FEB 15 1968

COO-1385-22.

~~Conf-680827--1~~

MASTER

Conf-680806--5

SOME EFFECTS OF CRYSTAL STRUCTURE ON PRODUCTION OF RADICALS IN IRRADIATED CRYSTALS[1]

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Abstract

A series of anhydrous and hydrated polycrystalline metal acetates have been irradiated at 77°K with 1 mev. electrons and the ESR spectra observed. The principal stable free radical found in the hydrated materials is methyl whereas other species predominate in the anhydrous acetates and methyl radical is not observed. The absolute yield of methyl radicals, as well as the ratio of methyl to other species, appears to increase with the number of molecules of water of hydration. The radicals obtained by breaking C-C bonds are also found in irradiated sodium perfluorosuccinate hexahydrate and acetamide and it appears that such species may be favored in crystals whose structures are largely determined by hydrogen bonding.

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Radicals produced in irradiated crystals may usually be identified by their ESR spectra and detailed studies of single crystals lead to a rather complete picture of their structures (1,17). There is now enough information concerning the nature of the radicals produced under given conditions so that one can hope to predict the products of radiation damage of organic crystals in favorable cases. In order to be able eventually to select conditions to observe a given radical of interest, however, it will first be necessary to study in detail the factors which influence the nature of the radicals produced. These include the structure of the species irradiated, the crystal structure, the nature of the radiation used and the thermal history of the crystal.

Where a large enough series of chemically related species have been irradiated it is often possible to formulate some rules governing the radical species likely to be found. Studies of aliphatic amides (22) show that C-H bonds on carbon adjacent to nitrogen are likely to be broken preferentially and where these are absent (in the unsubstituted amides) C-H bonds on carbon adjacent to the carbonyl group tend to be broken. Some general rules can also be formulated for simple carboxylic acids, dicarboxylic acids (30,31) and amino acids (6,28), since these have been extensively studied. Aliphatic fluorine compounds appear to behave similarly with a C-F bond of the group adjacent to -COOH or $-CONH_2$ being broken in $CF_3CF_2CONH_2$ (13) and $HOO\underline{C}-CF_2-CF_2-COOH$ (23). However,as mentioned below,C-C bonds are also broken in some cases and the present work is part of a general study to determine the conditions under which C-C bond breakage is favored over other processes.

The temperature at which crystals are irradiated and observed and the thermal history of the crystals after irradiation prove to be of major mportance in determining the nature of the radicals, their orientation in the crystal lattice and their thermal motions. Recent studies (6,28-30) have shown that for many molecules irradiated at low temperature (often 77°K) the first paramagnetic species is produced by adding an electron (or hole). This species is usually not stable at higher temperatures and decays to give a "primary neutral radical"(6). In some cases this radical may change its orientation in the lattice as the temperature is raised or may rearrange or react to give the final species seen at high temperature. Thus, irradiation of alanine (28) leads first to the ion-radical $CH_3CH(NH_3^+)COOH^-$, stable at 77°K, followed by loss of NH_3 to give $CH_3\overset{\circ}{C}HCOOH$ at 140-150°K and eventually to reorientation of this radical by room temperature to give the arrangement responsible for the room temperature spectrum. In the interesting case of irradiated α-amino-isobutyric acid (7) the radical $(CH_3)_2\overset{\circ}{C}COO^-$ stable at intermediate temperatures gives three different sets of ESR spectra corresponding to three distinct environments for the radical at different temperatures.

It is often the case that the electron (or hole) attachment product is not seen at 77°K but that a different radical is stable at 77°K from that seen at 25°K. Irradiation of sodium acetate trihydrate at 77°K gives methyl radical (24) but at 25°C the principal product is $\cdot CH_2COO^-$; also, irradiation of CF_3CONH_2 leads to $\cdot CF_3$ at 77°K but to $\cdot CF_2CONH_2$ at room temperature (14,25).

