Electron Spin Resonance Spectrum of an Intermediate in the Reduction of Benzoic Acid by e^-_{solv}

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NUMEROUS accounts[1] have appeared of e.s.r. spectra produced by the rapid oxidation of organic molecules in continuous-flow systems by powerful one-equivalent oxidants. We report one example of a continuous-flow reduction using the most effective reductant e^-_{solv}, in liquid ammonia to produce a new, simple aromatic radical anion.

When 10^{-2}M solutions of both $PhCO_2H$ and sodium in liquid ammonia are mixed continuously (flow rate 4—5 cm.^{3} sec.$^{-1}$) in the cavity of an e.s.r. spectrometer in a multicapillary mixing device based on a design of Moskowitz and Bowman,[2] the spectrum shown (Figure) is obtained. This has been analysed in terms of two equivalent protons of one kind (a 4·2 Oe), two equivalent protons of a second kind (a 0·82 Oe), and one further proton (a 7·7 Oe), and a computer-simulated spectrum based on these coupling constants is presented. The g value of the spectrum is 2·0034. In view of the extensive ionisation of the acid in liquid ammonia we assign the spectrum to the $PhCO_2^{2-}\cdot$ ion.

While e.s.r. spectra of the species $X\text{-}C_6H_4\text{-}CO_2^{2-}\cdot$ obtained by the reduction of $X\text{-}C_6H_4\text{-}CO_2H$ are well-documented in cases where X is sufficiently electron-attracting to stabilise the radical anion $PhX^-\cdot$ (*e.g.* $X = NO_2$,[3] $X = CN$,[4] $X = CO_2R$ [5]), it is only recently that accounts have appeared of unsubstituted analogues. Bennett and Gale[6] report that $PhCO_2H^-\cdot$ prepared in a solid matrix by the rotating-cryostat method, is characterised by a spectrum consisting of a poorly resolved basic quartet (a 5·8 Oe), which they assign on the basis of approximately equal splittings from the *o*- and *p*-protons. However, the similar radical, $PhCO_2Me^-\cdot$, prepared by Hirayama[7] by electrolytic reduction, shows a quite different pattern of coupling constants (a_2 4·20, a_3 0·94, a_4 7·64, and a_{Me} 0·94 Oe), as do the phthalate half-ester dianion radicals,[5] $RO_2C\cdot C_6H_4\cdot CO_2^{2-}\cdot$ (for R = Me,

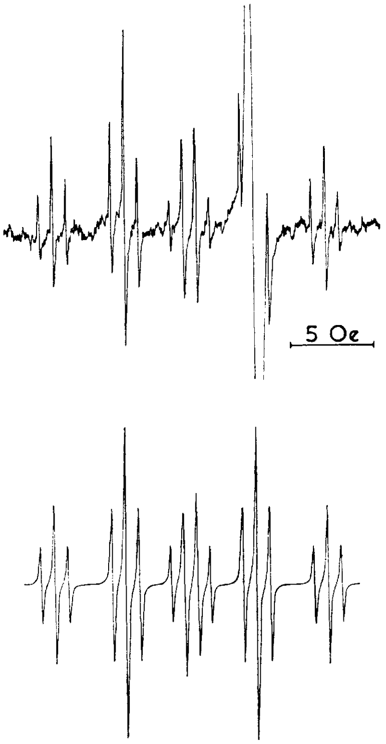

FIGURE. *The e.s.r. spectrum (top) of* $PhCO_2^{2-}\cdot$ *in liquid ammonia. The strong signal* (g = 2·0011) *on the right is due to* e^-_{solv}. *The computer simulation (bottom) is based on coupling constants given in the text.*

a_2 3·68, a_3 0·88, and a_4 7·35 Oe). Our results are in good agreement with those of Hirayama and Nelsen and indicate that the radicals have a spin-density distribution more similar to, say, the benzonitrile anion[4] (a_2 3·6, a_3 0·30, and a_4 8·42 Oe in dimethylformamide), than to the benzyl radical[8] (a_2 5·17, a_3 1·77, and a_4 6·19 Oe) as suggested by Bennett and Gale.

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