INTRODUCTION

It is well known that many organic molecules possessing low-lying orbitals form radical anions by electron attachment, and that several of these radical anions can initiate vinyl polymerization. However, there have been relatively few ESR studies of simple aliphatic radical anions, presumably because these species are generally too unstable to be observed under conventional experimental conditions in the liquid state. To some extent, this limitation set by the intrinsic chemical stability can be overcome by solid state studies at low temperatures, and this paper summarizes recent ESR work in this laboratory dealing with the identification and reactions of aliphatic

* Present address: Max-Planck-Institut für Kohlenforschung, Mülheim, West Germany
† Present address: Fuji Photo Film Co. Ltd., Research Laboratories, Tokyo, Saitama, Japan 351
radical anions in γ-irradiated crystalline solids. Incidental to this research, evidence has been obtained for weakly interacting radical-anion pairs formed by the dissociation of certain radical anions. Another aspect of this work which has received particular attention but will not be discussed here concerns the unexpected occurrence of hydrogen atom abstraction reactions by methyl radicals at 77°K (Sprague & Williams, 1971a). Detailed kinetic studies on a number of different systems (Wang & Williams, 1972) provide strong evidence for a large contribution from quantum mechanical tunneling in such reactions at low temperatures (LeRoy, Sprague & Williams, 1972).

RESULTS AND DISCUSSION

Only a brief survey of the main findings will be given here, and many historical and experimental details are of necessity omitted. Since the results are highly characteristic for each compound and even for the particular crystalline state in which it is γ-irradiated, each system is discussed separately.

Acetonitrile Crystal I

The photobleachable colour center produced by γ-irradiation of the metastabilized high-temperature phase of acetonitrile at 77°K has been identified as the dimer radical anion (Sprague, Takeda & Williams, 1971). All the ESR studies on the structure of the radical anions of
Acetonitrile have been carried out with deuterated compounds since the corresponding ESR spectra in CH₃CN are virtually unobservable because of proton hyperfine broadening and overlapping signals from other radicals. Representative ESR spectra from aligned crystals of CD₃¹⁴N and CD₃¹³¹⁴N are presented in Figure 1 and show hyperfine interaction of the unpaired electron with pairs of magnetically equivalent nuclei derived from two acetonitrile molecules. These results together with those for CD₃¹⁵N and CD₃¹³¹⁴N establish that the dimer radical anion possesses a center of symmetry, as provided by an antiparallel placement of molecules.

The experimental spin densities derived from the principal values of the hyperfine tensors (Takeda, 1971) show that the unpaired electron resides mainly in a single 2p orbital on each nitrogen atom ($\Sigma \rho_N = 0.68$) and the remaining fraction is accounted for by the spin densities on the methyl carbon ($\Sigma \rho_{CD} = 0.13$) and on the cyanide carbon ($\Sigma \rho_{CN} = 0.27$). Recent INDO calculations (Kerr, unpublished work) based on the structure shown in Figure 1 are in good agreement with these results and confirm the previous assignment (Sprague, Takeda & Williams, 1971) of the nitrogen spin density to the in-plane 2p orbitals between the molecules.

Evidence which establishes the anionic nature of the species comes from the results of photobleaching and electron scavenging experiments. The purple colour and the ESR spectrum of the dimer species in CD₃CN are removed on bleaching with red or white light.
(Bonin, Tsuji & Williams, 1968), and the only product observable by ESR is the \( \text{CD}_3 \cdot \) radical. Additional experiments with \( \text{CH}_3\text{CN} \) and \( ^{13}\text{CD}_3\text{CN} \) have verified that photodisociation gives the corresponding methyl radicals, so that the overall process can be represented by the equation,

\[
(\text{CD}_3\text{CN})_2 ^{-} \xrightarrow{\text{hv}} \text{CD}_3 \cdot + \text{CN}^- + \text{CD}_3\text{CN}
\]

