An ESR study of dibenzylmercury radical cations

Christopher J. Rhodes *,*

School of Chemistry, Thames Polytechnic, Wellington St., Woolwich, London SE18 6PF (U.K.)

and Hikmet Agirbas,

Department of Chemistry, Karadeniz University, Trabzon (Turkey)

(Received March 20th, 1989, appearence accidentally delayed)

Abstract

Following γ-irradiation of dilute solutions of dibenzylmercury and di(p-t-butyl-benzyl)mercury in Freon solvents at 77 K, ^{199}Hg and ^{201}Hg features were observed in their ESR spectra which are consistent with the formation of the parent radical cations, upon annealing at 150 K, unimolecular fragmentation occurs, with formation of benzyl radicals.

Introduction

Compared with the wide range of organic radical cations which have been studied by ESR spectroscopy following exposure of dilute solutions of their substrates in Freon solvents to ionising radiation at low temperatures [1,2], there have been relatively few studies of organometallic species. Such examples as there are include organotin [3–5], organosilicon [6–8], organogermanium [6,7] and organolead [9] species, and, pertinent to the present work, the radical cation from diethylmercury [10].

Results and discussion

We report ESR data for the radical cations of dibenzylmercury and di(p-t-butylbenzyl)mercury. The spectrum recorded from dibenzylmercury in $CFCl_3$ at 77 K is shown in Fig. 1, and contains well-resolved features arising from coupling to ^{199}Hg and ^{201}Hg nuclei. The low field ^{199}Hg $| + \frac{1}{2} >$ feature is almost isotropic owing to the close proximity of the parallel and perpendicular components, and shows an

---

* Present address: Department of Chemistry, Queen Mary College, University of London, Mile End Rd., London E1 4NS (U.K.).
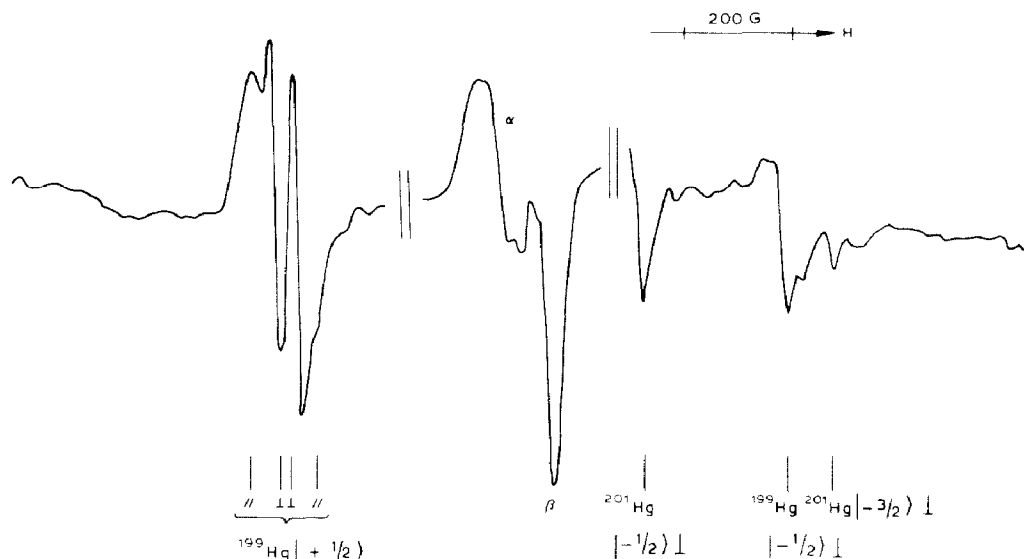
Fig. 1. ESR spectrum recorded from dibenzylmercury, following γ-irradiation as a dilute solution in CFCl$_3$ at 77 K, and assigned to the parent radical cations. α marks feature at $g = 2$; β marks perpendicular feature from non-magnetic mercury complexes at $g = 1.92$.

