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THE EFFECT OF SELFASSOCIATION OF MERCURATED CARBONYL COMPOUNDS ON MERCURY-199 CHEMICAL SHIFTS

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Summary

Temperature and concentration dependences of mercury-199 chemical shifts in benzene solutions of bis(methylethylketone)mercury $Hg(CH_2COC_2H_5)$ (I) and α-bis(methylacetoacetone)mercury $Hg(CH_2COCH_2COOCH_3)_2$ (II) are determined by the ^1H-$\{^{199}Hg\}$method. The NMR data obtained and the IR spectra are indicative of selfassociation of I and II in solution with the formation of weak intermolecular coordination bonds Hg ← :O=C. The enthalpies of complex formation calculated on the assumption of one mercury atom bonding with only one carbonyl function are equal to —3.2 ± 0.1 kcal/mol and —2.2 ± 0.1 kcal/mol for I and II, respectively.

Organomercury compounds give 1/1 and 1/2 complexes with many electron donor solvents (pyridine, dimethylsulphoxide, acetone, alcohols) [1]. This complex formation is an important factor controlling the directions and mechanisms of various reactions of these compounds in solution.

With symmetrical organomercury compounds, complex formation enthalpies are usually small and the complexes cannot be isolated while in solution, as the equilibria are strongly on the side of free components. Metallated carbonyl compounds can form inter- and intramolecular bonds $C{=}O\!: \rightarrow MR_n$ [2] whose strength is first of all determined by the metal electron withdrawing abilities and depends strongly on an effective positive charge on the metal. Thus, Group IVB elements can only participate in such bonding when linked with at least one strong electron acceptor, e.g. a halogen or oxygen. Complex formation may be detected by a splitting of the ν(C=O) bands in the IR spectrum. With intramolecular association in organomercury compounds, the possibility of formation of six-, five- and less frequently, four-membered cycles favours bonding [2—6].

^1H, ^{13}C and ^{19}F NMR spectroscopy has proved to be the most efficient tool for the study of specific solvation and complex formation phenomena in organometallics, in particular, in organomercury compounds, as these phenomena strongly affect spin—spin couplings involving magnetic metal isotope nuclei [7—11].

The first studies on mercury-199 chemical shifts (δ Hg) in various organomercury compounds revealed their strong dependence on the solvent and solution concentration [12—19]. Thus, δ Hg for dimethylmercury changes by more than 100 ppm on going from cyclohexane to dimethylsulphoxide, which is comparable with what is observed with another Group IIB metal dimethyl derivative, that of cadmium-113 [20], but exceeds the corresponding silicon-29 solvent shifts in $(CH_3)_4Si$ by two orders of magnitude [21,22] and tin-119, lead-207 [21] and selenium-77 [23] solvent shifts in their methyl derivatives by one order of magnitude. Mercury-199 chemical shifts thus offer much promise for the study of intermolecular interactions of organomercury compounds in solution, especially using the pulsed FT ^{199}Hg NMR technique.

In this paper we have studied mercury-199 chemical shifts in bismethylethylketonemercury (I), $Hg(CH_2COCH_3)_2$, and α-bis-methylacetoacetatemercury (II), $Hg(CH_2COCH_2COOCH_3)_2$, in benzene solutions and their concentration and temperature dependence.

Experimental

The synthesis of compounds I and II was described earlier [24]. The IR and NMR spectra of the products are consistent with the structures.

Mercury-199 chemical shifts were determined from ^1H-$\{^{199}Hg\}$ spectra measured on a Varian XL-100 instrument with internal proton stabilization on the solvent signal. The mercury-199 chemical shifts are given on the δ scale with reference to neat dimethylmercury (1 ppm = 17.92 Hz). The solvents were chromatographically pure. The concentrations were determined gravimetrically with accuracy to within 0.01 mol/l.

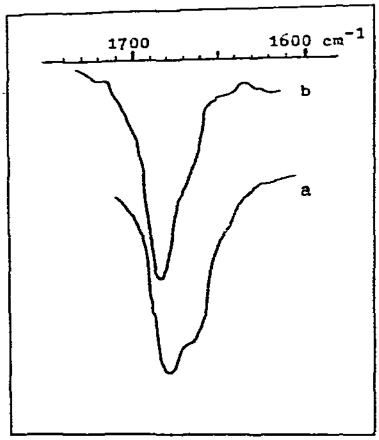
The temperature was monitored by measuring the proton NMR spectrum of a standard ethyleneglycol sample with accurary of ±1° C.