It is remarkable that this photobleaching reaction is thermally reversible, and the dimer radical anion recovers completely in \( \text{CD}_3\text{CN} \). The reaction occurs slowly on standing at \( 87^\circ \text{K} \) (\( t_{1/2} \approx 12 \text{ min} \)) but takes place within a few minutes at \( 100^\circ \text{K} \) (\( t_{1/2} \approx 1 \text{ min} \)). On the other hand, the recovery of the dimer radical anion in \( \text{CH}_3\text{CN} \) is much less complete, particularly below \( 100^\circ \text{K} \), and some of the methyl radicals decay irreversibly. This difference between the reactions in \( \text{CD}_3\text{CN} \) and \( \text{CH}_3\text{CN} \) is due to the intervention of a competitive process of hydrogen atom abstraction by the methyl radical from a neighboring \( \text{CH}_3\text{CN} \) molecule (Takeda & Williams, 1970), a reaction which exhibits a very large primary deuterium isotope effect (Sprague & Williams, 1971). The kinetics of these reactions have been studied extensively (Bonin, 1969; Sprague, 1971; Wang, 1972).

Definite confirmation that the dimer species is an anion rather than a cation is supplied by the results obtained using \( \text{CD}_3\text{CN} \) doped with methyl halides as competitive electron scavengers (Sprague & Williams, 1971b). In mixtures containing 10 mole % of \( \text{CH}_3\text{Cl} \) or \( \text{CH}_3\text{Br} \), dimer radical
anion formation is presented and scavenging is complete as evidenced by the absence of colour and the lack of any photobleaching effect on the ESR spectrum of the sample after γ-irradiation. Unexpectedly, the product of the scavenging reaction is of intrinsic interest. For the CH$_3$Br/CD$_3$CN mixture, the upper spectrum presented in Figure 2A can be analyzed into two separate quartets of quartets as indicated by the stick diagram, and these can be assigned to CH$_3^+$ radicals interacting with bromide ions ($^{79}$Br$^-$ and $^{81}$Br$^-$ are present in almost equal abundance). When the sample was pulse annealed, the spectrum changed to that of the familiar quartet due to free CH$_3^+$ radicals (see Figure 2A) showing that dissociation of the methyl radical-bromide ion pairs had occurred. As well as furnishing evidence that the paramagnetic dimer species in CD$_3$CN results from electron attachment, this experiment provides spectroscopic proof of dissociative electron capture by CH$_3$Br. Since the proton splitting in the spectrum of the unannealed sample is about 90% of the value for the free CH$_3^+$ radical, it seems more appropriate to describe the original species as a methyl radical-bromide ion pair than a methyl bromide radical anion.

The incorporation of methyl isocyanide into acetonitrile crystal I also resulted in efficient electron scavenging by the solute during γ-irradiation, and at sufficiently high concentration of scavenger (10 mole % CH$_3$NC in CD$_3$CN), the dimer radical anion of acetonitrile was not produced. In this case CH$_3^+$ radicals were produced directly during γ-irradiation so they must have originated from dissociative electron capture by CH$_3$NC (Wang, 1972). Although the reaction products are
presumably identical to those (methyl radical and cyanide ion) produced on photodissociation of the acetonitrile dimer radical anion, no evidence was obtained for the generation of a photobleachable radical anion in a subsequent thermal recombination reaction. The loss of CH$_3^*$ radicals by competitive hydrogen atom abstraction from CH$_3$NC (Wang and Williams, 1972) should be relatively unimportant in a largely deuterated matrix, so the failure to observe recombination can probably be attributed to the inverted position of the cyanide ion in the acetonitrile lattice.

Acetonitrile Crystal II. The lower crystalline phase of acetonitrile is prepared by slow cooling of the sample through a phase transition (Putnam, McEachern & Kilpatrick, 1965) at 215°C, about 12° below the melting point. On γ-irradiation of this phase at 77°C, the monomer radical anion is produced (Takeda & Williams, 1969). The identification is based largely on ESR studies of γ-irradiated CD$_3^{14}$N and CD$_3^{13}$C$^{14}$N. Although it is extremely difficult to grow single (aligned) crystals of this lower phase, this was achieved in some instances and particularly well resolved spectra were obtained in the case of CD$_3^{13}$C$^{14}$N.

