Evidence for Hydrogen Atom Abstraction by Methyl Radicals in the Solid State at 77°K[1]

Sir:

Since thermal reactions of free radicals by hydrogen atom abstraction in the gas and liquid states are generally characterized by activation energies in excess of 5 kcal mol^{-1}, it has been customary to exclude consideration of such processes in the solid state at 77°K.[2] From detailed studies on the reactions of methyl radicals in γ-irradiated acetonitrile at low temperatures, we have now obtained definitive evidence for a process of hydrogen atom abstraction with an activation energy of only 1.4 kcal mol^{-1}. This result suggests either a large contribution from tunnelling at low temperature or a drastic modification of the potential energy surface for the reaction upon going to the solid state.

When γ-irradiated acetonitrile is bleached with visible light at low temperatures (77–120°K), methyl radicals are produced.[3,4] Recent esr studies in this laboratory on single crystals of $^{13}CD_3CN$ and $CD_3{}^{13}CN$ have unambiguously confirmed this assignment. The subsequent thermal decay of these radicals in both acetonitrile-h_3 and acetonitrile-d_3 is now understood in terms of a simple kinetic competition between two parallel first-order processes.[5] Reaction 1 leads to the

$$\mathrm{CH_3\cdot + CN^- + CH_3CN \longrightarrow e^-(CH_3CN)_2} \qquad (1)$$

$$\mathrm{CH_3\cdot + CH_3CN \longrightarrow CH_4 + \cdot CH_2CN} \qquad (2)$$

recovery of the photobleachable electron-excess center,[4] while reaction 2 results in hydrogen atom abstraction from a neighboring acetonitrile molecule.[3,5–7] The results presented below refer to the high-temperature crystalline phase of acetonitrile which can be studied at low temperatures by quenching the sample to 77°K; in this phase the photobleachable center produced by γ-irradiation has been identified by esr as an excess electron bound to two acetonitrile molecules.[4,8]

In kinetic studies on the above reactions, the decay of $CH_3\cdot$ and the growth of $\cdot CH_2CN$ were followed simultaneously by esr, while the recovery of the electron-excess center was monitored in separate experiments by its optical absorption spectrum.[9] Table I summarizes the rate constants obtained from esr measurements on acetonitrile-h_3 at 77 and 87°K. The sum of the rate constants, $k_1 + k_2$, was obtained by following the decay of $CH_3\cdot$ in the dark after photobleaching. Independently, we evaluated k_2 both from the decay of $CH_3\cdot$ and by the growth of $\cdot CH_2CN$ during steady illumination. Under the latter conditions the methyl radicals decay only by means of reaction 2, since reaction 1 is continuously reversed by the photobleaching process. The kinetic coincidence as demonstrated by the essential agreement between the two values of k_2 at each temperature provides conclusive evidence that reaction 2 involves the loss of $CH_3\cdot$ by hydrogen atom abstraction to produce $\cdot CH_2CN$.

Table I. Rate Constants from Esr Studies on CH_3CN

Temp, °K	k_2,[a] min^{-1}	k_2,[b] min^{-1}	$(k_1 + k_2)$,[c] min^{-1}
77	0.025	0.028	0.025
87	0.071	0.081	0.084

[a] Calculated from $CH_3\cdot$ decay during photobleaching. [b] Calculated from $\cdot CH_2CN$ growth during photobleaching; the uncertainty in these values is *ca.* 10%. [c] Calculated from $CH_3\cdot$ decay in the dark after photobleaching; optical studies show that $k_1 \ll k_2$ at 77°K.

The rate constants obtained from optical studies on CH_3CN and the series of deuterated acetonitriles at 87°K are given in Table II. In this case we obtained $k_1 + k_2$ by following the recovery of the absorption due to the electron-excess center in the dark after photobleaching; the ratio $k_1/(k_1 + k_2)$ was also determined from the fraction which was ultimately recovered so k_1 and k_2 were thereby evaluated separately. In CD_3CN the recovery reaction 1 predominates so strongly that $k_1/(k_1 + k_2)$ exceeds 0.99 at 87°K and hence we can only state that k_2 is less than 7×10^{-4} min^{-1} in this case. A comparison of the results for CH_3CN in Tables I and II shows good agreement, and since k_2 is virtually unaffected by the experimental conditions (light or dark), we conclude that the abstraction reaction certainly does not involve hot methyl radicals. A salient feature of the results for the isotopic acetonitriles given in Table II is the almost linear variation of k_2 with the number n of H atoms in the acetonitrile molecule. This statistical result clearly verifies that reaction 2 is a simple H atom abstraction process from acetonitrile with a large primary kinetic isotope effect (*vide infra*).

