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The molecular and electronic structures of ions and radicals derived from alkylmercury(II) compounds: an SCF-MO study

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Abstract

Molecular geometries and energies have been calculated by the semi-empirical MNDO method for closed shell species and by the UHF-MNDO method for neutral radicals, radical-cations and radical-anions, for R_2Hg (R = Me, Et), RHgX(X = Cl, Br, I) and their radical-cations, fragment ions, and radicals (including RHg·, ·CH_2HgCH_3,·CH_2HgX, and CH_3·CHHgX) and $(HgMe_2)^-$. The radical-cations $(R_2Hg)^+$ have structures in which the organic substituents are nearly planar at the α-carbon; $(CH_3HgX)^+$ all have structures of C_{3v} symmetry, but while $(CH_3HgCl)^+$ has a ^2E ground state, both $(CH_3HgBr)^+$ and $(CH_3HgI)^+$ have $^2A_1$ ground states.

Introduction

The electron spin resonance spectra of γ-irradiated alkylmercury(II) halides RCH_2HgX (X = Cl, Br, or I) have been interpreted [1] in terms of neutral radicals $R\dot{C}HHgX$, whereas the spectra from similarly irradiated dialkylmercury(II) compounds R_2Hg were interpreted in terms of a range of products including $(R_2Hg)^+$, $(R_2Hg)^-$ and the neutral radicals RHg· [1,2]. Since in many cases the assignments rested on fairly qualitative interpretations of the hyperfine couplings to magnetic isotopes of mercury (^{199}Hg, $I = 1/2$; ^{201}Hg, $I = 3/2$), it is necessary to make more accurate calculations of the molecular and electronic structures of some of these radicals and radical ions. Here we present the results of an MNDO study of some organomercury radicals, including some not yet identified by electron spin resonance spectroscopy: this study allows confirmation of some of the previously reported assignments, and suggests alternatives to some others.

These results thus complement related studies on the molecular and electronic structures of organometallic radicals containing tin [3], germanium [4], and lead [5].

Calculations

All calculations of molecular properties were carried out using the MNDO method [6], as implemented in version 5.0 of the MOPAC system [7]. The PRECISE

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option for SCF and geometric convergence was used throughout, and atomic parameters were taken from the literature [6,8–11]. UHF wave functions were employed for all open shell species, and all geometric variables were, in every case, simultaneously optimised.

Results and discussion

Halogen-free ions and radicals

The neutral mercury(II) alkyls $HgMe_2$ and $HgEt_2$ optimised to structure of D_{3d} and C_{2h} symmetry respectively; the calculated geometries and energies were identical to those previously reported [11]. The dimethyl compound exhibited almost unrestricted rotation about the mercury–carbon-bonds, while in the diethyl derivative the lowest energy conformer had two hydrogens *transoid* to the mercury atom about the carbon–carbon-bonds. In each neutral compound, the dominant contribution to the HOMO, of a_{2u} symmetry in the methyl derivative and b_u symmetry in the ethyl, is from *p*-orbitals on mercury and the α-carbon atom giving an overall bonding combination. In $HgMe_2$, the LUMO, of a_{1g} symmetry, is predominantly a carbon–mercury antibonding orbital comprising the mercury *s*-orbital, and carbon *p*-orbitals.

Ionisation of $HgMe_2$ to the radical-cation $(HgMe_2)^+$ is accompanied, as expected from the character of the HOMO, by a lengthening and weakening of the mercury–carbon bonds, (Table 1): the D_{3d} symmetry is preserved. However, ionisation is accompanied by a very marked flattening of the methyl substituents; in the neutral $HgMe_2$, the HCH angle is calculated as 108.1°, so that the carbon atoms are very close to tetrahedral, while in the cation $(HgMe_2)^+$ the calculated HCH angle is 117.0°, indicative of almost planar methyl substituents. The net atomic charge calculated for mercury is the same, +0.38 *e*, for both $HgMe_2$ and $(HgMe_2)^+$, indicating loss of electron density, upon ionisation, from the methyl substituents; both $CH_3{}^+$ and CH_3 as isolated entities are planar.

