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EPR OF UV PHOTOLYZED TETRAMETHYLMONIUM ACETATE AND TRIBUTYLTIN ACETATE POWDERS

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ABSTRACT

The electron paramagnetic resonance investigation of tetramethylammonium acetate ($(CH_3)_4NCH_3COO$) and of tributyltin acetate ($(C_4H_9)_3SnCH_3COO$) powders under UV photolysis were carried out at 120 K. Some damage centers were formed by the UV photolysis which are attributed to \dot{CH}_3 and CO_2^- radicals in the first substance and to $CH_3\dot{C}OO$ radical in the second. The *g* values of the radicals were found to be 2.0642, 2.0305 and 2.0058 respectively. No signals were detected at different doses of the gamma irradiation and UV photolysis for both samples at the room temperature.

Key Words: EPR; UV photolysis; Tetramethylammonium acetate; Tributyltin acetate

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INTRODUCTION

It is well known that the irradiation of solids by gamma, x-rays, and UV light produce trapped radicals and that an EPR investigation of these radicals can provide very useful information. Free methyl radicals have been observed by many authors in various matrixes containing the methyl groups¹⁻⁷. CO_2^- radicals were reported in Tinoxsalate ($g_{av} = 2.0022$) and potassium format ($g_{av} = 2.0048$) by Atkins et al.⁸ and in some cereals, legumes and glucose samples under photolysis at 123 K (their g values were between 2.0010 and 2.0036) by Çakir et al.⁹ This radical was unstable at room temperature in these last matrixes and in lithium acetate by Nunome et al.⁷ In the literature, some EPR studies exist for free methyl radical. $CH_3\dot{C}OO$ -radical in gamma irradiated acetylcholine bromide single crystals and powders¹⁰, and $CH_3CO_2^{2-}$ radical in x-ray irradiated strontium and zinc acetate single crystals¹¹ have been reported.

In this paper, we report the EPR spectra of UV photolysing products. To our knowledge $(C_4H_9)_3SnCH_3COO$ (TBTA) and $(CH_3)_4NCH_3COO$ (TMAA) powders at 120 K have not previously been investigated. The spectra indicate the occurrence of \dot{CH}_3 and CO_2^- radicals in TMAA, and the $CH_3\dot{C}OO$ radical in TBTA. In both substances, no radical was observed by gamma irradiation and by UV photolysing at room temperature.

EXPERIMENTAL

The $(CH_3)_4NCH_3COO$ used for this experiment was prepared from $(CH_3)_4NI$ and $AgCH_3COO$, both of which were obtained commercially. When the aqueous solution of $(CH_3)_4NI$ and $AgCH_3COO$ were prepared, they were mixed in a 1:1 stoichiometric proportion in order for anion or cation exchange. The precipitated AgI was then filtered out and the residual aqueous solution was $(CH_3)_4NCH_3COO$. Since this substance is highly hydroscopic, we could not obtain its single crystals in several attempts in a desiccator.

Tributyltin acetate was also obtained from a commercial source. It gives very fine and flexible crystals by slow evaporation in acidic medium. Therefore its powder form was used for the EPR experiment.

The ultraviolet photolysis was carried out directly in the EPR cavity by a Conrad Hannovia 1 kW Xenon lamp. The EPR spectra were recorded with an X-band Varian E-109C model EPR spectrometer using 10 dB microwave power and 100 kHz modulation. The low temperature measurements were carried out using a Varian variable temperature control unit. The g values were determined by comparison with a standard DPPH sample



of $g = 2.0036$. Gamma-irradiation of the powders of TMAA and TBTA have been made at ambient temperature by a ^{60}Co source of ≈ 1.5 Mrad/h.