The observed concentration dependences were processed using a specially designed iteration programme on a 620f spectrometer computer. This programme finds unknown parameters by minimization of the rms deviations of the calculated concentration dependence from the experimental one.

The IR spectra were obtained on an UR-20 spectrometer.

Results and discussion

The occurrence of selfassociates of mercury carbonyl compounds has been suggested on the basis of their IR spectra [25]. It has been noted that the carbonyl group stretching frequency (ν(C=O) decreases by 30—40 cm^{-1} in the solid state from solutions in various solvents. IR spectra of benzene solutions of I measured in this work contain an asymmetric ν(C=O) band (Fig. 1); the intensity of the low-frequency component corresponding to the carbonyl group in associates decreases noticeably as the solution concentration lowers. Too small a frequency separation of components (ca. 20 cm^{-1}) hinders a detailed study of



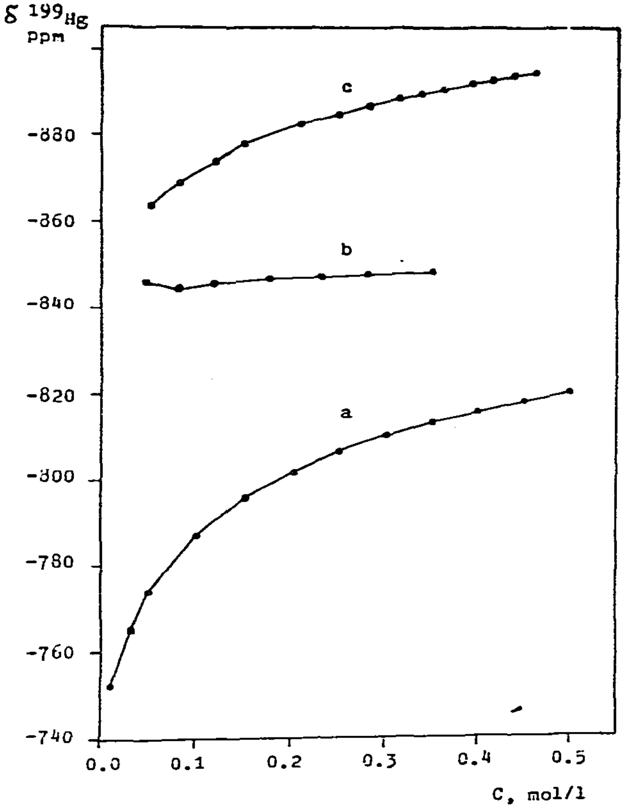


Fig. 1. IR spectra of benzene solutions of I, (a) c = 0.0133 mol/l (b) c = 0.0067 mol/l.

Fig. 2. Concentration dependences of ^{199}Hg chemical shifts in solutions of I in benzene (a) and acetone (b) and in solutions of II in benzene (c).

the selfassociation by the IR method.

Lowering of the concentrations of benzene solutions of I and II results in a marked downfield shift of the mercury-199 signal (see Fig. 2), by 70 and 30 ppm, respectively. As a temperature rise also causes downfield shifting (Figs. 3, 4), the phenomenon may be explained by intermolecular selfassociation of the compounds studied. This suggestion is substantiated by the fact that practically no concentration dependence of δ Hg is observed in acetone (Fig. 2) where the solvent is present in large excess and binds the solute to the complex and thus shifts the mercury-199 signal to the higher field.

Selfassociation in solutions may be described by the equilibrium

$$nA \rightleftharpoons A_n\,, \quad A = \mathrm{I} \text{ or } \mathrm{II}\,. \tag{1}$$

Clearly, n may take on any value and the percentage of selfassociates with $n \geqslant 2$ should increase with concentration. It is difficult to say a priori what the dependence of the mercury-119 chemical shifts on n will be. The shift value should first of all depend on the mercury coordination number, i.e. on the number of oxygen atoms bound to mercury. Most probably, mercury would