interesting substructure. A similar low-field feature was observed in the spectrum of the diethylmercury cation [10], which showed a 40 G (1G 10^{-4} T) triplet structure, ascribed to proton coupling. However, we consider that substantial proton coupling is unlikely in the present case, and assign the substructure to an anisotropic coupling to a ^{19}F nucleus from a single solvent molecule. Solvent superhyperfine couplings have been observed previously [1,2] for radical cations in Freon matrices. The data are given in Table 1, and indicate that ca. 5% of the total spin density is delocalised on to fluorine via what is essentially a F$_{2p}$ orbital, given the fluorine p/s

Table 1

Hyperfine coupling data for dibenzylmercury radical cations (G)^{a,b}

Radical	Coupling constants		T (K)
(PhCH$_2$)$_2$Hg$^{+\cdot}$	$A_\perp$ (^{199}Hg)	-952	77
	$A_\perp$ (^{201}Hg)	370	
	$A_\parallel$ (^{19}F)	123	
	$A_\perp$ (^{19}F)	13	
	$A_\parallel$ (^{199}Hg) ca. -800 ^{c}		
(p-Bu^{t}C$_6$H$_4$CH$_2$)$_2$Hg$^{+\cdot}$	$A_\perp$ (^{199}Hg)	-932	77
	$A_\perp$ (^{201}Hg)	365	
	$A_\parallel$ (^{19}F)	115	
	$A_\perp$ (^{19}F)	20	
	$A_\parallel$ (^{199}Hg) ca. -800 ^{c}		
PhCH$_2$	A(3H) 5.0; A(2H) 16.3		150
p-Bu^{t}C$_6$H$_4$ĊH$_2$	A(2H) 5.0; A(2H) 16.0		150

^{a} 1 G 10^{-4} T. ^{b} Couplings correct to second order. ^{c} Assuming $g_\parallel = 2$.

ratio of 16. Support for this assignment is provided by the fact that this substructure was not observed when the experiments were repeated with a CCl_4 matrix.

The absence of a clearly defined parallel $^{199}Hg \mid -\frac{1}{2}>$ feature precludes a precise determination of $A_{\parallel}(^{199}Hg)$ but an estimate of ca. 800 G may be obtained if it is assumed that the $g_{\parallel}$ component from non-magnetic mercury complexes is contained in the $g = 2$ feature (α in Fig. 1). Given that $A_{\parallel} < A_{\perp}$, for a positive ^{199}Hg magnetic moment, A_{iso} must be negative, with $2B$ positive. For ^{201}Hg, with a negative magnetic moment, although the signs of $A_{\parallel}$ and $A_{\perp}$ (^{201}Hg) will be positive, $2B$ will be negative, and so the relation $A_{\parallel} < A_{\perp}$ will again hold. Use of the couplings predicted from the atomic wavefunctions calculated by Morton and Preston [11], along with our approximate $2B$ value of 100 G, suggests that the $6p$-orbital spin density on mercury is ca. 17%. Since a comparable contribution to the SOMO from the $6s$ orbital is expected for nearly linear C–Hg–C bonding, which would provide a substantial positive contribution to A_{iso}, the observation that $A_{\parallel} < A_{\perp}$ shows that the negative spin density arising from exchange polarisation of the lower lying s-electrons on mercury is very large and dominates the isotropic coupling. This was also the case for the $Et_2Hg^{+\cdot}$ cation [10] and for a Tl^0 centre in a KCl matrix [12].

We note that the $A_{\perp}$ coupling in the $(PhCH_2)_2Hg^{+\cdot}$ cation is reduced to 60% of the ca. 1600 G reported for the diethylmercury cation; this is most likely due to "benzylic" delocalisation of spin density into the aromatic rings in the structure I. In I, the solvent fluorine $2p$ orbital is colinear with the C–Hg–C unit, and so the $^{199/201}Hg$ and ^{19}F hyperfine tensors are parallel, thus accounting for the observed anisotropy. The position of the perpendicular feature due to non-magnetic mercury isotopes (β in Fig. 1) gives $g_{\perp} = 1.92$ and reflects a shift from free-spin of ca. 54% of that in the $Et_2Hg^{+\cdot}$ cation (where $g_{\perp} = 1.85$), in good accord with the above estimate of the reduction in the spin density on mercury in $(PhCH_2)_2Hg^{+\cdot}$. The results for the p-t-butyl derivative are very similar; the small reductions in $A_{\perp}$ (^{199}Hg) and $A_{\perp}(^{201}Hg)$ are probably due to an additional delocalisation into the t-butyl groups, as found for the free benzyl radicals [13].