A photobleachable triplet spectrum (Figure 1) is produced in CD$_3^{14}$N indicating that the unpaired electron interacts with only one $^{14}$N nucleus. This is verified by the single crystal spectrum from CD$_3^{13}$C$^{14}$N which is seen to consist of a doublet of triplets with a
large $^{13}\text{C}$ splitting. The principal values of the $^{13}\text{C(CN)}$ hyperfine tensor in gauss are [71.7, 59.6, 53.0] from which the spin densities in the $2s$ and in-plane $2p$ orbitals of the cyanide carbon are calculated to be 0.06 and 0.19, respectively. These values give a $p/s$ hybridization ratio of 3.51 and by a well known formula (Atkins & Symons, 1967) this leads to a calculated CCN angle of 130°. This result corresponds closely to the HCN angle of 131° in the isostructural molecule HCN$^-$ (Adrian et al., 1969). The structure of the acetonitrile monomer radical is indicated in Figure 1 and it should be noted that the total spin density on the carbon in the cyanide group ($\rho_{\text{CN}}^C = 0.32$) is slightly larger than that on nitrogen ($\rho_{\text{N}}^N = 0.29$). This is expected in view of the electronegativity difference between carbon and nitrogen which should concentrate the charge distribution in the antibonding orbital more in favour of the carbon of the cyanide group. Another point of interest is the presence of substantial spin density on the carbon of the methyl group ($\rho_{\text{CD}}^{\text{CD}_3} = 0.31$). The large isotropic $^{13}\text{C}$ splitting of ~88 gauss from this carbon suggests that in the contributing structure $\text{CD}_3 \cdot \text{CN}^-$, the configuration at the methyl carbon atom is tetrahedral rather than planar.

The photobleaching and thermal recovery reactions of the acetonitrile monomer radical anion are strikingly similar to those already described for the dimer species in Crystal I, thereby providing strong confirmation of the radical anion assignment. Recovery of the
monomer radical anion from the methyl radical produced on photo-
dissociation proceeds to completion in CD$_3$CN as before, but the
reaction rate for monomer recovery in Crystal II is about a factor
of ten slower than that for dimer recovery in Crystal I at the
same temperature although the activation energies have very nearly
the same value (4.5 ± 0.5 kcal mole$^{-1}$) within experimental error.
In the case of CH$_3$CN the recovery reaction competes with hydrogen
atom abstraction by methyl radicals, again paralleling the results
in Crystal I.

Adiponitrile. Monomer and dimer radical anions of NC(CD$_2$)$_4$CN
have also been identified by ESR. The monomer radical anion is formed
by γ-irradiation at 77°K of the crystalline phase produced directly
from the melt whereas the dimer is produced on irradiation of the phase
prepared by crystallization from the glass at low temperature. Excellent
single crystals of the former phase were grown and enabled the deter-
mination of the principal values for the $^{14}$N hyperfine tensor of the
monomer radical anion (Takeda, 1971). These values in gauss are [21,0,0]
which hardly differ from the corresponding results for HCN$^-$ (Adrian et al.,
1969). Only powder spectra could be obtained from the other crystalline
phase but the parallel features of a quintet ESR spectrum are clearly
displayed with $A_{\parallel} (^{14}$N) = 17.2 gauss which is almost identical to that
found for the dimer radical anion in acetonitrile Crystal I. Both monomer
and dimer radical anions are photobleached but only the monomer shows
appreciable thermal recovery.
Succinonitrile. In contrast to the results for acetonitrile and adiponitrile, the dimer radical anion is formed in both crystalline phases of succinonitrile. Identification is based in each case on the powder ESR spectrum of succinonitrile-$d_4$ which closely resembles the corresponding spectra of the dimer radical anions of acetonitrile, propionitrile, and adiponitrile. The formation of the $\cdot CH_2CH_2CN$ radical is observed in both crystal phases of succinonitrile-$h_4$ after photobleaching but it is remarkable that thermal recovery to the dimer radical anion proceeds only in Crystal II (Campion & Williams, 1971). Similar results were obtained with succinonitrile-$d_4$. Presumably the radical produced on photobleaching in Crystal I relaxes to a position in the lattice which prevents the regeneration of the dimer radical anion.

