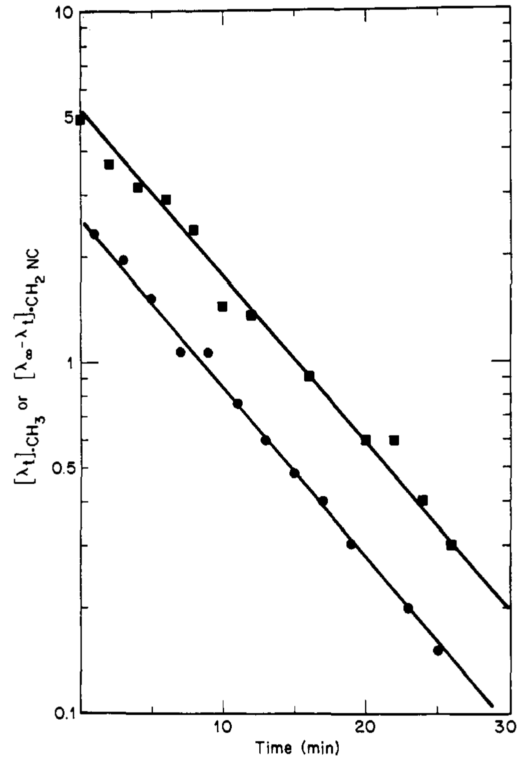

Figure 3. First-order kinetic plots obtained from esr spectra of γ-irradiated CH_3NC at 106°K: (●) $CH_3\cdot$decay, λ_t represents height of the low-field outer line recorded at a gain of 400; (■)$\cdot CH_2$-NC growth, λ_t represents height of the center line recorded at a gain of 630.

Effect of Temperature. There is a well-defined curvature to the Arrhenius plot in Figure 4 and the slopes at 90 and 120°K give apparent activation energies of 1.4 and 4.5 kcal mol^{-1}, respectively. Between 77 and 87°K we can use the $t_{1/2}$ values of 210 and 54 min at these respective temperatures to obtain an apparent activation energy of 1.8 kcal mol^{-1}, but this value is subject to a greater uncertainty because kinetic measurements by esr become much less reliable when the reaction time is lengthened to several hours. It appears from these results that the apparent activation energy increases rapidly above 90°K.

Isotope Effect. Before discussing the decay of the $CD_3\cdot$ radical in CD_3NC, it is appropriate to present evidence concerning the stability of the $\cdot CH_2NC$ radical in the CH_3NC matrix. The spectrum displayed in Figure 5a was recorded at 133°K at which temperature there was little or no decay over a period of 10–15 min. This radical disappeared within a few minutes when the sample temperature was raised above 150°K.

In contrast to the results obtained for $CH_3\cdot$ decay in CH_3NC, the $CD_3\cdot$ radical was found to be stable in γ-irradiated CD_3NC to much higher temperatures. A slow decay was observable at 120°K and the change was followed nearly to completion over 2.6 hr. This was manifested (Figure 5b) by a very marked reduction in the intensity of the seven inner components without any change in the strength of the outermost lines. A

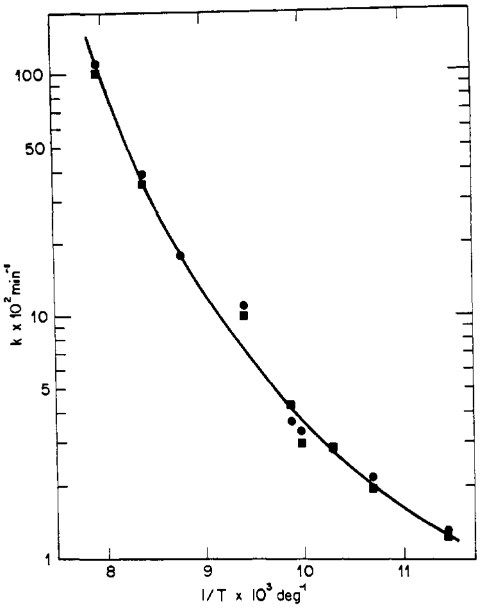

Figure 4. Arrhenius plot of first-order rate constants for reaction 2: (●) derived from $CH_3\cdot$decay; (■) derived from $\cdot CH_2NC$ growth.

subtraction of the residual spectrum from the initial spectrum yields a septet with intensity ratios of 1.1:3:6:7:6:3:1.0 close to that expected for $CD_3\cdot$. The residual spectrum in Figure 5b is assigned mainly to $\cdot CD_2NC$ since the intensities of the four low-field lines are approximately in the correct ratios for a 1:2:4:4:5:4:4:2:1 spectrum derived from the parameters, $2A_{iso}(D) = A_{iso}(N) = 6.5$ G. Because of the smaller deuterium hfs, the anisotropic broadening is expected to be much less important here than in the case of $\cdot CH_2NC$ discussed earlier, and so the powder spectrum of $\cdot CD_2NC$ should resemble the isotropic spectrum.

