^{199}Hg Hyperfine Coupling in the E.S.R. Spectra of Mercurated Arene Radical Cations: Evidence for an Alternative Mechanism of Mercuration

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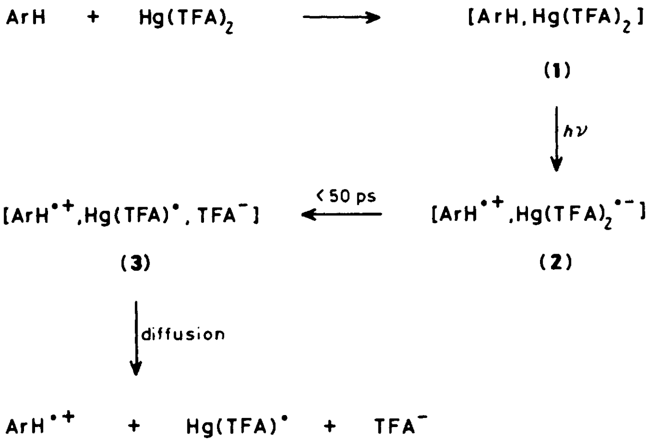
The mercuration of various arenes is promoted when they are photolysed in trifluoroacetic acid containing mercury(II) trifluoroacetate, and ^{199}Hg hyperfine coupling can be observed in the e.s.r. spectra of the radical cations which are formed.

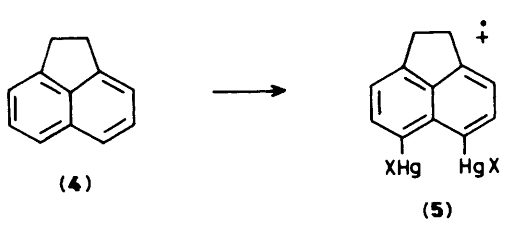
One of the most useful methods for generating hydrocarbon radical cations for e.s.r. studies was developed by Lau and Kochi,[1] and involves the photolysis of a solution of the hydrocarbon (ArH) in trifluoroacetic acid (TFAH) containing mercury(II) trifluoroacetate. From a detailed study of the reaction of hexamethylbenzene,[2] they concluded that the initial step was photoassisted electron transfer within a charge transfer complex (**1**). The high quantum efficiency of the reaction results from the rapid dissociation of $Hg(TFA)_2^{\cdot-}$ in the radical pair ($\mathbf{2} \rightarrow \mathbf{3}$), which minimises energy wastage by back electron transfer.

Their attempts to observe ^{199}Hg hyperfine coupling in the e.s.r. spectra were unsuccessful, and our experience with this system is similar. Indeed there appears to be no report in the literature of the detection of ^{199}Hg coupling.†

We have used this reagent to generate the radical cations of a variety of hydrocarbon π-electron systems.[3] We report here the observation of ^{199}Hg hyperfine coupling resulting from mercuration of the aromatic rings in some of these compounds.



Scheme 1



Scheme 2

For example acenaphthene (**4**) reacts with $SbCl_3$ to form the corresponding radical cation ($\mathbf{4}^{\cdot+}$) with the e.s.r. hyperfine coupling constants listed in Table 1.[4] Photolysis of a solution of (**4**) in Kochi's reagent shows the spectrum illustrated in Figure 1.

