The Electron Spin Resonance Spectra of Styrene Monomer Radical-anions

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Summary Reduction of styrene and *m*-fluorostyrene by solutions of sodium in liquid ammonia in a flow system yields the monomeric radical-anions identified by e.s.r.

THE monomeric radical-anion of styrene ($\text{sty}^{\overline{\cdot}}$) has long evaded definitive spectroscopic characterisation despite its well-established role as the reactive monomer species in the copolymerisation of styrene and methyl methacrylate by suspensions of lithium in tetrahydrofuran[1] (THF) and the anionic polymerisation of styrene by solutions of sodium naphthalene in THF.[2] The most authentic optical spectrum is that of Hamill and his co-workers[3,4] who γ-irradiated 0·1M solutions of styrene in 2-methyltetrahydrofuran at 77° K to obtain $\text{sty}^{\overline{\cdot}}$ by electron capture from the solvent ($\lambda_{\max}$ 410 and 600 nm, $\epsilon_{410} = 2{\cdot}3 \times 10^4$ l.mole^{-1}cm.$^{-1}$, $\epsilon_{600} = 5 \times 10^3$ l.mole^{-1}cm.$^{-1}$). This assignment is partly supported by the quite similar spectrum of $\text{sty}^{\dot{+}}$ obtained by the same group[4] on γ-irradiation of 0·3M styrene in sec-butyl chloride at 77° K. Efforts to obtain an optical spectrum of $\text{sty}^{\overline{\cdot}}$ by pulse radiolysis (p.r.) have resulted in a confused situation. P.r. of pure liquid styrene produces several absorptions with differing decay times,[5,6] but that at 370 nm ($t_{\frac{1}{2}}$ *ca.* 4 μsec) has been assigned[5] to $\text{sty}^{\overline{\cdot}}$; p.r. of dilute solutions of styrene in cyclohexane[7] and dioxan[8]

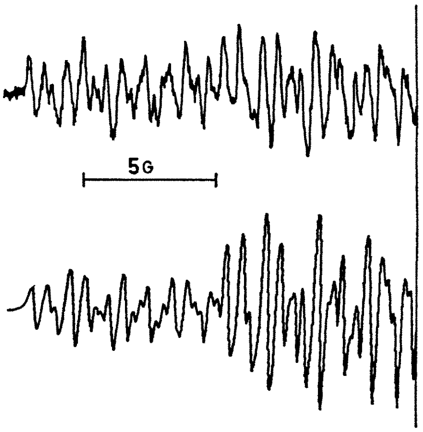
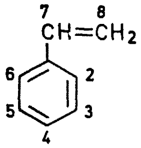


FIGURE. *E.s.r. spectrum* (*top*) *of styrene radical-anion and* (*bottom*) *computer simulation using coupling constants given in the text* (*only half the spectrum is shown*).

produces absorptions at 390 and 320 nm respectively but these are not assigned to sty$^{\overline{\cdot}}$. E.s.r. studies of sty$^{\overline{\cdot}}$ and its analogues in irradiated low-temperature glasses are frustrated by the broad nature of the resulting spectra.[9]

We have obtained reasonably well-resolved e.s.r. spectra of sty$^{\overline{\cdot}}$ and *m*-fluorosty$^{\overline{\cdot}}$ by flowing and rapidly mixing *ca.* 10^{-2}M solutions of sodium and of the corresponding styrene both in liquid ammonia in the spectrometer cavity using a multi-capillary mixing device described previously.[10] Analysis of the spectrum of sty$^{\overline{\cdot}}$ (Figure) gives coupling constants corresponding to six different single protons and one pair of equivalent protons. Preliminary theoretical calculations indicate the tentative assignments shown in the Table; at present a definite assignment cannot be made between the two *ortho* and the *meta* positions.

Coupling constants (in Gauss) for sty and$^{\overline{\cdot}}$ m-*fluorosty*$^{\overline{\cdot}}$



	sty$^{\overline{\cdot}}$	m-fluorosty$^{\overline{\cdot}}$
a_8	7·35	7·66
a_7	1·51	1·55
a_2,a_6	3·82,2·00	3·98,2·43
a_3,a_5	0·86,0·59	1·00,1·22(F)
a_4	5·50	5·23

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[1] K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Science*, 1958, **31**, 115, 123.

[2] M. Szwarc, M. Levy, and R. Milkovich, *J. Amer. Chem. Soc.*, 1956, **78**, 2656.

[3] M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Amer. Chem. Soc.*, 1962, **84**, 4230.

[4] T. Shida and W. H. Hamill, *J. Chem. Phys.*, 1966, **44**, 4372.

[5] D. J. Metz, R. C. Potter, and J. K. Thomas, *J. Polymer Science*, 1967, **A5**, 877.

[6] C. Schneider and A. J. Swallow, *J. Polymer Science*, 1966, **B4**, 277.

[7] J. P. Keene, E. J. Land, and A. J. Swallow, *J. Amer. Chem. Soc.*, 1965, **87**, 5284.

[8] K. W. Chambers, E. Collinson, F. S. Dainton, W. A. Seddon, and F. Wilkinson, *Trans. Faraday Soc.*, 1967, **63**, 1699.

[9] J. Lin, K. Tsuji, and F. Williams, *Trans. Faraday Soc.*, 1968, **64**, 2896 and references cited therein.

[10] A. R. Buick, T. J. Kemp, G. T. Neal, and T. J. Stone, *J. Chem. Soc.* (*A*), 1969, 666.