Table II. Rate Constants from Optical Studies at 87°K

Compound	k_1,[a] min^{-1}	k_2,[b] min^{-1}	n[c]
CH_3CN	0.013	0.071	3
CH_2DCN[d]	0.016	0.043	2
CHD_2CN[d]	0.029	0.025	1
CD_3CN	0.071	<0.0007	0

[a] This rate constant refers to the recovery reaction of the center $e^-(CH_nD_{3-n}CN)_2$. [b] This rate constant refers to abstraction from $CH_nD_{3-n}CN$. [c] Number of H atoms in acetonitrile. [d] The isotopic purity of the partially deuterated acetonitriles was *ca.* 85% in each case, according to mass spectrometric analyses.

The apparent activation energy for reaction 2 is calculated from the data in Table I to be 1.4 kcal mol^{-1}. This is considerably lower than the value of 10.0 ± 0.5 kcal mol^{-1} obtained for hydrogen atom abstraction from CH_3CN by $CD_3\cdot$ in the gas phase[10] over the temperature range from 373 to 573°K. Quantum mechanical tunnelling would appear to provide an attractive explanation for the very low activation energy in the solid at low temperatures, and in this respect it can be shown that the present results are at least qualitatively consistent with Bell's theory.[11,12] An alternative explanation suggested to us by the referees is the possible

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(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2968. This is AEC Document No. ORO-2968-54.

(2) For a review, see J. E. Willard in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley-Interscience, New York, N. Y., 1968, p 599.

(3) P. B. Ayscough, R. G. Collins, and T. J. Kemp, *J. Phys. Chem.*, 70, 2220 (1966).

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(6) M. A. Bonin, Ph.D. Thesis, The University of Tennessee, 1969.

(7) F. P. Sargent, *Can. J. Chem.*, **48**, 1780 (1970).

(8) R. J. Egland and M. C. R. Symons, *J. Chem. Soc. A*, 1326 (1970).

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(11) R. P. Bell, *Proc. Roy. Soc., Ser. A*, **148**, 241 (1935).

(12) R. P. Bell, *Trans. Faraday Soc.*, **55**, 1 (1959).

distortion of the potential energy surface in the crystal as compared to the gas phase. However, at the present time we know of no basis for meaningful estimates of such possible effects.

A primary kinetic isotope effect, k_2^H/k_2^D, in excess of 10^6 rather than a "normal" effect of $\approx 10^2$ at 87°K would provide clear support for a large degree of tunnelling. Unfortunately there are serious problems in obtaining accurate measurements of k_2^D under the conditions which apply here. We attempted to measure the decay of $CD_3\cdot$ in CD_3CN at 87°K by esr over a period of 12 hr while the sample was being continuously photobleached, but because of difficulties connected with spectrometer stability, we can only state with confidence at this time that k_2^D is definitely less than 5×10^{-4} min^{-1}. Thus k_2^H/k_2^D exceeds 140 at 87°K. In future work, we hope to be able to devise experiments to measure the actual value of this ratio.

Regardless of which theory applies to the process, hydrogen atom abstraction would seem to be important in the general consideration of free-radical reactions in organic compounds at low temperatures.[13] Progress in this field has been hindered by the experimental difficulty of establishing the reaction path with certainty in the vast majority of systems, so the present result may be of wide significance and we plan to examine other cases of potential interest.

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[13] *Cf.* S. H. Chin and S. I. Weissman, *J. Chem. Phys.*, **53**, 841 (1970); these authors have observed the rapid migration of hydrogen atom vacancies in a solid solution of the free radical bis(trifluoromethyl) nitroxide, $(CF_3)_2NO$, in its hydroxylamine, $(CF_3)_2NOH$, at 110°K.