From these observations, it is evident that the initial concentration ratio of $\cdot CD_2NC$ to $CD_3\cdot$ is quite small, and this accords with the original distribution of analogous radicals in the CH_3NC system. Also, the stability of the residual $\cdot CD_2NC$ radical at 120°K parallels the previous findings for $\cdot CH_2NC$. On the other hand, there is a remarkable difference between the CH_3NC and CD_3NC systems in that the decay of $CD_3\cdot$ in CD_3NC at 120°K is not accompanied by a concomitant growth of $\cdot CD_2NC$. This suggests that $CD_3\cdot$ radicals decay by combination with other $CD_3\cdot$ radicals after diffusion, and the process of deuterium atom abstraction does not compete to any significant extent at 120°K. At a somewhat lower temperature, the diffusive decay mechanism appeared to be frozen out, so we attempted to determine the rate of deuterium atom abstraction at 110°K. A γ-irradiated mixture consisting of 10 mol % CH_3NC in CD_3NC at 110°K was used for this purpose because of the analytical advantage that any significant decay of $CH_3\cdot$ radicals can be observed unambiguously from the change in intensity of the outer esr line at low field. On the basis of the previous results for CH_3NC and CD_3NC, we reasoned that all the $CH_3\cdot$ (and $CD_3\cdot$) radicals which had vicinal CH_3NC molecules would decay rapidly at 110°K by abstraction leaving behind $\cdot CH_2NC$, whereas $CH_3\cdot$ (and $CD_3\cdot$) radicals caged by CD_3NC molecules would be much more stable. The objective of the experiment was to measure the decay (if any) of these latter $CH_3\cdot$ radicals.

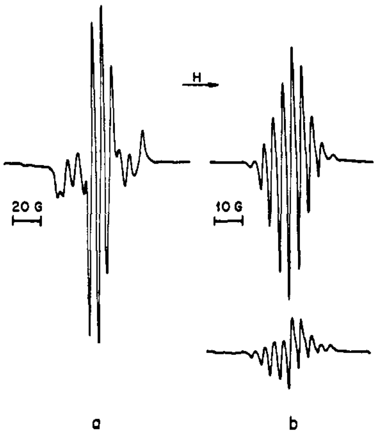

Figure 5. (a) Esr spectrum of γ-irradiated CH_3NC at 133°K; (b) esr spectra of γ-irradiated CD_3NC recorded under identical conditions before (upper spectrum) and after (lower spectrum) standing for 2.6 hr at 120°K.

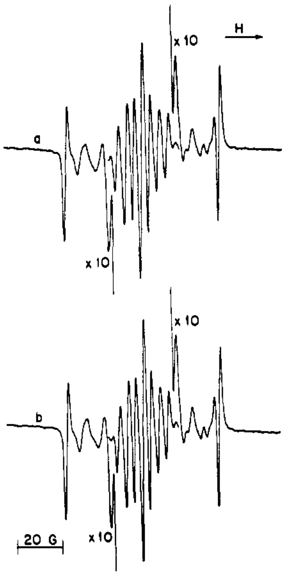

Figure 6. Esr spectra of γ-irradiated 10 mol % CH_3NC in CD_3NC recorded under identical conditions before (a) and after (b) standing for 8.5 hr at 110°K.

The esr spectrum displayed in Figure 6a clearly shows the outer lines of the $CH_3\cdot$ quartet as well as features from $\cdot CH_2NC$. Also, the innermost lines in the portion of the spectrum recorded at higher gain are attributable to the $\cdot CD_2NC$ spectrum which was discussed before. The center portion of the spectrum consists of overlapping components from $CD_3\cdot$, $CH_3\cdot$, $\cdot CD_2NC$, and $\cdot CH_2NC$. Comparison of the two spectra a and b in Figure 6 shows that over a period of 8.5 hr at 110°K, there was virtually no change in the intensity of the entire spectrum beyond that normally attributable to spectrometer fluctuations. In particular, there is no evidence for an alteration in the relative intensities of the various spectral components and neither a decrease in $CH_3\cdot$ nor a growth in $\cdot CD_2NC$ can be observed. Once again these negative results make it impossible to arrive at a value of k_2^D for the abstraction reaction so we must be content to estimate an upper limit. Based on our expectation that a conversion of 5% would have been detectable during the course of this experiment, we estimate k_2^D is less than 1.0×10^{-4} min^{-1} at 110°K. The value of k_2^H at this temperature is 1.1×10^{-1} min^{-1} (Figure 4) which means that k_2^H/k_2^D exceeds 1.1×10^3. When the temperature of the γ-irradiated isotopic mixture of methyl isocyanides was raised above 120°K, the esr components from $CH_3\cdot$ and $CD_3\cdot$ were both observed to decay gradually with no indication of deuterium atom abstraction, paralleling the previous results for CD_3NC.