Acrylonitrile. The ESR spectra of $\gamma$-irradiated acrylonitrile differ according to the nature of the crystalline phase (Chung, Takeda & Williams, 1970). A photobleachable triplet spectrum was observed in the low-temperature phase and has been tentatively assigned to the monomer radical anion. Only the spectrum of the CH$_3$CHCN radical could be identified in quenched samples of the high-temperature phase.

tert-Butyl isocyanate. The ESR spectrum of crystalline tert-butyl isocyanate after $\gamma$-irradiation (Figure 3A) shows the well resolved lines of the tert-butyl radical spectrum with a hfs of 22.0 gauss and three central components with a hfs of 4.8 gauss. The latter structure
is selectively removed by photobleaching with visible light and this change is accompanied by a considerable increase in the intensity of the tert-butyl radical spectrum, as shown in the lower spectrum of Figure 3A. By analogy to the studies on nitriles, the photobleachable species with the triplet spectrum can be assigned to the radical anion of tert-butyl isocyanate. Further evidence for this assignment comes from experiments using samples doped with tert-butyl iodide, an effective electron scavenger. As shown in Figure 2B, a rather complicated ESR spectrum is obtained after such mixtures are γ-irradiated at 77°K, and there is no photobleaching effect, suggesting that electron scavenging has occurred. On rapid annealing at higher temperatures, the spectrum gradually changes to that of the tert-butyl radical. Although the original spectrum of the doped sample is not easily analyzed, it can be interpreted reasonably well as the spectrum of tert-butyl radical-iodide ion pairs formed when tert-butyl iodide undergoes electron capture. The thermal dissociation of these radical-anion pairs parallels the results (Figure 2A) for the methyl radical-bromide ion pairs in acetonitrile Crystal I.

**tert-Butyl Isothiocyanate.** As shown in the upper spectrum of Figure 3B, the ESR spectrum of γ-irradiated tert-butyl isothiocyanate is composed of both a broad singlet feature and the multiplet spectrum of the tert-butyl radical. This particular spectrum was recorded while the sample was exposed to red light and the lines of the tert-butyl radical
multiplet are much sharper than in the spectrum recorded with the sample in the dark, although the singlet feature was unaffected. This effect of line sharpening by red light was found to be completely reversible. On illuminating the sample with unfiltered tungsten light, the singlet spectrum was photobleached irreversibly and there was a large increase in the intensity of the tert-butyl radical spectrum, as shown in the middle spectrum of Figure 3B recorded during this exposure to visible light. When the lamp was turned off, the lines of the tert-butyl radical spectrum broadened. Again these lines could be sharpened by illumination with red light and the relative increase in signal height was similar to that observed before photobleaching. Further experiments showed that light in the near-infrared region (λ > 1250 nm) was responsible for the photodynamic effect on the tert-butyl radical spectrum in this system (Chung & Williams, 1972).

On the basis of the photobleaching reaction, the singlet spectrum is assigned to the radical anion. Since the reversible line broadening is observed for the tert-butyl radicals produced by photodissociation of the radical anion as well as those formed directly by γ-irradiation, this suggests that the broadening is due to the interaction of the tert-butyl radical with the thiocyanate anion. Moreover, a strong resemblance to the alkyl radical-halide ion pairs is indicated by comparison with the spectrum of the methyl radical-chloride ion pair which consists of the familiar quartet spectrum of the methyl radical broadened by hyperfine coupling with the chloride ion (Sprague, 1971). Although the exact nature of the magnetic resonance interaction responsible for line broadening in the tert-butyl radical-thiocyanate anion pair is not directly evident,
the reversible photodynamic behavior can probably be attributed to motional effects which lead to an overall reduction in the \( g \) anisotropy (Chung & Williams, 1972).

**SUMMARY**

This paper has been concerned with the identification and reactions of radical anions and radical-anion pairs derived by electron attachment to simple organic molecules. The chemistry observed in these systems can be conveniently summarized by the following set of basic processes, where \( R \) is an alkyl group and \( X \) is either a halogen (Cl, Br, I) or a pseudo-halogen (CN, NC, NCO, NCS). The analogous reactions involving dimer radical anions \((RX)^-\_2\) can also be accommodated by this scheme.

