SHORT PAPER

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Electron paramagnetic resonance of gamma irradiation damage centres in acetyl and carbamyl-β-methyl choline chloride

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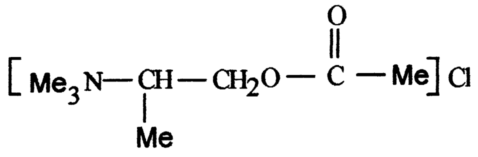
The EPR spectra of γ-irradiated powders of acetyl-β-methyl choline chloride (AβMCCl) and carbamyl-β-methyl choline chloride (CβMCCl) indicated the existence of the $[\mathrm{Me_3N\dot{C}MeCH_2OCOMe}]\mathrm{Cl}$ radical in the former and of the $[\mathrm{Me_3N\dot{C}MeCH_2OCONH_2}]\mathrm{Cl}$ radical in the latter.

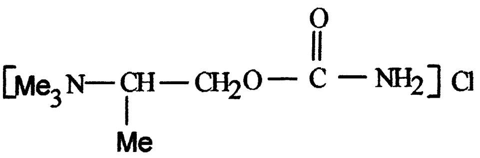
Keywords: EPR, γ-irradiation, acetyl-β-methyl choline chloride

The radiation sensitivity of biologically important choline derivatives has long been recognised.[1,2] Selective deuteration of choline chloride has been employed to establish the localisation of the unpaired electron in the radical using EPR techniques.[3] Although the spectra were not well resolved they were attributed to the radical $\dot{\mathrm{C}}\mathrm{H_2CH_2OH}$. The EPR spectra of radiation-damage centres in choline chloride were interpreted[4] also as being due to a biradical. The EPR spectra of irradiated choline iodide and choline sulfate were examined; it was observed that the radicals formed in all analogues except choline chloride and choline bromide were not hydroxyethyl radicals, but a detailed analysis of their spectra was not attempted.[5] In addition, the EPR studies of γ-irradiated acetyl choline iodide and bromide,[6] carbamyl choline chloride[7] and methoxycarbamylcholine picrate hemihydrate[8] were investigated. To our knowledge, acetyl-β-methylcholine chloride **(1)** and carbamyl-β-methylcholine chloride **(2)** have not been studied so far, and we have now undertaken a study of these compounds.



$[\mathrm{Me_3N{-}CH(Me){-}CH_2O{-}C({=}O){-}Me}]\,\mathrm{Cl}$

1



$[\mathrm{Me_3N{-}CH(Me){-}CH_2O{-}C({=}O){-}NH_2}]\,\mathrm{Cl}$

2

The EPR spectrum of the γ-irradiated AβMCCl powder at room temperature is shown in Fig.1.The unpaired electron couples with three equivalent methyl protons and one of the methylene protons, which are all magnetically equivalent ,and shows a multiplet, with intensity distribution of 1:4:6:4:1 (five lines), which is further split by coupling to the nitrogen (I=1). Therefore, the radical formed by abstraction of a proton from the AβMCCl is given in structure **3**.

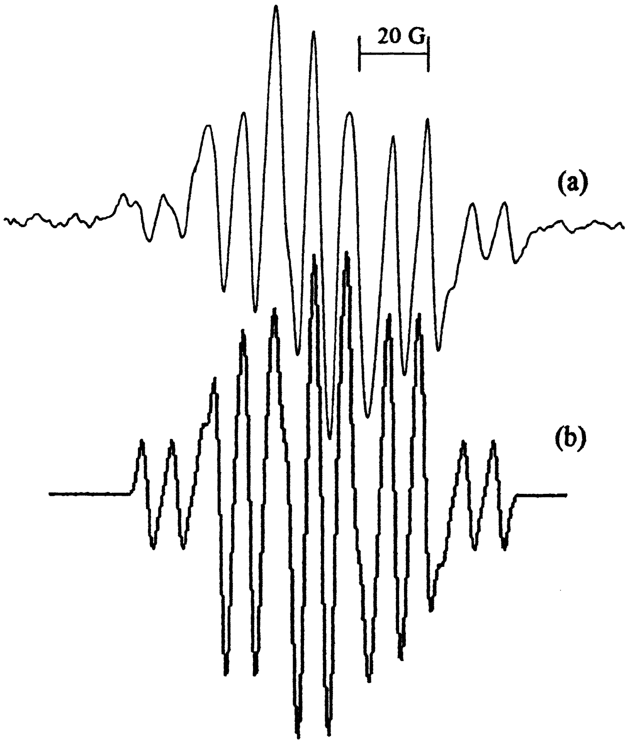
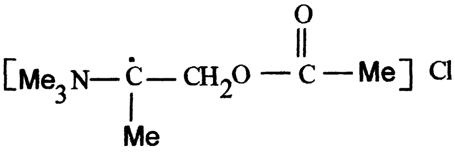


Fig. 1 The EPR spectrum of γ-irradiated acetyl β-methyl choline chloride powder at room temperature (a), and simulation of the spectrum (b).