Reactions of radicals first formed with other species in the crystal may also occur on warming or on standing. Intermolecular transfer of spins has been demonstrated in deuterium substituted alanine where $CH_3\overset{\circ}{C}HCOO^-$ comes to equilibrium with $CD_3\overset{\circ}{C}DCOO^-$ and partly deuterated species on standing at room temperature for a year or on heating at 150°C for an hour (15). The radical $\cdot CF_2COO^-$

produced in irradiated sodium chlorodifluoroacetate reacts with ions of the lattice, on standing for a year, to give $\cdot CFClCOO^-$ (26) and reacts very readily with oxygen gas to give a peroxide radical (27).

The effect of radiation on the nature of the stable radicals produced has not been systematically studied to any extent. Rather random observations available at present indicate that x-rays, γ-rays and high-energy electrons give about the same radicals. Photolysis often leads to similar radicals but by varying the wavelength of irradiation the products may be varied (5). It has also been found that bombardment by hydrogen atoms leads to stable radicals (9) and has the advantage that only one radical species is produced Saturated organic compounds suffer hydrogen abstraction whereas unsaturated molecules add a hydrogen atom in the examples studied (9).

One factor about which little is as yet known is the effect on the nature of the radicals produced of changes in the structure of the host crystal. It has been reported that the CO_2^- radical, which is obtained on irradiating sodium formate(19)is also present in the irradiated potassium salt and in several other irradiated metal formates(4).Similarly,irradiation of the potassium, calcium and lithium salts of glycollic acid (2,3),as well as the acid itself (2), leads to the radical $\overset{\circ}{H}C(OH)CO_2^-$. It is interesting that some of the hyperfine splittings differ substantially in the case of irradiated anhydrous lithium glycollate (20) and it has been proposed that the geometry of the radical is slightly different in this lattice. Cases are also known where essentially the same radical is produced on irradiating chemically different materials. The radical $\cdot CH_2COO^-$ (or its protonated form) is observed (26) in sodium acetate trihydrate irradiated at 25°C but is also a product of the irradiation of glycine (6,18). The radical $HOOCCH_2\dot{C}HCOOH$ is obtained from room temperature irradiation of succinic acid (21), maleic acid (10) and *dl*-aspartic acid (11).

We report here some observations on irradiated metal salts of acetic acid which suggest that changing the crystal structure by changing the number of molecules of water of crystallization may lead to quite different stable radicals at 77°K. It is hoped that further studies of the effects of crystal structure on the nature of the free radicals obtained on irradiation may aid in choosing conditions under which a given desired radical might be stable.

Experimental

The metal acetates were commercial reagent grade materials. Single crystals, where used, were grown from saturated aqueous solutions of the salts. Trapped radicals were produced by irradiation with the 1 m.e.v. beam of a General Electric Resonant Transformer and crystals could be irradiated at 77°K and observed at that temperature.

ESR spectra were taken with a Varian V-4200-10A spectrometer equipped with 100 kHz modulation. Hyperfine splittings were obtained by placing proton markers on the spectra and g-values were obtained from a measurement of the Klystron frequency.

Results

The ESR spectra of polycrystalline acetates irradiated and observed at 77°K lead to the g-values and hyperfine splitting constants shown in Table I. Details of the analysis of the spectra, where available, are given under the heading "Comments". The spectra for three representative crystals are shown in Fig. 1.

Discussion

It may be seen (Table I and Fig. 1) that the methyl radical becomes relatively more stable, and more are produced for a given dosage of radiation, as the number of molecules of water of crystallization increases. The spectra of the anhydrous acetates are too complex to interpret in detail but both the absolute concentration, and the relative amount of the methyl radical compared to other radical species, must be small.