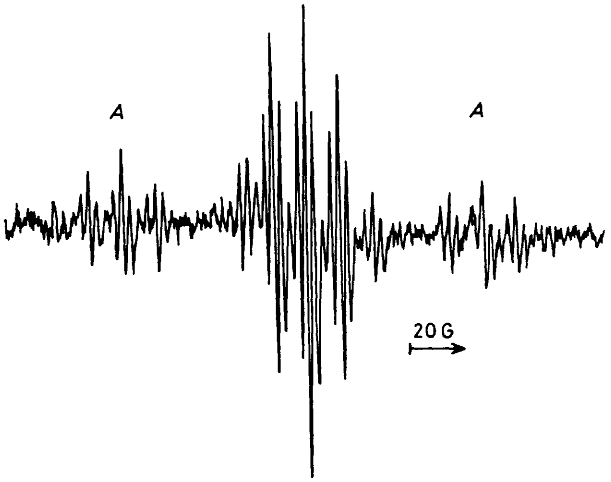
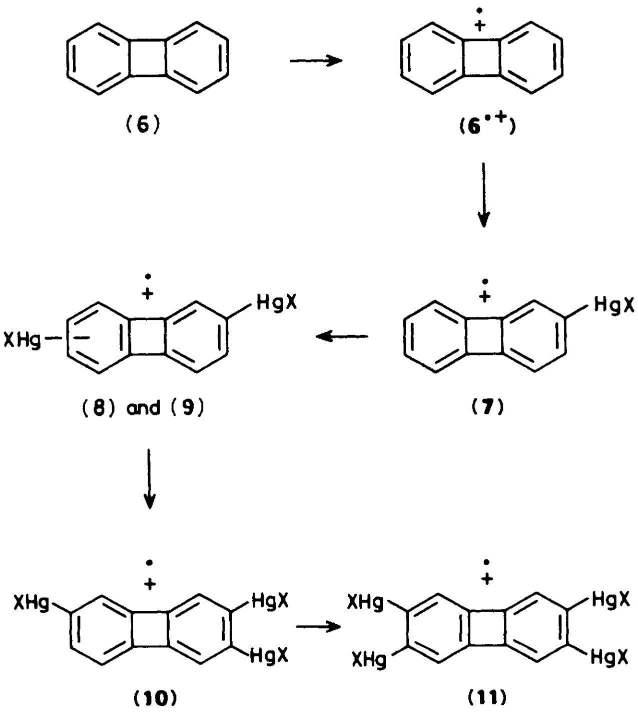


Figure 1. E.s.r. spectrum of the radical cation of dimercurated acenaphthene (**5**), in trifluoroacetic acid at 262 K, showing ^{199}Hg satellites *A*.



Scheme 3

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† Natural abundance: ^{196}Hg, I 0, 0.14%; ^{198}Hg, I 0, 10.02%; ^{199}Hg, I $\frac{1}{2}$, 16.84%; ^{200}Hg, I 0, 23.13%; ^{201}Hg, I 3/2, 13.22%; ^{202}Hg, I 0, 29.80%; ^{204}Hg, I 0, 6.85%. No hyperfine coupling was apparent from ^{201}Hg.