<table>
<thead>
<tr>
<th>Process</th>
<th>Example</th>
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<tbody>
<tr>
<td>Electron Attachment</td>
<td>( RX + e \rightarrow [R^* \quad X^-] )</td>
</tr>
<tr>
<td></td>
<td>(la) CH(_3)NC (in CD(_3)CN)</td>
</tr>
<tr>
<td></td>
<td>( RX^- )</td>
</tr>
<tr>
<td>(lb) CH(_3)Br (in CD(_3)CN)</td>
<td></td>
</tr>
<tr>
<td>(lc) CH(_3)CN</td>
<td></td>
</tr>
<tr>
<td>Photodissociation</td>
<td>( RX^- + h\nu \rightarrow R^* + X^- )</td>
</tr>
<tr>
<td></td>
<td>(2a) (CH(_3))(_3)CNCO</td>
</tr>
<tr>
<td></td>
<td>[R*- --- X^-]</td>
</tr>
<tr>
<td>(2b) (CH(_3))(_3)CNCS</td>
<td></td>
</tr>
<tr>
<td>Thermal Dissociation</td>
<td>([R^* \quad X^-] \rightarrow R^* + X^- )</td>
</tr>
<tr>
<td></td>
<td>(3a) (CH(_3))(_3)Cl (in CH(_3))(_3)CNCO</td>
</tr>
<tr>
<td>Thermal Recovery</td>
<td>( R^* + X^- \rightarrow RX^- )</td>
</tr>
<tr>
<td></td>
<td>(4) CH(_3)CN</td>
</tr>
</tbody>
</table>
A few generalizations can be made about the scope of these reactions. Electron attachment to alkyl halides is generally found to be dissociative giving rise to either separated fragments as in (1a) or to a radical-anion pair as in (1b). On the other hand, electron attachment to molecules possessing π electron systems is predominantly non-dissociative, as in (1c), although CH₃NC constitutes an exception to this trend. The interconversions of the different paramagnetic species as represented by reactions (2a), (2b), (3a), and (4) are of particular interest. Both the radical anion RX⁻ and the radical-anion pair [R⁺ −− X⁻] can be regarded as intermediate stages in the overall process of dissociative electron attachment. However, if the dissociation of the radical anion is an endothermic process, the fragments produced by photodissociation in (2a) can recombine thermally in (4) to regenerate the radical anion. This type of behavior is exemplified by the nitrile systems.

There is a certain arbitrariness about defining a radical-anion pair in crystalline solids according to the observation of a magnetic resonance interaction between the nominally paramagnetic and diamagnetic fragments. At present it is impossible to state whether the radical-anion pair represents a true minimum in the potential energy curve or merely reflects constraints imposed by the crystalline lattice.

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REFERENCES


LEGENDS TO FIGURES

Figure 1. ESR spectra and spin density distributions for dimer (left side) and monomer (right side) radical anions of acetonitrile. The upper and lower spectra were obtained using CD$_3$C$^{14}$N and CD$_3$C$^{13}$C$^{14}$N, respectively. The dimer and monomer radical anions were produced in Crystal I and Crystal II, respectively, of acetonitrile by $\gamma$-irradiation at 77°K in the dark.

Figure 2. (A) ESR spectra of $\gamma$-irradiated 5 mole % CH$_3$Br in CD$_3$CN at 88°K. The upper spectrum was recorded before annealing. The middle and lower spectra were recorded after the sample had been warmed to 175°K for a few seconds. For comparison, the upper and middle spectra were recorded at the same gain whereas the lower spectrum was recorded at half the modulation amplitude and one-tenth the gain. (B) ESR spectra of $\gamma$-irradiated ca. 10 mole % tert-butyl iodide in tert-butyl isocyanate at 77°K. The upper spectrum was recorded before annealing and the middle spectrum was recorded at the same gain setting after 1 min at 150°K. The lower spectrum was recorded at a reduced gain (X 1/3) after prolonged annealing at ca. 150°K.

Figure 3. (A) ESR second-derivative spectra of $\gamma$-irradiated tert-butyl isocyanate at 77°K. The upper and lower spectra were recorded at the same gain settings before and after photobleaching with unfiltered
tungsten light. (B) ESR spectra of γ-irradiated crystalline tert-butyl isothiocyanate at 77°K. The upper spectrum was recorded during exposure of the sample to red light (Corning Filter No. 2030) and the middle spectrum during subsequent exposure to unfiltered tungsten light. The lower spectrum was recorded subsequently with the sample in the dark. These last two spectra were recorded at a reduced gain (X 0.8).
Figure 1  Bonin et al.