A detailed analysis of the single-crystal ESR spectra of sodium acetate trihydrate at 77°K has been given (24);in that crystal the hyperfine interaction is nearly isotropic, with $A \cong 23$ Gauss, presumably as a result of rapid reorientation of the methyl group about its threefold axis combined with accidental near equality of $(A_{xx} + A_{yy})$ and A_{zz} for the anisotropic C-H interactions. The radical was identified as $\cdot CH_3$ (rather than $CH_3\overset{\circ}{C}OO^{-2}$) by the ^{13}C hyperfine interactions which are observed for $^{13}CH_3COONa \cdot 3H_2O$ but not for $CH_3{}^{13}COONa \cdot 3H_2O$. On this basis we assign the quartets with $A_H \cong 23G$ to $\cdot CH_3$ in all the irradiated acetates although ^{13}C substituted materials have not been examined. The methyl radical is also apparently present in irradiated acetamide and ammonium acetate although again, in the absence of ^{13}C hyperfine interaction data, there is also the possibility that these quartets with $A \cong 23$ Gauss are from radicals formed by electron attachment to a molecule of the lattice (or electron loss).

In irradiated anhydrous sodium and potassium acetate the principal radicals show anisotropic proton hyperfine interactions. The principal values observed (±28.5, ±20, ±9 Gauss) and (±32, ±23.6, ±14.5 Gauss) are not greatly different from values typical of $\cdot CH_2COO^-$; in irradiated malonic acid at 25°C (17) the principal tensor components for $\cdot CH_2COO^-$ are [-32.8,-21,-13.2] and [-32.5,-19.7,-10.7], while in $CH_3COONa.3H_2O$ at room temperature the values (26) are [±31.3,±19.0,±8.0]. On the basis of these observations the principal radical present in irradiated CH_3COONa and CH_3COOK is beleived to be $\cdot CH_2COO^-$. The precursor radical-ion $CH_3\dot{C}OO^{2-}$ with A_H = 21.0 G and g = 2.0030 has been reported (8) in irradiated sodium acetate at 77°K although it was not stated whether the salt was anhydrous or not. We have thus far failed to observe a radical with these parameters in either hydrated or anhydrous sodium acetate at 77°K ; the quartet in the ESR spectrum of the hydrated salt has A_H = 22.5 G and g = 2.0028 and almost certainly arises from the methyl radical (24).

It appears that the methyl radical is more stable in crystals with the more open structure characteristic of two- or three-dimensional hydrogen-bonded networks.The structure of zinc acetate dihydrate,for example, is known (32) and the acetate ions are tied together by hydrogen bonds in two-dimensional sheets with only weak Van der Waals forces between layers.Since the formation of $\cdot CH_3$ in hydrated acetates presumably is the result of dissociation of a precursor of the type $CH_3\dot{C}OO^{2-}$,which would be formed from the ion by gain (or possibly loss) of an electron, the CO_2 might be more readily lost in the more open crystal structure. In the anhydrous salt abstraction of a hydrogen atom from an ion of the lattice by the precursor radical to give $\cdot CH_2COO^-$ can be postulated. Spin-flip satellites, which are displaced from the main lines by ±5.6 G,are observed for $\cdot CH_3$ in the hydrated salts;they show that the radicals interact weakly with neighboring protons. The $\cdot CH_3$ lines disappear on warming for all the crystals in which they appear and are replaced at higher temperatures by the lines of $\cdot CH_2COO^-$ .We beleive this change is the result ofhydrogen abstraction by methyl (26). Strangely enough methyl radicals do not appear to be an important product of the irradiation of acetic acid itself at 77°K (16).

There is also some evidence that C-C bonds may be broken in amides.The methyl radical appears to be a product of the irradiation of acetamide (Table I) and the trifluoromethyl radical has been conclusively shown to be the principal product of the irradiation of CF_3CONH_2 at 77°K (25). Evidence that $\cdot CCl_3$ is the principal product of the irradiation of CCl_3CONH_2 (26) has also been found. Until complete single-crystal data are available for acetamide there remains a possibility that the quartet could arise from a species such as $(CH_3CONH_2)^{+ \text{ or } -}$ rather than $\cdot CH_3$; however,the molecule-ion,if present, should show extra hyperfine interactions which we do not see.