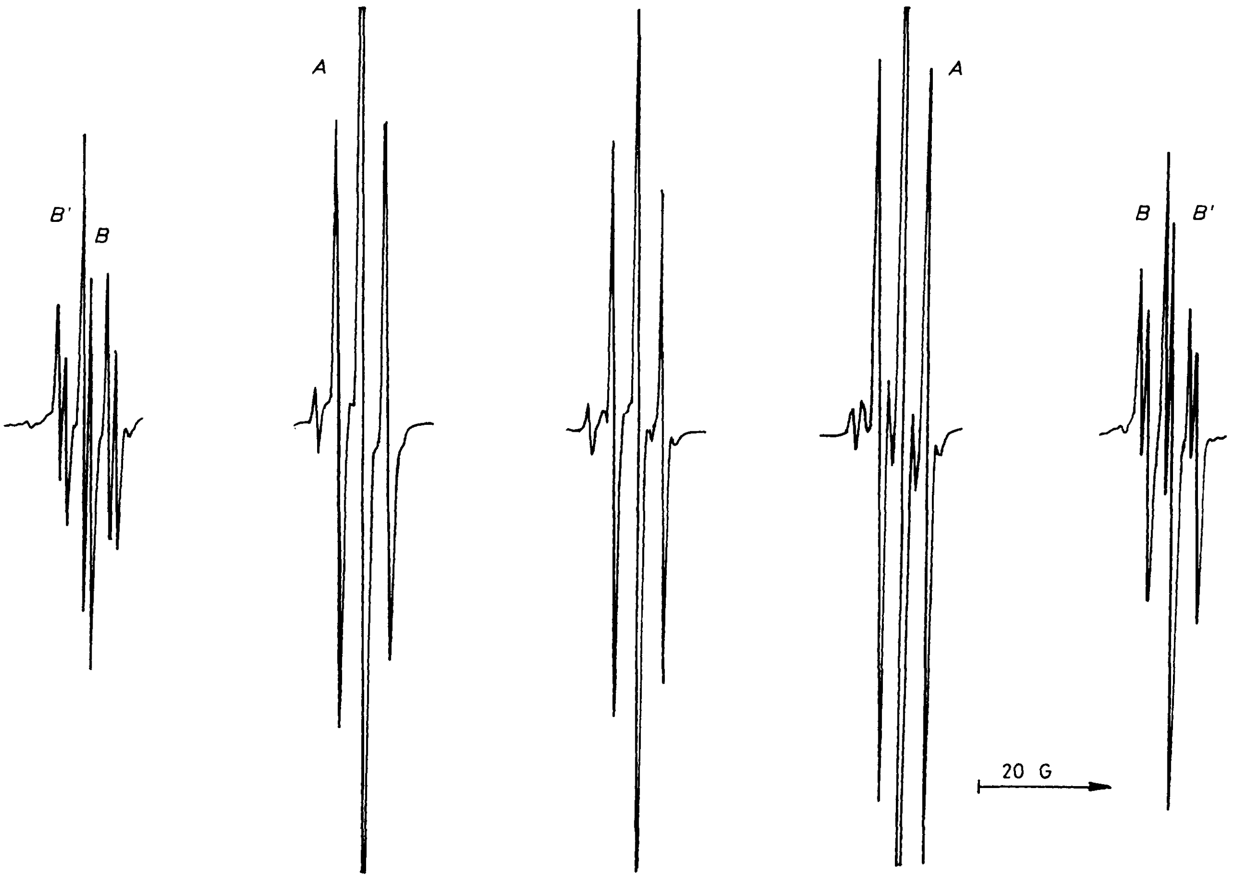


Figure 2. E.s.r. spectrum of the radical cations of the dimercurated biphenylenes (**8**) and (**9**), in trifluoroacetic acid at 262 K, showing primary ^{199}Hg satellites *A*, and secondary satellites *B* and *B'*.

The central feature of the spectrum can be simulated on the basis of the same hyperfine coupling constants which relate to ($4^{\cdot+}$), but without the coupling which is ascribed to the protons H(3) and H(4). Outside this central feature, satellites (*A*) due to ^{199}Hg coupling can be observed with $a(^{199}\text{Hg})$ 141.6 G (G = 10^{-4} T). The relative intensities of the satellites and of the central feature confirm that the protons have been replaced by two mercury atoms, but the signal-to-noise ratio is not high enough for the secondary satellites in molecules containing two ^{199}Hg atoms to be detected.

We conclude that dimercuration is occuring at positions C(3) and C(4) to give (**5**) as shown in Scheme 2.

Similarly, biphenylene (**6**) in sulphuric acid shows an e.s.r. spectrum of the corresponding radical cation ($6^{\cdot+}$) with the hyperfine coupling constants listed in Table 1.[5] If a solution of biphenylene in Kochi's reagent is photolysed with u.v. light, there is a progressive decrease in the number of protons which show the hyperfine coupling at 3.58 G, and the development of satellites due to ^{199}Hg hyperfine coupling.

At an early stage in the reaction, the e.s.r. spectrum observed is that of the corresponding radical cation ($6^{\cdot+}$). The spectrum then reduces to a quartet and ^{199}Hg satellites appear (see Table 1), showing the formation of the monomercurated species (**7**). After *ca.* 1 h the spectrum illustrated in Figure 2 is obtained which shows primary (*A*) and secondary (*B* and *B'*) sets of ^{199}Hg satellites which at this resolution appear as triplets. Hyperfine coupling constants are given in Table 1. We conclude that dimercuration has occurred at two of the β positions, to give two isomeric products [probably (**8**) and (**9**); Scheme 3].

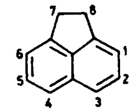
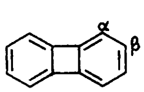
Further reaction leads to a tri-β-mercurated compound (**10**), with a spectrum which shows a central doublet, for which primary, secondary, and tertiary satellites can now be identified. Ultimately the central feature of the spectrum (at the resolution shown in Figure 2) collapses to a singlet, but the quaternary satellites in the molecules (**11**) containing four ^{199}Hg atoms were too weak to be detected. Expansion of all these lines shows that the small hyperfine coupling by the protons at the α-positions is still present.