(I)
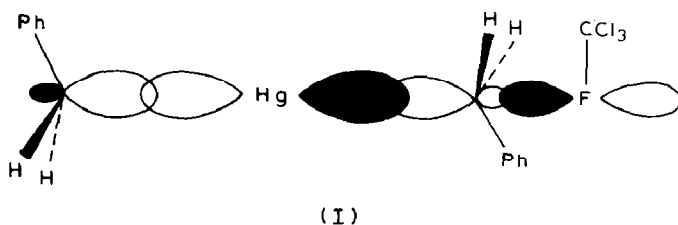
On annealing of either sample at 150 K, ESR signals attributable to the corresponding benzyl radicals, formed by unimolecular fragmentation of the cations I, are observed.

$$PhCH_2-Hg-CH_2Ph^{+\cdot} \rightarrow PhCH_2 \cdot + \overset{+}{Hg}-CH_2Ph$$

(1)
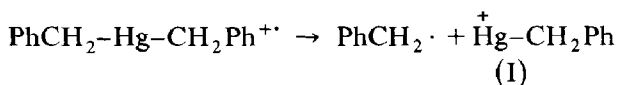
The $\overset{+}{Hg}-CH_2Ph$ moiety (or $\overset{+}{CH_2}Ph$ cation formed by loss of mercury from $\overset{+}{Hg}-CH_2Ph$) may be stabilised by bonding to a solvent molecule, as suggested for the ring-opened $\overset{+}{CH_2}CH_2\dot{CH_2}$ cation [14].

Experimental

The dibenzylmercury compounds were prepared by standard methods [15]. Dilute solutions (ca. 0.1 mole%) of the mercurials were prepared in trichlorofluoromethane (Aldrich) and were γ-irradiated at 77 K with a ^{60}Co source. The ESR spectra were recorded using a Varian E109 spectrometer; samples were annealed in a Varian variable temperature apparatus.

Acknowledgement

References

1 M.C.R. Symons, Chem. Soc. Rev., 13 (1984) 393.
2 M. Shiotani, Magn. Reson. Rev., 12 (1987) 333.
3 M.C.R. Symons, J. Chem. Soc., Chem. Commun., (1982) 869.
4 M.C.R. Symons, J. Chem. Soc., Chem. Commun., (1981) 1251.
5 A. Hasegawa, S. Kaminaka, T. Wakabayashi, M. Hayashi, M.C.R. Symons and J. Rideout, J. Chem. Soc., Dalton Trans., (1984) 1667.
6 B.W. Walther and F. Williams, J. Chem. Soc., Chem. Commun., (1982) 270.
7 J.T. Wang and F. Williams, J. Chem. Soc., Chem. Commun., (1981) 666.
8 C.J. Rhodes, J. Organometal. Chem., 336 (1987) 317.
9 B.W. Walther, F. Williams, W. Lau and J.K. Kochi, Organometallics, 2 (1983) 688.
10 J. Rideout and M.C.R. Symons, J. Chem. Soc., Chem. Commun., (1985) 129.
11 J.R. Morton and K.F. Preston, J. Magn. Reson., (1978) 30. 577.
12 S.V. Nistor, E. Goovaerts, A. Bouwen and D. Schoemaker, Phys. Rev. B, 27 (1983) 5797, and ref. therein.
13 J.M. Dust and D.R. Arnold, J. Am. Chem. Soc., 105 (1983) 1221; ibid., 105 (1983) 6531.
14 M.C.R. Symons, Chem. Phys. Lett., 117 (1985) 381.
15 S. Dincturk, R.A. Jackson, M. Townson, H. Agirbas, N.C. Billingham and G. March, J. Chem. Soc., Perkin Trans. 2, (1981) 1121.