Another example of a hydrated salt which gives the stable radicals obtained from C-C bond breakage is sodium perfluorosuccinate hexahydrate. When irradiated at room temperature the principal product is $^{-}OOC\text{-}CF_2\text{-}\dot{C}F\text{-}COO^{-}$ (23) but at 77°K the ESR spectrum of CF_2COO^{-} is also seen (26). In this case the magnitude of the fluorine hyperfine splitting rules out the electron attachment products such as $^{-}OOC\text{-}CF_2\text{-}CF_2\text{-}\dot{C}OO^{-2}$ since β-fluorine splittings are much smaller. In a detailed study of the 77°K irradiation products of succinic acid (8) only the radical-ion $HOOC\text{-}CH_2\text{-}CH_2\text{-}\dot{C}OOH^{-}$ was mentioned. More recently it is claimed (12) that some of the weak lines are from $HOOC\text{-}CH_2\text{-}CH_2\cdot$, but $HOOC\text{-}CH_2\cdot$ has not been reported.

It has been shown that the nature of the stable radicals produced on irradiation of a given species, in this case acetate ion, can be influenced in an important way by the crystal structure of the host. At 77° the anhydrous alkali metal acetates give $\cdot CH_2COO^{-}$ as a principal product but the hydrated metal acetates give $\cdot CH_3$. We conclude that the products of breaking C-C bonds are more stable in crystals with water of hydration than in anhydrous crystals and tentatively suggest that one should expect such species to be favored in crystals where hydrogen bonding is important in determining the structure. The products of the irradiation of acetamide, trifluoroacetamide and sodium perfluorosuccinate hexahydrate are in agreement with this hypothesis but much more extensive data will be needed to develop a full understanding of this subject.

Acknowledgment

This work was supported through a contract with the Atomic Energy Commission and this is AEC Document No. C00-1385-20. We are indebted to the Department of Agricultural Engineering, Michigan State University, for the irradiations.

Table I. Production of $\cdot CH_3$ and $\cdot CH_2COO^-$ radicals in irradiated polycrystalline acetates and other crystals at 77°K.

Substance	$A \cdot CH_3$	$g \cdot CH_3$	$\cdot CH_2COO^-$ observed	Comments*
CH_3COONa	None	----	yes	Principal A values are 28.5, 20, 9 G.
$CH_3COO\ K$	none	---	yes	Principal A values 32, 23.6, 14.5 G. Very asymmetric pattern
$(CH_3COO)_2\ Hg$	None	----	,	Radicals not identified, very asymmetric pattern
$(CH_3COO)_2\ Ag$	None	----	?	Triplet observed at low microwave power
CH_3CONH_2	23.1	----	$\cdot CH_2CONH_2$	Both radicals present
CH_3COONH_4	23.0	2.0028	No	
$CH_3COO)_2 \cdot Ca\ H_2O$	23.0	2.0027	No	Very asymmetric pattern, other radicals present
$(CH_3COO)_2 \cdot Zn\ 2H_2O$	22.8	2.0027	No	$\cdot CH_3$ predominates, lines saturate easily
$(CH_3COO)_2Pb \cdot 3H_2O$	22.5	2.0029	No	Also a center line at $g = 2.0024$
$CH_3COO\ Na \cdot 3H_2O$	22.5	2.0028	No	Lines are 100x intensity of those for CH_3COONa
$(CH_3COO)_2Mg.\ 4H_2O$	22.5	2.0026	No	

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*All irradiations and ESR observations were at 77°K with about the same radiation dosage and the same microwave power attenuation (15 db). The error in the proton hyperfine splittings is estimated to be ±0.5 Gauss.