Discussion

This work provides additional evidence for hydrogen atom abstraction by methyl radicals in the solid state at 77–125°K. As shown in Table I, the apparent activation energies of reactions 1 and 2 are quite similar at comparable temperatures, and this suggests that processes of this type may be of fairly general occurrence at low temperatures. It is interesting that for each of these reactions, the apparent activation energy increases with temperature in the solid state. Although no value is available for abstraction from CH_3NC at high temperature in the gas phase, the combined data in Table I strongly suggest that the apparent activation energy is primarily a function of temperature rather than of phase.

Table I. Apparent Activation Energies for Hydrogen Atom Abstraction by Methyl Radicals

Substrate molecule	Phase	Temp, °K	Arrhenius activation energy, kcal mol^{-1}
CH_3CN	Solid[a]	77–87	1.4[b]
CH_3NC	Solid	90	1.4[c]
CH_3CN	Solid[a]	93–108	2.4[d]
CH_3NC	Solid	120	4.5[c]
CH_3CN	Gas	373–573	10.5[e]

[a] High-temperature phase. [b] Reference 6. [c] This work. [d] Unpublished work by J. D. Skelton, K. Takahashi, and F. Williams. [e] Reference 7; abstraction by $CD_3\cdot$ radicals.

It would have been useful to obtain detailed results on the deuterium isotope effect in the methyl isocyanide system as a function of temperature, but such measurements were precluded by experimental difficulties. At temperatures appreciably above 110°K, there is an additional process of methyl radical decay which predominates to the exclusion of deuterium atom abstraction. On the other hand, in the region below 110°K where there appears to be virtually no decay of methyl radicals by other mechanisms, the deuterium abstraction reaction is much too slow to obtain reliable data by the esr method. In these circumstances, it could only be established that k_2^H/k_2^D is greater than 1.1×10^3 at 110°K. From the difference of 751.4 cm^{-1} between the antisymmetric C–H and C–D stretching frequencies in CH_3NC and CD_3NC,[15] the maximum zpe isotope effect at 110°K is $\sqrt{2}\ \exp(375.7/76.5) = 1.92 \times 10^2$. Thus, the experimental isotope effect exceeds the maximum classical value.

The unusual kinetic characteristics of the abstraction reaction, as evidenced by the low activation energies, the positive curvature in the Arrhenius plot, and the magnitude of the deuterium isotope effect, are consistent with the hypothesis that the reaction proceeds mainly by quantum mechanical tunnelling. However, other explanations should also be considered. One possibility which has been suggested repeatedly to us is that the potential energy surface might be modified considerably in the solid by strong cage effects, resulting in a lower potential energy barrier relative to that for the reaction in the gas phase. We find it difficult to reconcile this explanation with the marked temperature dependence of the activation energy for the reaction in the solid state. Moreover, there is no physical evidence to support the idea that the states of the reactant molecules are strongly perturbed in the crystalline solid. Thus, the differences between the vibrational frequencies of acetonitrile in the gas and the solid phases are quite small;[20] also, the isotropic esr spectrum of the methyl radical in the solid state is virtually the same as that in solution indicating that a planar configuration is maintained.

Finally, we wish to draw attention to the remarkable isotope effect in these systems on the overall course of methyl radical disappearance at low temperatures. Thus we have now observed in γ-irradiated methyl isocyanide at 120°K that $CH_3\cdot$ radicals in CH_3NC decay by abstraction to give $\cdot CH_2NC$, whereas $CD_3\cdot$ radicals in CD_3NC decay much more slowly without giving $\cdot CD_2NC$. Similarly, it was found before[6,11,21] in γ-irradiated acetonitrile crystal I at 77°K that $CH_3\cdot$ radicals in CH_3CN disappear almost exclusively by abstraction to give $\cdot CH_2CN$, whereas $CD_3\cdot$ radicals in CD_3CN undergo another reaction leading to the complete recovery of the acetonitrile dimer radical anion. These all-or-nothing isotope effects which appear to be unique in the annals of chemistry are entirely understandable in terms of a simple competition between abstraction and other decay processes, for which only the former displays a large deuterium isotope effect ($>1 \times 10^3$).

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