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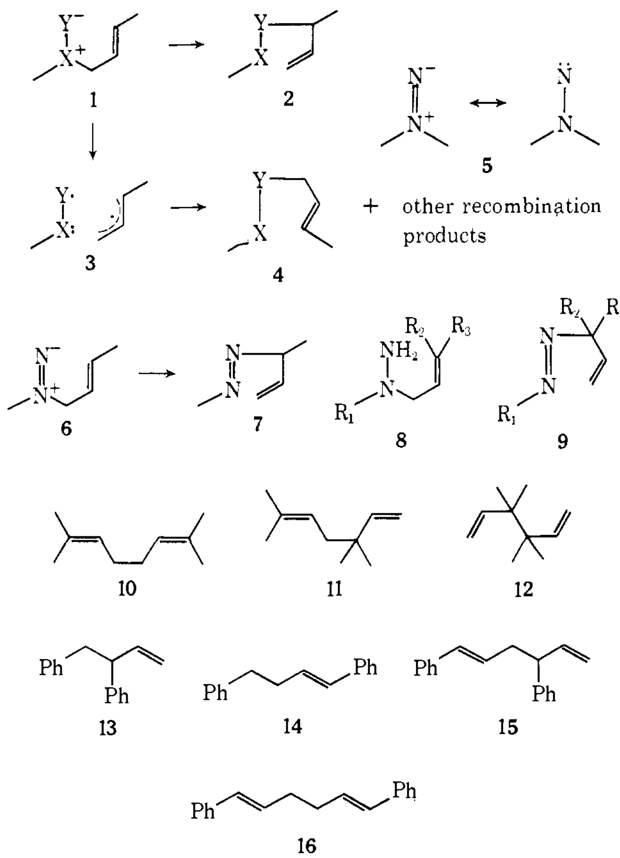
Sigmatropic Rearrangements of Diazenes

Sir:

Recently we have adumbrated[1] a general scheme for ylide rearrangements of type **1** to **2**, and have presented evidence for a duality of mechanism in such processes, namely the facile orbital symmetry conserved[2] process **1** to **2** and the competing homolytic dissociation–recombination path, through **3**, to **4**. This latter process is in general less facile and competes only at high temperatures and in special structural environments with the concerted pathway. Since the diazene function[3] **5** may, in its dipolar form, be described as an ylide, and since the nonbonding electrons on the terminal nitrogen would be ideally located to participate in the suprafacial transformation, **1** to **2**, as in **6** to **7**, we have investigated the properties of such species **6**. Furthermore, as a recent note[4] describes work whose interpretation is in contradiction to our own findings we report here our analysis of this problem.[5]



We prepared a series of allylic hydrazines **8a–g**,[6] Table I, and subjected them to a variety of oxidants, designed to produce the diazene **6**, namely mercuric oxide,[7] lead tetraacetate, manganese dioxide, and *tert*-butyl hypochlorite. The metal oxides at or below 0°, in CCl_4 suspension, produced the allylic azo compounds in

Table I. Hydrazines and Azo Compounds

	R_1	R_2	R_3
a	C_6H_5	CH_3	CH_3
b	C_6H_5	H	H
c	CH_3	CH_3	CH_3
d	CH_3	H	C_6H_5
e	3-Methyl-2-butenyl	CH_3	CH_3
f	Allyl	H	H
g	Benzyl	H	C_6H_5

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[1] J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970).

[2] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[3] For an excellent review of diazenes see: D. M. Lemal in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, Chapter 10.

[4] W. D. Ollis, I. O. Sutherland, and Y. Thebtaranoth, *Chem. Commun.*, 1199 (1970).

[5] An earlier report (C. L. Bumgardner and J. P. Freeman, *J. Amer. Chem. Soc.*, **86**, 2233 (1964)) describes the reaction of diallylamine with difluoramine, a reaction which was presumed to produce the diallyldiazene, to yield *N*-allylpyrazoline. In our case we have isolated the azo compound **9f**, and have observed its slow rearrangement to acrolein allylhydrazone.

[6] The hydrazines were prepared by alkylation with allylic halides or by reduction (Al–Hg) of the corresponding nitrosamines.

[7] An early report (A. Michaelis and K. Luxembourg, *Chem. Ber.*, **26**, 2174 (1893)), described the oxidation with mercuric oxide of **8b** to **9b**. Despite an assertion to the contrary, ref 3, p 390, we have confirmed their observation.