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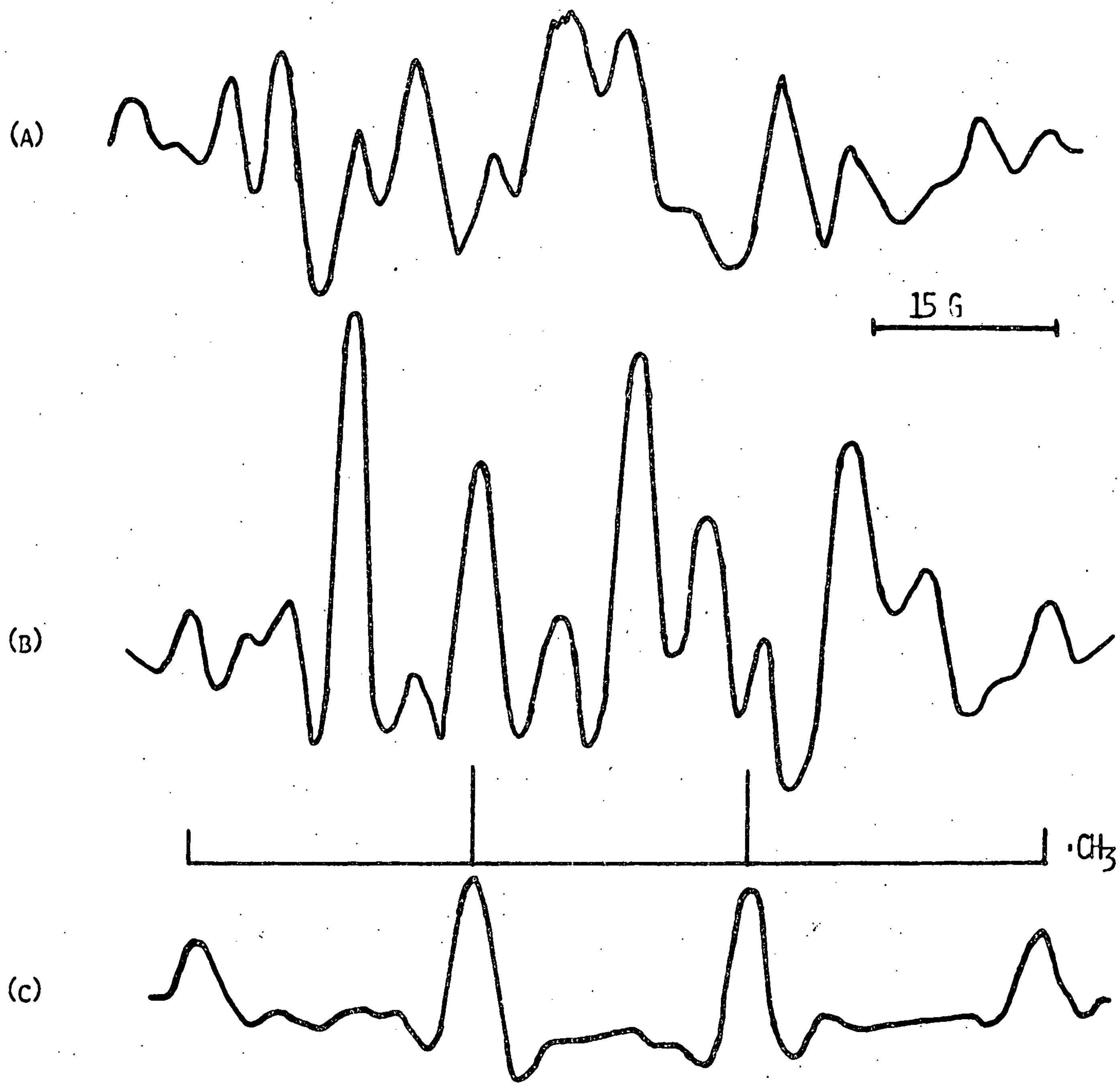

Fig. 1. Second-derivative ESR spectra of polycrystalline (A) potassium acetate, (B) calcium acetate monohydrate, and (C) magnesium acetate tetrahydrate irradiated and observed at 77°K with 15 db attenuation.