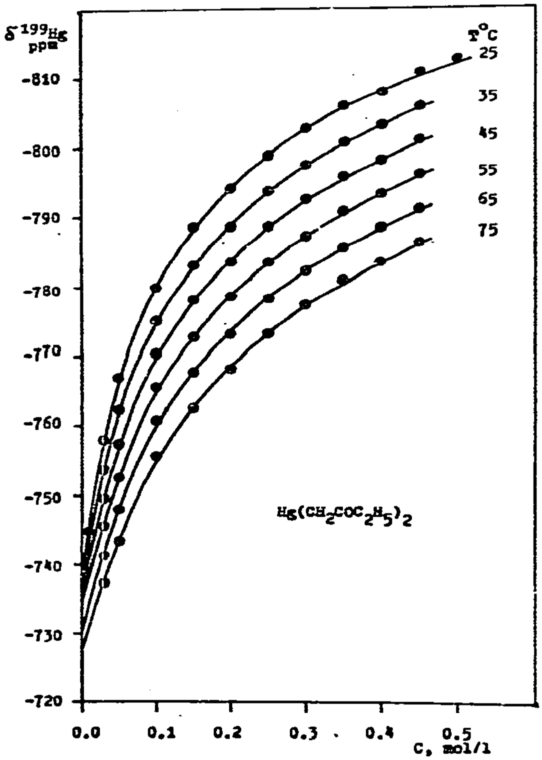


Fig. 3. Concentration dependences of ^{199}Hg chemical shifts in solutions of I in benzene at various temperatures. The points correspond to the experimental values, and the curves to the calculated ones.

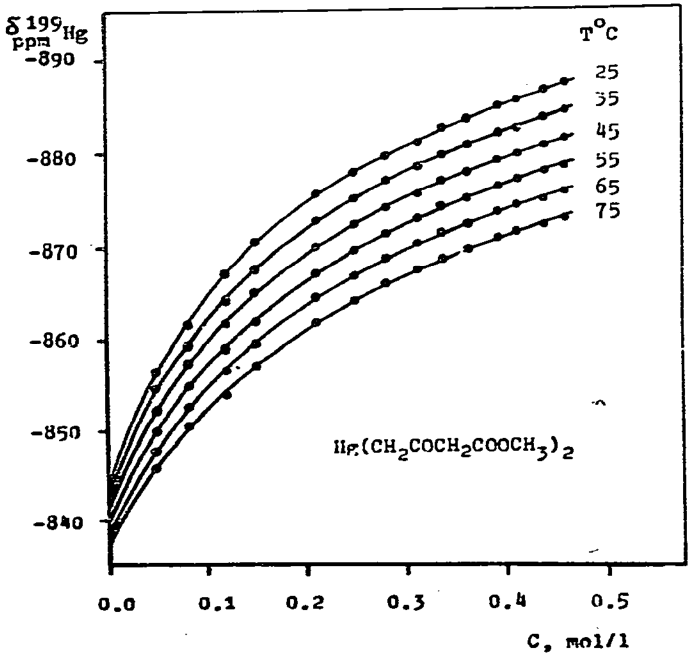
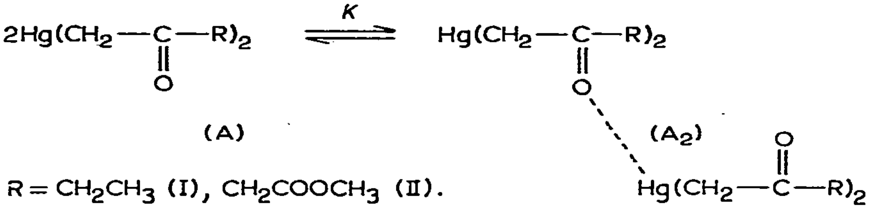


Fig. 4. Concentration dependence of ^{199}Hg chemical shifts in solutions of II in benzene of various temperatures. The points correspond to the experimental values, and the curves to the calculated ones.

preferably bind only one oxygen atom in the concentration range studied, because the formation of tetracoordinate mercury complexes is only characteristic for organomercury salts and cations [1]. We have therefore chosen the following model as the first approximation:



R = CH2CH3 (I), CH2COOCH3 (II).

Under fast interconversion conditions the observed mercury-199 chemical shift has an averaged value

$$\delta_{\text{obs}} = p_{\text{A}}\delta_{\text{A}} + p_{\text{A}_2}\delta_{\text{A}_2} \tag{3}$$

where p_{A} and p_{A_2} are the mole fractions of free molecules and selfassociates, and δ_{A} and δ_{A_2} are their chemical shifts. By expressing the mole fractions p_{A} and p_{A_2} via the solute concentration (C_{A}) and equilibrium constant (K) we obtain for the chemical shift concentration dependence:

$$\delta_{\text{obs}} = \delta_{\text{A}_2} + \left(\frac{-1 + \sqrt{1 + 4C_{\text{A}}K}}{2\,C_{\text{A}}K}\,(\delta_{\text{A}} - \delta_{\text{A}_2})\right) \tag{4}$$