RESULTS AND DISCUSSION

Tetramethylammonium Acetate

The EPR spectrum of TMAA powder UV photolyzed for 15 min exhibits a quartet with intensity distribution of 1:3:3:1 with 23.0 \pm 0.5 Gauss line spacing and a broad singlet starting at the end of quartet at 120 K as shown in Fig. 1. When the temperature is raised to room temperature, all of the signals disappear. It is, therefore, concluded that the species is not stable at room temperature. The quartet and its relative intensity indicate that the unpaired electron spin interacts with a methyl group. This can be interpreted in terms of the $\dot{\text{C}}\text{H}_3$ radical, which was also observed by Rogers and

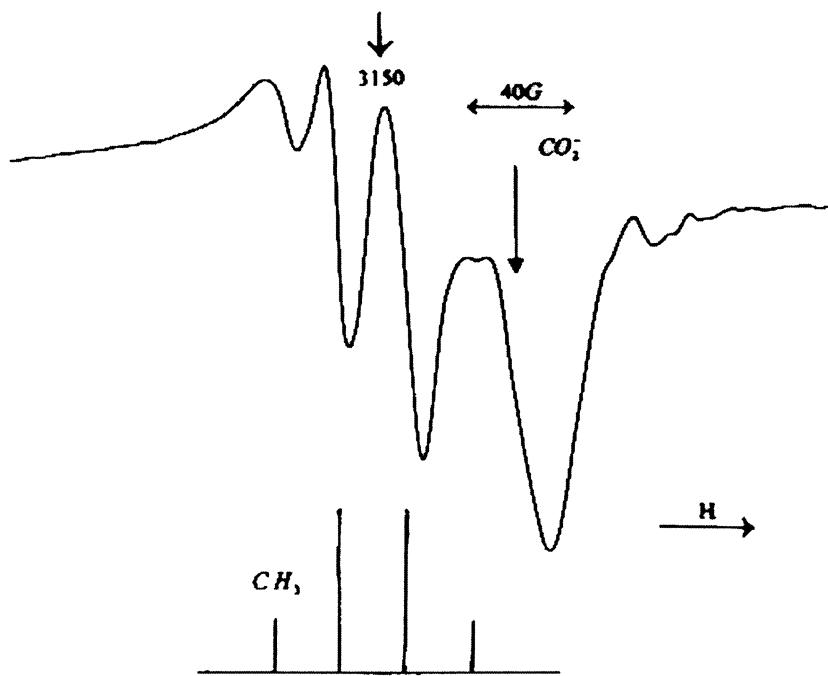


Figure 1. The EPR spectrum of TMAA powder UV photolyzed for 15 min at the 120 K temperature.



Kispert⁵ in sodium acetate trihydrate irradiated by 1 MeV electrons under similar conditions and by also Tolles et al.⁴ in zinc acetate dihydrate irradiated by x-rays. In the latter study, the decay of initially formed methyl radical is accompanied by a corresponding increase in another species shown to be the $CH_2CO_2^-$ radical. The suggested mechanism for this was a simple abstraction of a hydrogen atom by the methyl radical from a neighbouring acetate ion. The g value of the radical was found to be $g = 2.0642 \pm 0.0005$. In the present work, this value is somewhat greater than the values obtained by other workers¹. However the hyperfine coupling agrees well with the hyperfine coupling constant of freely tumbling methyl radical in the solution and in an inert-gas matrix that is 23.023 G (see reference 5).

A broad singlet in the spectrum is attributed to the CO_2^- radical. This signal appears together with the \dot{CH}_3 radical signal after a few minutes of UV photolysis. This radical was observed to be unstable at room temperature as seen by Çakir et al.⁹ as found in some cereals, legumes, and glucose samples under UV photolysis at 123 K. In addition to the \dot{CH}_3 and $\dot{CH}_2CO_2^-$ radicals, EPR studies of triplet radical pairs of CO_2^- were reported in gamma-irradiated single crystals of $LiCH_3COO \cdot 2H_2O$ at 77 K by Nunome et al.⁷. Upon annealing the irradiated crystals to room temperature for 2 min, a single line spectrum which was attributed to the isolated CO_2^- radicals appeared together with the $\dot{CH}_2CO_2^-$ radicals. The isotropic value of g tensor of the isolated CO_2^- radicals were found to be 2.0003.