Similarly, when $HgEt_2$ is ionised to $(HgEt_2)^+$, the molecular symmetry and the preferred extended conformation are both preserved, but the detailed geometry changes in a manner somewhat different from that found in the methyl system. The Hg–C bonds are lengthened and weakened upon ionisation (Table 1) as expected, but the CH_2CH_3 groups centred on the α-carbon atoms, as well as being very much flattened are also strongly tilted away from the carbon–mercury vectors. Thus the angles HCH and HCC at the α-carbon are both increased, from 106.7 and 109.2° respectively, in the neutral $HgEt_2$, to 116.7° in the radical-cation $(HgEt_2)^+$, indicative of developing $\cdot CH_2CH_3$ character in the ethyl substituents; at the same time the HgCC angle is increased to 129.0°, as the HgCH angles are reduced to only 85.9°, both indicative of a major tilt at the α-carbon. As with the methyl system, there is no difference between the net charges of mercury in $HgEt_2$ and in $(HgEt_2)^+$, again confirming that ionisation draws electron density exclusively from the substituents. Both cations, $(HgMe_2)^+$ and $(HgEt_2)^+$ have molecular and electronic structures to which a major contributor is the spin-doublet canonical form $(RHg^+ \cdot R)$ (for R = Me or Et): the very high spin densities at mercury (Table 1 and below) are consistent with this.

Alkyl-group loss from HgR_2 [or from $(HgR_2)^+$] provides the neutral radicals $\cdot HgR$ [1]. Of these $\cdot HgCH_3$ was calculated to have C_{3v} symmetry, with a calculated

Table 1

Optimised properties of halogen-free organomercury radicals

Radical	Optimised point-group	ΔH_f° (kJ mol^{-1})	d(Hg–C) (Å)	p(Hg–C)	ρ[Hg(6s)]	$A(^{199}Hg)$ (G)	ρ[H(1s)]	$A(^1H)$ (G)	Ref. for A values
$[(CH_3)_2Hg]^+$ [a]	D_{3d}	+913.1	2.074	0.528	−0.5208		−0.0176		
$[(CH_3)_2Hg]^-$ [a]	C_{2v}	+52.7	2.073	0.571	+0.5744	2674	−0.0125(×6)	20(6H)	1
$[(C_2H_5)_2Hg]^+$ [b]	C_{2h}	+873.4	2.140 [c]	0.466	−0.6046	"Large"[2]	−0.0155 (CH_2)		2
							+0.0094 (H_β,×4)		
							0.0517 (H_β,×2)	42(2H)	
$CH_3Hg\cdot$	C_{3v}	+109.4	1.993	0.732	+0.5678		−0.0173		
$C_2H_5Hg\cdot$	C_s	+108.2	2.021 [d]	0.711	+0.5687	3693	−0.0212 (CH_2)		1
							+0.0061 (CH_3)		1
$CH_3HgCH_2\cdot$	C_s	+166.5	1.987						
			(CH_3)	0.922	−0.0496	220	−0.0531 (CH_2)	21(2H)	
			1.947						
			(CH_2)	0.871			+0.0013 (CH_3)		

[a] Neutral $(CH_3)_2Hg$ has calculated d(Hg–C), 1.989 Å; p(Hg–C), 0.901. [b] Neutral $(C_2H_5)_2Hg$ has calculated d(Hg–C), 2.014 Å; p(Hg–C), 0.889. [c] Calculated d(C–C), 1.498Å; p(C–C), 0.999. [d] Calculated d(C–C), 1.517 Å; p(C–C), 0.988.

$\Delta H_f°$ value some 11.5 kJ mol^{-1} lower than that reported by Dewar [11]. The radical $\cdot HgC_2H_5$ was calculated to have only C_s symmetry, as expected. As for the cation radicals $(HgR_2)^+$, so too the neutral radicals $\cdot HgR$ are calculated to have very large spin densities at the mercury atom: the relationship between calculated spin densities and the hyperfine couplings observed in the electron spin resonance spectra will be discussed below.