Unknown parameters K, δ_{A} and δ_{A_2} from (4) have been determined using the iteration programme "HG". The value extrapolated to infinite dilution and the chemical shift value found for acetone solutions have been used as starting approximations of δ_{A} and δ_{A_2}. As seen from Figs. 3 and 4, the model of selfassociation chosen provides a fairly good fit to the observed concentration dependence of mercury-199 chemical shifts in compounds I and II in the concentration and temperature ranges studied. The results are listed in Tables 1 and 2. The downfield shifts of δ_{A} and δ_{A_2} caused by a temperature increase are worth mentioning. These may be due to intramolecular selfassociation and to changes in populations of higher rotational and vibrational states.

The thermodynamic parameter values calculated from the temperature dependences of selfassociation constants (Table 3) are indicative of a rather low

TABLE 1

SELFASSOCIATION CONSTANT, K, AND FREE MOLECULE (δ_{A}) AND SELFASSOCIATE (δ_{A2})-MERCURY-199 CHEMICAL SHIFTS FOR COMPOUND I AT VARIOUS TEMPERATURES

T(°C)	K (l/mol)	$-\delta_{\text{A}}$ (ppm)	$-\delta_{\text{A2}}$ (ppm)
25	8.7 ± 0.3 [a]	735.9 ± 0.5 [a]	858.6 ± 0.9 [a]
35	7.1 ± 0.4	735.1 ± 0.9	857.2 ± 1.5
45	6.1 ± 0.4	733.0 ± 0.9	855.3 ± 1.8
55	5.3 ± 0.4	730.6 ± 0.9	853.8 ± 2.3
65	4.5 ± 0.4	728.0 ± 1.0	852.7 ± 3.0
75	3.9 ± 0.4	725.3 ± 1.0	852.3 ± 3.7

[a] Standard deviation.

TABLE 2

SELFASSOCIATION CONSTANT, K, AND FREE MOLECULE (δ_A) AND SELFASSOCIATE (δ_{A2}) MERCURY-199 CHEMICAL SHIFTS FOR COMPOUND II AT VARIOUS TEMPERATURES

T(°C)	K (l/mol)	$-\delta_A$ (ppm)	$-\delta_{A2}$ (ppm)
25	4.1 ± 0.3 [a]	843.3 ± 0.6 [a]	932.8 ± 1.4 [a]
35	3.7 ± 0.2	842.3 ± 0.4	931.3 ± 1.1
45	3.3 ± 0.1	841.1 ± 0.3	930.1 ± 1.0
55	3.0 ± 0.2	839.9 ± 0.4	928.9 ± 1.5
65	2.7 ± 0.2	838.5 ± 0.6	927.9 ± 2.3
75	2.4 ± 0.3	837.2 ± 0.7	927.2 ± 3.4

[a] Standard deviation.

TABLE 3

THERMODYNAMIC PARAMETERS OF SELFASSOCIATION IN I AND II

Compound	ΔH (kcal/mol)	ΔS (e.u.)
I	−3.2 ± 0.1 [a]	−6.5 ± 0.5 [a]
II	−2.1 ± 0.1	−4.4 ± 0.5

[a] Standard deviation.

stability of intermolecular Hg ← :O=C bonds. Comparison of equilibrium constants and complex formation enthalpies for I and II shows that I gives more stable selfassociates. The possible reason for this may be occurrence of competing intramolecular selfassociation in II leading to unstrained six-membered cycles.

We also tried to take into account the formation of trimeric species A_3 in selfassociation.

$$A + A + A \overset{K}{\rightleftharpoons} A_2 + A \overset{K'}{\rightleftharpoons} A_3 \qquad (5)$$

In this model, the observed chemical shift is a function of five variables δ_A, δ_{A_2}, δ_{A_3}, K, K'. Processing of the experimental data in terms of this model yields enthaply values for the formation of one Hg ← :O=C coordination bond similar to those obtained for the dimer—monomer equilibria. As the number of the experimental points exceeds the number of parameters to be determined only insignificantly, the results obtained by the iteration procedure depend strongly on the starting approximations. The formation of more complex selfassociates in solution is certainly possible. The parameters obtained, nevertheless, provide an estimate of the Hg ← :O=C intermolecular coordination bond strength in mercurated carbonyl compounds.

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