Electron Spin Resonance Spectrum of the Acetyl Radical

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Although the formyl radical has been studied in detail by e.s.r. spectroscopy and its structure elucidated,[1–3] the e.s.r. spectrum of the acetyl radical has not been conclusively identified. Indeed, previous assignments of the spectrum of the acetyl radical have differed considerably. Morton and Falconer[4] observed a spectrum consisting of four hyperfine lines (splitting 16·4 Oe), when biacetyl was photolysed at 77° K, which they attributed to the acetyl radical. Judeikis and Siegel[5] observed a quartet (splitting 5·2 Oe) during the photolysis of ethanol at 77° K and suggested that it arose from the acetyl radical. In the liquid phase, Chiang *et al.*[6] have attributed a quartet (splitting 21·2 Oe), which was observed during the reaction between Ti^{III}–H_2O_2 and acetaldehyde in an aqueous flow system, to the acetyl radical.

We report the preparation of the acetyl radical by the reaction between acetyl chloride and potassium atoms at 77° K in a rotating cryostat and the subsequent observation and analysis of its e.s.r. spectrum. Briefly, the technique,[7] consists of laying down alternate layers of acetyl chloride and potassium atoms from the gas phase on the outer surface of a stainless-steel drum which is filled with liquid nitrogen and rotates rapidly in a high vacuum. Secondary reactions are prevented by using a third, inert, material as the bulk of the deposit in which the primary acetyl radical is trapped.

The acetyl radical has been trapped successfully in matrices of D_2O, C_6D_6, cyclohexane, and camphane. The e.s.r. spectra of the acetyl radical in all of the matrices are virtually the same; that observed in C_6D_6 is shown in

Figure (a). This spectrum can be analysed in terms of approximately axially symmetric g- and hyperfine tensors, the values of which are: $g_\perp = 2{\cdot}0034 \pm 0{\cdot}0005$, $A_\perp(\mathrm{CH_3}) = 4{\cdot}6 \pm 0{\cdot}5$ Oe; $g_\parallel = 1{\cdot}9952 \pm 0{\cdot}0005$, $A_\parallel(\mathrm{CH_3}) = 6{\cdot}0 \pm 0{\cdot}5$ Oe.

The spectrum of the deuteriated acetyl radical, $\mathrm{CD_3\dot{C}O}$, [Figure (b)] confirms the assignment of the principal g-values, the corresponding values being, $g_\perp = 2{\cdot}0036 \pm 0{\cdot}0005$; $g_{\parallel} = 1{\cdot}9960 \pm 0{\cdot}0005$.

The principal values of the g-tensor for the acetyl radical are almost identical with those of the formyl radical,[1] $g_x = 2{\cdot}0041$; $g_y = 2{\cdot}0027$; $g_z = 1{\cdot}9960$, and this suggests that the structures of the two radicals are very similar. E.s.r. studies[1,2] of the formyl radical show that it is a σ-radical with the unpaired-electron located mainly in an sp hybrid orbital on the carbon atom. The H–C–O angle has been determined from measurements[3] of the carbon-13 hyperfine coupling-constants to be 125°, which is in good agreement with the values[8,9] (120° and 124°) obtained by optical spectroscopy.

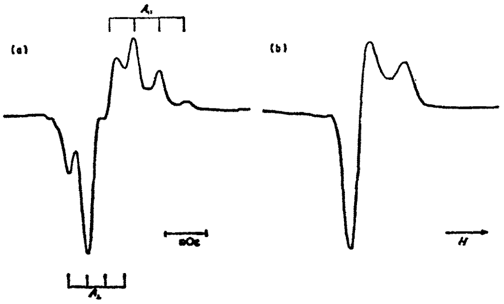

FIGURE *First derivative e.s.r. spectra at* 77° K *of* (*a*) $\mathrm{CH_3{\cdot}\dot{C}O}$, (*b*) $\mathrm{CD_3{\cdot}\dot{C}O}$

The isotropic hyperfine coupling in the acetyl radical is 5·1 Oe which is close to the value obtained by Judeikis and Siegel[5] in irradiated ethanol and confirms their tentative identification of the radical. The small hyperfine-coupling contrasts markedly with the very large coupling (136 Oe) observed in the formyl radical, which has been attributed mainly to the participation of the excited state, H· :C=O, in the structure of the radical.[1] For the methyl coupling in the acetyl radical it is not essential to postulate a similar delocalization of the electron as the observed splitting could arise from the normal interactions operative in π-radicals. However, as the R–CO bond strengths in both radicals are very low (10—20 kcal. mole^{-1}) it is feasible that a comparable participation of the excited state, $\mathrm{\dot{C}H_3}$:C=O, may also occur in the acetyl radical. Thus, it is interesting to compare the ratio of the hyperfine coupling-constant in $\mathrm{H\dot{C}O}$ to that of the free hydrogen atom with the corresponding ratio for $\mathrm{CH_3\dot{C}O}$ and $\mathrm{\dot{C}H_3}$. These ratios are $A(\mathrm{HCO})/A(\mathrm{H}) = 0{\cdot}27$ and $A(\mathrm{CH_3CHO})/A(\mathrm{CH_3}) = 0{\cdot}22$, which, when any other coupling mechanisms are neglected, represent the corresponding spin densities on the substituent groups, and thus show that the contributions of the excited states are similar in both the formyl and acetyl radicals.

(*Received, November* 8*th*, 1968; *Com.* 1522.)

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