Hydrogen atom loss, as opposed to methyl radical loss, from $HgMe_2$ provides the neutral carbon-centred radical $CH_3HgCH_2\cdot$ [1], calculated to have C_s symmetry, and to be linear at mercury and accurately planar at the radical centre, as expected for a substituted methyl radical $\cdot CH_2X$, with substituent ($X = CH_3Hg$) of comparatively low electronegativity: in keeping with this, the spin density at mercury is low (Table 1).

The LUMO of neutral $HgMe_2$ is calculated to be of a_{1g} symmetry, and to be primarily localised in the C–Hg–C framework as an antibonding orbital, comprising mainly Hg(6*s*) and C(2*p*). Electron attachment to form $(HgMe_2)^-$ leads to a bent skeleton and overall C_{2v} symmetry, with the unpaired electron in an orbital of a_1 symmetry arising from mixing of the LUMO of the neutral with the previously empty in-plane *p*-orbital on mercury. The calculated C–Hg–C angle in $(HgMe_2)^-$ is 120.7°; the non-linear structure is some 30 kJ mol^{-1} more stable than the D_{3d} isomer.

Halogen-containing ions and radicals

The neutral methylmercury(II) halides, CH_3HgX (for X = Cl, Br, or I) all optimised to structures of C_{3v} symmetry, as observed experimentally by microwave spectroscopy [12]. In these molecules, the calculated binding energies for the essentially non-bonding, lone-pair electrons on the halogen are 12.01, 11.09, and 10.20 eV for X = Cl, Br, I respectively: the binding energies for the bonding σ(C–Hg–X) level, localised primarily in the C–Hg portion, are 11.67, 11.51 and 10.98 eV respectively. This means that for CH_3HgCl, the σ(C–Hg–X) level is the HOMO, of a_1 symmetry, while for CH_3HgBr and CH_3HgI the HOMO, of *e* symmetry, is the halogen lone pair orbitals. It is thus somewhat surprising to find, because of the extensive re-ordering of the molecular energy levels which attend ionisation to $(CH_3HgX)^+$ and subsequent geometric relaxation, that $(CH_3HgCl)^+$ is in a ^2E state, with the unpaired electron in a lone-pair type orbital, while $(CH_3HgBr)^+$ and $(CH_3HgI)^+$ are both $^2A_1$ systems. These different electronic states doubtless are responsible for major differences in Hg–X bond orders, and in spin-densities calculated for X = Cl on the one hand, and X = Br or I on the other (Table 2).

An alternative process to ionisation of CH_3HgX is hydrogen atom loss to provide neutral, carbon-centred radicals $\cdot CH_2HgX$, as observed [1] upon irradiation. Each of the radicals $\cdot CH_2HgX$ (for X = Cl or I) optimised to structures of C_{2v} symmetry, in each of which the SOMO is an almost pure carbon 2*p* orbital perpendicular to the H_2CHg plane: in each case the SOMO contains a small contribution from the corresponding mercury 6*p* and halogen *np* orbitals, in bonding and anti-bonding senses respectively. These radicals can thus be regarded, like $\cdot CH_2HgCH_3$, as methyl radicals containing a single substituent of low electronegativity. As in $\cdot CH_2HgX$ is changed from chlorine, via bromine, to iodine there is a steady decrease in the carbon–mercury bond order, accompanied by a steady increase in

Table 2

Optimised properties of halogen-containing organomercury radicals

Radical	Optimised point-group	ΔH_f° (kJ mol$^-$)	d(C–Hg) (Å)	p(C–Hg)	d(Hg–X)[a] (Å)	p(Hg–X)[a]	ρ[Hg(6s)]	A(^{199}Hg) (G)	ρ[H(1s)]	A(^{1}Hg) (G)	ρ[X(ns)][a]	Ref. for A values
$\cdot CH_2HgCl$	C_{2v}	+53.6	1.937	0.941	2.285	0.891	−0.0918		−0.0522		+0.0002	
$\cdot CH_2HgBr$	C_{2v}	+140.2	1.939	0.928	2.378	0.899	−0.0883	439	−0.0523	23	+0.0002	1
$\cdot CH_2HgI$	C_{2v}	+184.5	1.943	0.898	2.475	0.979	−0.0707	410	−0.0521	21	+0.0006	1
$CH_3\dot{C}HHgCl$	C_s	+30.6	1.961	0.927	2.285	0.875	−0.0952	450	−0.0518[b]	21	+0.0002	1
$CH_3\dot{C}HHgBr$	C_s	+116.9	1.962	0.915	2.376	0.903	−0.0918		−0.0517[b]		+0.0002	
$CH_3\dot{C}HHgI$	C_s	+160.3	1.967	0.885	2.474	0.983	−0.0733		−0.0518[b]		+0.0005	
$(CH_3HgCl)^+$	$C_{3v}(^2E)$	+947.6	2.089	0.385	2.228	1.126	+0.1446		−0.0095		−0.0004	
$(CH_3HgBr)^+$	$C_{3v}(^2A_1)$	+979.5	2.035	0.351	2.671	0.693	+0.5331		+0.0131		+0.0010	
$(CH_3HgI)^+$	$C_{3v}(^2A_1)$	+924.3	2.040	0.323	2.717	0.565	+0.5297		+0.0140		+0.0047	

