# The Radical Cation of Diethyl Mercury: an E.S.R. Study

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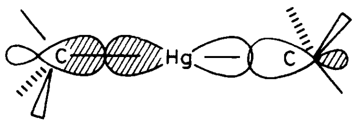
Exposure of diethyl mercury in fluorotrichloromethane to $^{60}$Co $\gamma$-rays at 77 K gave a radical cation whose e.s.r. features are as expected for $(EtHgEt)^{\cdot+}$.

The formation of radical species in dialkyl mercury derivatives has been studied by Fullam and Symons.[1] Species positively identified by e.s.r. spectroscopy include $R_2\dot{C}HgR'$ and $\cdot HgR$. Formation of $(Me_2Hg)^{\cdot-}$ was also considered to be probable but there was no evidence for the presence of the primary cations. Photoelectron spectroscopic studies have shown that the first ionization is from the $\sigma_u$ orbital, which can be depicted as (**1**),[2,3] the resulting vertical ionization potentials being *ca.* 9.3 eV for $Me_2Hg$ and 8.9 eV for $Et_2Hg$.[3] Thus these molecules should readily form cations in halogenoalkane solvents on irradiation.[4—6] This technique has been used to form $\cdot SnR_4^+$ cations, which are a good source of alkyl radicals,[7—9] and it seemed of interest to widen this study to include $R_2Hg^{\cdot+}$ cations.

We have studied $Me_2Hg^{\cdot+}$, $(CD_3)_2Hg^{\cdot+}$, and $Et_2Hg^{\cdot+}$. In all cases, spectra of the type shown in Figure 1 were obtained. Those for the methyl derivatives were complicated by weak solvent interactions and will be discussed elsewhere. Here we consider the analysis of the spectrum shown in Figure 1. This comprises central ($g$ = 2) features, which are in part due to impurity cations, an intense perpendicular type 1 : 2 : 1 triplet at $g$ = 1.85 (A), a nearly isotropic line of *ca.* one quarter the intensity on the low-field side (B), and a much weaker

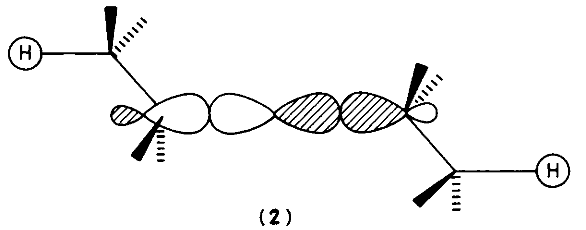


(**1**)

**Figure 1.** The e.s.r. spectrum of $(EtHgEt)^{\cdot+}$.

high-field perpendicular component (C). Other still weaker features can also be seen in Figure 1. In all cases, the features are split into 42 G† triplets, showing that they belong to the same radical species. Since we expect to find $g_{\perp} < g_{\parallel} \leqslant 2.00$ for the $6p^1$ configuration of mercury having relatively strong linear σ-bonding, we assign triplet A to the perpendicular component of the non-magnetic mercury complexes and B and C to the $M_I = \pm\frac{1}{2}$ perpendicular components for $^{199}$Hg complexes ($I = \frac{1}{2}$, 16.84% abundance). Feature B clearly also contains the parallel component (hence its high intensity) but, as is often the case for such systems, the $|-\frac{1}{2}>$ parallel line is not readily located. The extra features are assigned to the less abundant $^{201}$Hg complexes [$I = \frac{3}{2}$, 13.24% abundance]. Because of our uncertainty regarding the precise location of the parallel lines other than the $M_I = +\frac{1}{2}$ line, we are not yet able to quote good values for the $^{199}$Hg hyperfine tensor components. However, it is clear that $|A_{\perp}| = ca.$ 1 600 G and that $|A_{\parallel}| < |A_{\perp}|$. This situation is unusual for normal radicals, for which $|A_{\parallel}| > |A_{\perp}|$ is a general rule, but is quite characteristic of $np^1$ systems ($n$ = 4, 5, 6) and can be taken as being diagnostic thereof.[10] In that case, both $A_{\parallel}$ and $A_{\perp}$ are negative. Hence $A_{iso}$ is large and negative, whereas $2B$ is positive, as required for structure (**1**). The negative value for $A_{iso}$ stems largely from spin polarisation of the 5s and inner s electrons.

Since the value of $2B$ cannot be obtained with the required precision (it probably lies in the 200—300 G region), we turn to the $^1$H hyperfine coupling to obtain some measure of the delocalisation of the SOMO onto the alkyl ligands. This requires $^{13}$C labelling for an accurate estimate, but the following argument seems to give a reasonable result. The $^1$H coupling for $Me_2Hg^{\cdot+}$ is small, as required for structure (**1**). {*E.g.* the $^1$H coupling for the unique methyl protons in $[Me_3C{\cdot}CH_3]^+$ cations is *ca.* 40 G.}[11] Hence the large coupling for two protons in $Et_2Hg^{\cdot+}$ is assigned to two β-protons, as in (**2**). This structure is reminiscent of that for the ethane cation,[6] which exhibits hyperfine coupling to two strongly-coupled protons (152 G). If there is no major distortion of the structure at the methylene carbon, then a comparison of these results (42 ÷ 152 = 0.28) gives a rough measure of the extent of delocalisation onto the two ethyl groups. This should be reduced somewhat for the dimethyl derivative, which accords with its slightly greater coupling with $^{199}$Hg.



(**2**)

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## References

1 B. W. Fullam and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1974, 1086.
2 T. P. Fehlner, J. Ulman, W. A. Nugent, and J. K. Kochi, *Inorg. Chem.*, 1976, **15**, 2544.
3 D. K. Creber and G. M. Bancroft, *Inorg. Chem.*, 1980, **19**, 643.
4 T. Kato and T. Shida, *J. Am. Chem. Soc.*, 1979, **101**, 6869.
5 I. G. Smith and M. C. R. Symons, *J. Chem. Res. (S)*, 1979, 382.
6 K. Toriyama, K. Nunome, and M. Iwasaki, *J. Chem. Phys.*, 1982, **77**, 5891.
7 M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1981, 1251.
8 A. Hasegawa, S. Kaminaka, T. Wakabayashi, M. Hayashi, M. C. R. Symons, and J. Rideout, *J. Chem. Soc., Dalton Trans.*, 1984, 1667.
9 B. W. Walther, F. Williams, W. Lau, and J. K. Kochi, *Organometallics*, 1983, **2**, 688.
10 S. V. Nistor, E. Goovaerts, A. Bouwen, and D. Schoemaker, *Phys. Rev. B*, 1983, **27**, 5797.
11 K. Nunome, K. Toriyama, and M. Iwasaki, *J. Chem. Phys.*, 1983, **79**, 2499.

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† 1G = $10^{-4}$ T.