Another species from the $\dot{CH}_2CO_2^-$ radical was also observed in freshly irradiated zinc acetate dihydrate crystals at room temperature⁴. This unidentified species appears as a broad singlet at $g = 2.0000$ and disappears at room temperature in about one day. This unidentified species was also observed in irradiated sodium acetate and was not attributed to the any radical¹².

The observed value of CO_2^- radicals in TMAA is $g = 2.0305 \pm 0.0005$, and this value is greater than the values given in literature^{7,8,9}. This case may be explained by effects of polarization.

Tributyltin Acetate

The EPR spectrum of TBTA powder UV photolyzed for 20 min exhibits a quartet with an approximate intensity distribution of 1:3:3:1 with a line spacing of 16.0 ± 0.5 Gauss at 120 K temperature, as shown in Fig. 2. The spectra do not change significantly between 120 K and 200 K, but the intensity of signals decreased after 200 K and completely disappeared at room temperature. This behaviour observed in the spectra is due to the



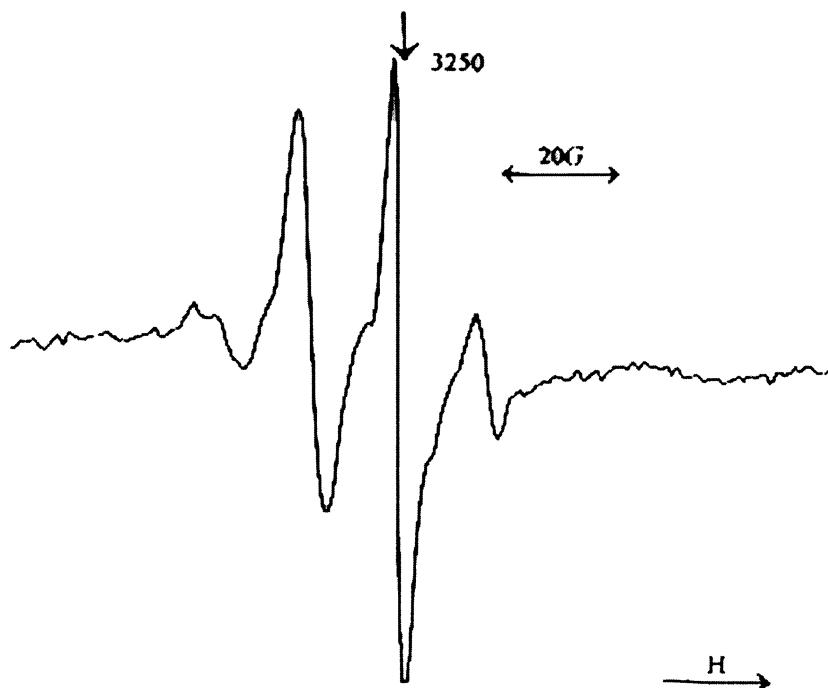


Figure 2. The EPR spectrum of TBTA powder UV photolyzed for 20 min at the 120 K temperature.

$CH_3\dot{C}OO$ radical. A similar radical was also observed in x-ray irradiated acetic acid¹³. In this study the hyperfine coupling of the unpaired electron to the CH_3 protons was found to be 15 Gauss. A similar radical was also observed in gamma irradiated acetylcholine bromide and in acetylcholine iodide single crystals¹⁰. In Ref.¹⁰ for both substances the coupling was found to have a value of 17 Gauss, and the $CH_3\dot{C}OO^-$ radical was seen to be stable at room temperature. The coupling of the β protons in the CH_3 radical occurs primarily through hyperconjugation and its magnitude should depend on the dihedral angle, θ , between the β -proton $C-H$ bond and α -proton $2p_z$ orbital which contains the unpaired electron. The proton coupling constant is given by¹⁴

$$A_\beta = B_0 + B_1 \cos^2 \theta \quad (1)$$

where B_0 is a constant includes contributions from spin density which arise from conformation – independent mechanisms, in particular spin



polarisation, B_1 includes the hyperconjugate contributions. In the case of rapid rotation about $C_\alpha - C_\beta$ bond the average value of A becomes