[a] X = Cl, Br, or I. [b] Refers to α-hydrogen; for β-hydrogen, ρ[H(1s)] is +0.0260 (for X = Cl, Br, or I).

the mercury-halogen bond order: the same is true of closely-related radicals CH_3CHHgX (Table 2).

Other mercury radicals

In addition to the organomercury radicals $C_2H_5Hg\cdot$ and $CH_3\dot{C}HHgCl$ derivable from C_2H_5HgCl [1], a third radical can be derived from this source, which has been tentatively identified as neutral $\cdot HgCl$ [1]. Similar, related, radicals, variously identified as Hg^+, $Hg_2{}^+$ or $Hg_2{}^{3+}$, HgOH or $(HgOH)^{2+}$, and $HgOC_2H_5$ or $(HgOC_2H_5)^{2+}$ have likewise been reported [13] to arise from γ-irradiation of aqueous and/or ethanolic solution of various mercury salts.

Of these, Hg^+ has calculated spin density $\rho[Hg(6s)]$ of unity, while $Hg_2{}^+$ has a corresponding spin density of 0.6195: attempts to optimise the structure of the tri-positive ion, $Hg_2{}^{3+}$, on the other hand, led to smooth dissociation to Hg^+ and Hg^{2+}. For $(HgOH)^{2+}$, the calculated spin density $\rho[Hg(6s)]$ was only -0.0750, seriously inconsistent with the observed $A(^{199}Hg)$ value of 4734 G [13]: on the other hand for the neutral analogue HgOH, the calculated ρ value was 0.7309. Similarly, for neutral HgOEt, the calculated $\rho[Hg(6s)]$ was 0.7982, but attempts to optimise the structure of $(HgOEt)^{2+}$, described [13] as having $A(^{199}Hg)$, of 4525 G led to smooth dissociation to Hg^+ and EtO^+. For both these systems $(HgOH)^x$ and $(HgOEt)^x$ the calculations are more consistent with $x = 0$, than with $x = 2$, as suggested previously [13]. Formation of the species having $x = 0$ can readily be rationalised as coordination of Hg^+ by either OH^- or OEt^-, whereas formation of the $x = 2$ species is less easy to understand on purely chemical grounds.

Calculated spin densities and experimental A values

For most of the radicals studies here, the data in Tables 1 and 2 show a clear distinction between those, such as $(R_2Hg)^+$ or RHg, where the SOMO is localised largely on mercury and where both the calculated spin density $\rho[Hg(6s)]$ and the observed A value are large and those, such as $\cdot CH_2HgX$, where the SOMO is largely carbon-centred, having small values for both ρ and A. Overall, the corresponding values of ρ and A lie close to a smooth curve, qualified on some cases by significant solvent variation in the experimental A values: as an extreme example the A (^{199}Hg) value observed [13] for Hg^+ ranges from 13860(100) G in sulphuric acid as solvent to 11490(300) G in ethanol solution. For practical purposes, the curve may be regarded as biphasic, with two linear portions: for low A (^{199}Hg) and ρ values these are linearly related with a scale factor of ca. 5000 G, while for high values A (^{199}Hg) is approximated by $(19000\rho - 7000)$ G, with a switch-over at $\rho = 0.5$.

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