From these and similar experiments, the following generalisations can be drawn. (i) When mercuration occurs, the hyperfine coupling constants of the remaining protons remain essentially unchanged; the introduction of mercury does not significantly alter the π-electron distribution in these non-degenerate aromatic systems. (ii) Mercuration occurs at the aromatic position where a(H) is highest, *i.e.* where the electron density in the SOMO is greatest. (iii) The ratio between the hyperfine coupling constants of the mercury atom which is introduced, and the proton which it displaces, $a(^{199}\text{Hg}) : a(^{1}\text{H})$, is *ca.* 21.5 : 1 (see Table 1). If we accept that there is no change in electron distribution in the π-system when mercuration occurs (see above), it follows that ^{199}Hg hyperfine coupling can be described by equation (1), where the McConnell constant Q_{Hg} is *ca.* 573 G.[6] (iv) Mercuration leads to a reduction of the g value of the radical.

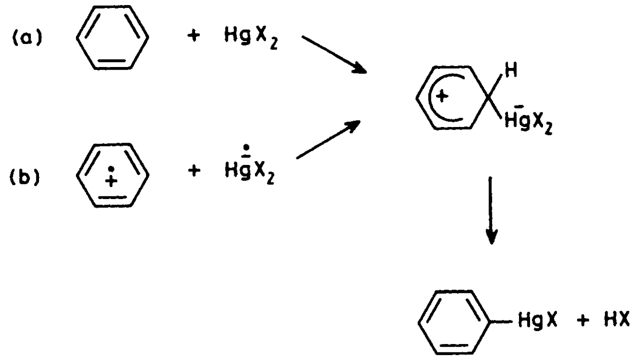
$$a(^{199}\text{Hg}) = \rho_{\text{C}\alpha} Q_{\text{Hg}} \qquad (1)$$

The electrophilic mechanism for the mercuration of an arene by mercury(II) trifluoroacetate is shown in Scheme 4,

Table 1. E.s.r. spectra of arenes and mercurated arenes.

Reactant	Radical cation	Hyperfine coupling constants[a]				a(Hg)/a(H)	g
		H(1,6)	H(2,5)	H/Hg(3,4)	H(7,8)		
	(**4**$^{\cdot+}$)	3.13(2H)	0.59(2H)	6.59(2H)	13.18(4H)		2.0027
	(**5**)	3.13(2H)	0.59(2H)	141.6 (2Hg)	13.13(4H)	21.49	1.9950
		H(α)	H(β)	Hg(β)			
	(**6**$^{\cdot+}$)	0.21(4H)	3.58(4H)				2.0025
	(**7**)	0.21(4H)	3.58(3H)	76.5(1Hg)		21.37	2.0014
	(**8**)	0.21(4H)	3.58(2H)	76.45(2Hg)		21.22	2.0007
	(**9**)	0.21(4H)	3.58(2H)	77.32(2Hg)		21.46	2.0007
	(**10**)	0.21(4H)	3.58(1H)	76.5(3Hg)		*ca.* 21.5	*ca.* 2.0003
	(**11**)	0.21(4H)		*ca.* 77(4Hg)		*ca.* 21.5	*ca.* 2.0003

[a] In trifluoroacetic acid at 262 K.



Scheme 4

path (a)[7,8] and an alternative mechanism involving radical ion intermediates is shown in Scheme 4, path (b). Lau and Kochi thoroughly investigated the scope of these two reactions in the mercuration of homologous methylbenzenes under thermal conditions, and they concluded that in this system, mercuration follows only the electrophilic mechanism [Scheme 4, path (a)],[8] although the corresponding thallation reaction with $Tl(OCOCF_3)_3$ does proceed by dual electrophilic and radical ion mechanisms.[9]

Identical solutions of biphenylene (**5**) were prepared in Kochi's reagent in e.s.r. tubes. One sample was kept in the dark and the other was photolysed in the e.s.r. cavity until the spectrum showed that dimercuration was complete (*cf.* Figure 2).‡ The first sample was then introduced into the cavity, when the e.s.r. spectrum showed that negligible mercuration had occurred.

This implies that there is a mechanism for mercuration which can be stimulated by photolysis. We conclude that for suitable substrates under photolytic conditions, and perhaps also under thermal conditions, mercuration can proceed through a mechanism other than that of Scheme 4, path (a), and that this mechanism probably involves radical pair intermediates as shown in Scheme 4, path (b).

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‡ Reaction with thallium(III) trifluoroacetate under the same conditions shows a strong spectrum of the biphenylene radical cation (**6**$^{\cdot+}$), but gives no evidence of thallation of the aromatic ring. The study of this system is continuing.

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