A simulation of the spectrum is shown in Fig.1, using the hyperfine coupling constants a_{CH3} = 23 G and a_{CH} = 21 G, a_{N} = 9.6 G. The measured value of the g factor is g = 2.0048±0.0005.



$[\mathrm{Me_3N{-}\dot{C}(Me){-}CH_2O{-}C({=}O){-}Me}]\,\mathrm{Cl}$

3

In spite of several attempts, a single crystal of CβMCCl was not obtained. The γ-irradiated powder of this compound gives the spectrum shown in Fig.2 at room temperature. The

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

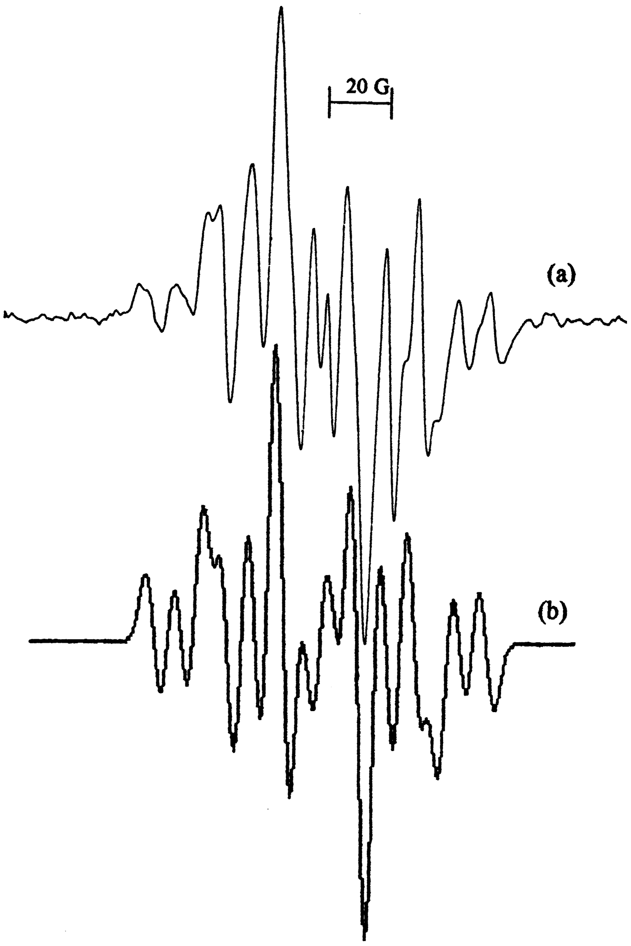
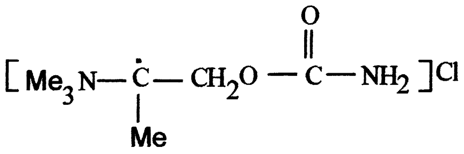


Fig. 2 The EPR spectrum of γ-irradiated carbamyl β-methyl choline chloride powder at room temperature (a), and simulation of the spectrum (b).



$$\left[\mathrm{Me_3N{-}\underset{\underset{Me}{|}}{\dot{C}}{-}CH_2O{-}\overset{\overset{O}{\|}}{C}{-}NH_2}\right]\mathrm{Cl}$$

4

spectrum can again be interpreted as a 1:1:1 triplet of 1:4:6:4:1 quintets. With the hyperfine constants a_{CH3} = 23 G, a_{CH} = 18 G, a_N = 9 G and the g factor is g = 2.0048±0.0005.

Therefore, the paramagnetic centre can be attributed to the radical **(4).** The simulation of the powder spectrum, with the values given above, is shown in Fig.2.

In both the radicals 3 and 4, only one of the two methylene protons shows a resolvable coupling. This can be ascribed to the fact that β-coupling is angle-dependent as expressed in Equation (1).

$$a_\beta = B_o + B_1 \cos^2\theta \qquad (1)$$

where B_o is the spin polarisation contribution (B_o = 0-3.5 G), B_1 is the hyperconjugative contribution (≈ 50 G) and θ is the angle between the π orbital and the C–H bond projections on a plane perpendicular to the C_α–C_β bond direction.

Presumably the "invisible" proton lies close to the model plane of the singley-occupied *p*-orbital, so that θ = *ca*90°, and the major second term in the equation is close to zero.

In conclusion we can state that γ-irradiation produces free radicals in AβMCCl and CβMCCl by loss of the hydrogen atom from the CHMe group.

Experimental

The compounds used in this study were obtained from commercial sources: Aldrich and Sigma catalogues. The samples were irradiated at room temperature with a ^{60}Co γ- ray source at 1.5 Mradh^{-1} for 1h. The EPR spectra were recorded at room temperature with a Varian X-band E-109 C model spectrometer by using 100 kHz modulation. The *g* factors were determined by comparison with a diphenylpicryl-hydrazyl sample of *g* = 2.0036.

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