Electron Spin Resonance Spectra of Cyclohexadienyl Radicals

By Peter G. Cookson, Alwyn G. Davies,* and Brian P. Roberts
(*Chemistry Department, University College London,* 20 *Gordon Street, London* WC1H 0AJ)

Summary The e.s.r. spectra of a number of radical adducts, [XArH]·, of 1,3,5-tris(trimethylsiloxy)benzene [ArH] have been measured in hydrocarbon solvents; the rate constant for the self-reaction of the radicals is 1·7 × 10^6 l mol^{-1} s^{-1} (at −88 °C) when X = $PhCO_2$, and 5·7 × 10^6 l mol^{-1} s^{-1} (at −86 °C) when X = F_3C.

The contribution which e.s.r. spectroscopy has made to the understanding of homolytic aromatic substitution has been restricted by the limited conditions under which the spectra of the intermediate cyclohexadienyl radicals have been observed. Partly as a consequence of this, the system is beset by many unsolved problems.[1] The adducts of hydroxyl radicals with a number of arenes have been observed in aqueous solution under rapid flow conditions,[2] but this technique is not readily adapted to the study of the adducts of other radicals, or to other solvents, or to kinetic analysis over a range of temperature.

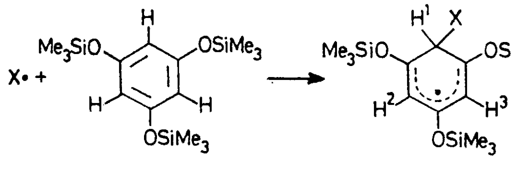
Table. E.s.r. spectra of cyclohexadienyl radicals (II).

Precursor of X·	X·	T/°C	$a(H^1)$/G[a]	$a(H_2,H^3)$/G
$Bu^t{}_2O_2$	$Bu^tO\cdot$	−85	11·0	6·4
$(Et_3Si)_2O_2$	$Et_3SiO\cdot$	−20	21·2	2·5[a]
$(PhCO)_2O_2$	$PhCO_2\cdot$	−70	11·1	6·3[b]
$CF_3I + Me_6Sn_2$	$F_3C\cdot$	−85	24·5	2·8
$PhI+Me_6Sn_2$	$C_6H_5\cdot$	+30	33·0	2·5[d]
p-$FC_6H_4I+Me_6Sn_2$	*p*-$FC_6H_4\cdot$	−80	33·5	2·5
m-$FC_6H_4I+Me_6Sn_2$	*m*-$FC_6H_4\cdot$	0	31·3	2·4[e]
$C_6F_5I+Me_6Sn_2$	$C_6F_5\cdot$	−85	36·6	[f]

[a] The spectrum of the ethyl radical was also observed at low temperature.[5] [b] Toluene was used as solvent. Up to 40 °C in cyclopropane and 80 °C in heptane, the spectrum which we ascribe to the adduct (II; X = Ph) was not apparent. [c] a(F) 2·1 G (3F); g = 2·0031. [d] The same but weaker spectrum was obtained from PhBr + Me_6Sn_2. [e] a(F) 1·1G (1F). [f] Complex multiplet.

Ingold and his co-workers recently attempted to render the cyclohexadienyl radicals more persistent, so that their spectra could be observed in non-polar solvents, by introducing sterically protecting groups into the molecule, but 1,3-di-t-butylbenzene frequently gave two or more radical adducts, and 1,3,5-tri-t-butylbenzene gave a detectable adduct only with the pentafluorophenyl radical.[3]

In order to investigate the relative reactivity of different radicals towards various substrates, we sought an arene which forms e.s.r.-observable adducts in non-polar solvents, and we now report that 1,3,5-tris(trimethylsiloxy)benzene (I) is suitable for this purpose. The arene is readily prepared as a low melting solid (b.p. 280 °C at 760 mmHg; m.p. 35 °C) by the trimethylsilylation of phloroglucinol,[4] and it is very soluble in non-polar solvents.



(I) (II)

Radicals X· were generated photolytically in the presence of the arene (I), usually in cyclopropane solvent, giving strong well resolved spectra of the cyclohexadienyl radicals (II). Spectroscopic data on some of the adducts (II) are given in the Table, and a typical spectrum is illustrated in the Figure.

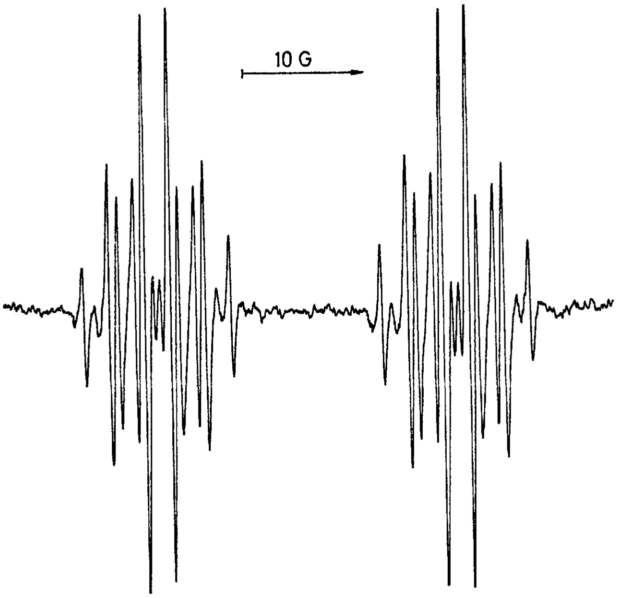


Figure. E.s.r. spectrum of the radical (II; X = CF_3) in cyclopropane at −85 °C.

The arene (I) was chosen partly because the siloxy substituents might be expected to activate the aromatic ring towards attack by 'electrophilic' radicals, by an electronic effect,[1] and to render the adducts (II) more long-lived by a steric effect.[3]

The factor of activation is apparent in the relative reactivity towards $CF_3\cdot$ and $CH_3\cdot$ radicals; whereas the former give an adduct (see Figure), photolysis of acetyl peroxide in the presence of (I) between −100 and −50 °C gave only the spectrum of the methyl radical.

The lifetimes of the radicals (II, X = $PhCO_2$ and CF_3) were measured by the method of intermittent illumination.[6] Both decayed by a second-order reaction, with rate constants of $1{\cdot}70 \times 10^6$ (at −88 °C in toluene) and $5{\cdot}72 \times 10^6$ (at −86 °C in cyclopropane) $l\ mol^{-1}\ s^{-1}$ respectively, some two or three powers of ten less than the value which might be expected[7] for the self-reaction of unhindered cyclohexadienyl radicals.

This ability to observe the e.s.r. spectra of a series of adducts of siloxyarenes such as (I) should help in determining the structure of and electron distribution in cyclohexadienyl radicals, and in elucidating the mechanism of homolytic aromatic substitution.

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