$$a_\beta = B_0 + B_1/2 \quad (2)$$

In this equation $B_0 = 0 - 3.5 \text{ G}^{14,15}$ and $B_1 = 32.1 \text{ G}^{16}$ which was earlier measured as 30 G assuming that the methyl group ceased its rotation around the $C_\alpha - C_\beta$ bond at 77 K, and one of the $C-H$ bonds is coplanar with the p orbital¹³. If these values are replaced in Eq. (1), $a = 16.05 - 19.55 \text{ G}$ can be obtained. In this study the value $a_\beta = 16 \text{ G}$ was found in the same range. The spin density distribution on the CH_3 protons of $CH_3\dot{C}OO$ radical is only 70% of that found for the free methyl radical. This value is also in agreement with the β -proton couplings for $(CH_3 - CH_2)_3\dot{C}$ (17.3 G) $(CH_3)_2\dot{C}CH_2CH_3$ (17.6 G), $> \dot{C}-CH_3$ (17.16 G)^{17,18} and $CH_3\dot{C}OO^-$ (17 G)¹⁰.

Methyl groups undergo restricted reorientation about a $C-C$ bond. In cases such as the $CH_3CHCOOH$ radical trapped in alanine^{19,20}. Their rotation is nearly quenched below 100 K, but the methyl group of the radical $CH_3C(COOH)_2$ in irradiated malonic acid executes nearly free rotation even at 4.2 K²¹. Restricted torsional motion of a methylene group about a $C-C$ bond was also been found in an irradiated crystal of hexamethylene-diammonium adipate²². An EPR study of x-ray irradiated single crystals of zinc acetate dihydrate, $Zn(CH_3COO)_2 \cdot 2H_2O$, was reported by Ohigashi and Kurita²³. In their study the trapped radicals were identified as CH_3 and CH_2COO at 77 K. Free methyl radical disappears above 150 K but the second is stable and persists up to 370 K. A marked temperature dependency has been found in the absorption spectra of the radical CH_2COO from which it is concluded that the motion (*i.e.*, rotation about the $C-C$ bond) of CH_2 group is quenched at low temperatures but undergoes rapid reorientation around the $C-C$ bond above room temperature.

In the EPR study of x-ray irradiated single crystals of strontium acetate hemihydrate, the $CH_3\dot{C}O_2^{2-}$ radical was observed which is a different methyl radical as seen in other acetates¹¹. At higher temperature this radical was seen to be replaced with two magnetically distinct $\dot{C}H_2CO_2^-$ radicals. In the presence of the propionate ion, further reaction takes place at about -30°C to yield one rotamer of one magnetically distinct $CH_3\dot{C}HCO_2^-$ radical. In $CH_3\dot{C}O_2^{2-}$ radical the unpaired electron is localized on one of the oxygen atoms. The four-line isotropic hyperfine coupling is 33.15 MHz (11.8 G) reported in Ref. ¹¹ By comparing isotropic hyperfine values of the $CH_3\dot{C}OO^-$ radical with the $CH_3\dot{C}O_2^{2-}$ radical it can be seen that unpaired electron density on the methyl group is more favourable than the $CH_3\dot{C}O_2^{2-}$ radical.



The g value for the $CH_3\dot{C}\bar{O}O$ radical is 2.0058 ± 0.0005 and this is slightly larger than the $g = 2.0044$ of the $CH_3\dot{C}\bar{O}O$ -radical¹⁰; and that of $g = 2.0032$ for the $CH_3\dot{C}OOH$ radical¹⁶. The g tensor for the $CH_3\dot{C}\bar{O}O$ -radical appears to be slightly anisotropic. This anisotropy is attributed to the spin distribution of the unpaired electron as well as the oxygen atoms that lower the symmetry. This same phenomenon should also be true for the $CH_3\dot{C}\bar{O}O$ radical and contribute to the asymmetry of the spectrum together with partly restricted rotation or torsion of the methyl group radical. No signal was observed in gamma irradiated and UV photolyzed TMAA and TBTA at room temperature probably due to instabilities of the produced species.

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