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## THE EFFECT OF THE SOLVENT UPON THE RATES AND MECHANISMS OF ORGANOMETALLIC REACTIONS

### VI. THE COMPLEXATION OF DIBENZYL MERCURY IN SOLUTIONS STUDIED BY PMR SPECTROSCOPY

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#### Summary

The concentration and temperature dependence of  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  values for solutions of dibenzylmercury in various solvents show clearly that if the solvent is of the monodentate electron-donating type 1/1 complexes are formed predominantly, the 1/2 complexes existing only at very low temperatures. The results suggest that the 1/1 complexes are very weak and have planar T-shaped structures, whereas the 1/2 complexes are probably tetragonal pyramids. In complexes of the former type the relative content of s-electrons in the Hg-C-H site is higher than in the 1/2 complexes.

#### Introduction

It has recently been emphasized [1] that to understand the nature of the solvent effect upon the rates and mechanisms of organometallic reactions, it is important to study the redistribution reaction kinetics for various organometallic compounds in various solvents and, simultaneously, the solvation of these organometallic molecules in the ground and transition states. Therefore, we have studied the effect of the solvent upon rates of redistribution between various organic derivatives of tin and mercury [2], and the solvation of these organotin [3, 5, 6] and organomercury [4–6] molecules. One of the model compounds chosen for this study is dibenzylmercury which reacts readily with organic and inorganic derivatives of mercury [7, 8] and tin [9] in various solvents. In the present work we have used PMR spectroscopy to study the behaviour of dibenzylmercury in those solvents for which the kinetics of the reaction with molecules of the type  $\text{CF}_3\text{HgX}$  ( $\text{X} = \text{Cl}, \text{I}, \text{OCOCF}_3$ ) were studied earlier [2].

## Results and discussion

In our previous studies of solvation of organomercury molecules [4-6] it was shown that the changes of proton chemical shifts in organomercury compounds on going from one particular solvent to another are not due solely to the electronic effects involved in the complexation. Unfortunately, there are other contributions (reaction field, anisotropy effect, dispersion forces) which cannot be evaluated correctly at present. Therefore we focussed our attention on the study of  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  spin-spin coupling constants which are known [10] to be a good source of information on the distribution of electrons in organomercury molecules and their complexes. Bearing in mind that organomercury molecules and monodentate ligands can form 1/1 and 1/2 complexes [11-13] we have studied the concentration and temperature dependence of  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  for solutions of  $\text{Bz}_2\text{Hg}$  in carbon tetrachloride, tetrachloroethylene, methylene chloride, benzene, acetone- $d_6$ , pyridine, DMF- $d_7$ , and DMSO- $d_6$ . It is important to note at the outset that for solutions in  $\text{CCl}_4$  and  $\text{C}_2\text{Cl}_4$   $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  does not depend either on concentration or on temperature, and is equal to 130.0 Hz. The data for other solvents are given in Table 1.

It is evident from the results in Table 1 that when  $\text{CCl}_4$  and  $\text{C}_2\text{Cl}_4$  are replaced by other solvents  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  increases slightly in benzene and

TABLE 1

CONCENTRATION AND TEMPERATURE DEPENDENCE OF  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  FOR  $\text{Bz}_2\text{Hg}$  IN VARIOUS SOLVENTS

Solvent	D/A <sup>a</sup>	$J(^{199}\text{Hg}-\text{C}-^1\text{H})(\text{Hz})$							
		-30°	-10°	-5°	+25°	+40°	+50°	+60°	+70°
Benzene	19				133.8		132.9	132.5	132.1
	56				134.9		133.8	133.2	132.9
	76				134.9		133.8	133.2	132.9
	112				134.9		134.1	133.2	132.9
$\text{CH}_2\text{Cl}_2$	27			135.1	134.5				
	78	138.2	137.3	136.4	135.7				
	106	138.2	137.3	136.5	135.7				
	157	138.2	137.3	136.5	135.7				
	314	138.2	137.3	136.5	135.7				
Acetone- $d_6$	272	142.6	141.8		139.6				
Pyridine	17				139.1		137.3	136.9	
	62		142.4		141.5		139.9	139.4	
	83		142.4		141.8		140.8	140.1	
	124		142.5		141.8		141.0	140.6	
	247		142.5		141.8		141.0	140.7	
DMF- $d_7$	17				141.0	140.2			138.6
	54				142.8	142.3			141.0
	65				142.9	142.3			141.4
	130				143.0	142.3			141.4
DMSO- $d_6$	94				145.2		144.0	143.7	
	140				145.2		144.0	143.7	
	280				145.2		144.0	143.7	

<sup>a</sup> D/A = [solvent]/[ $\text{Bz}_2\text{Hg}$ ].

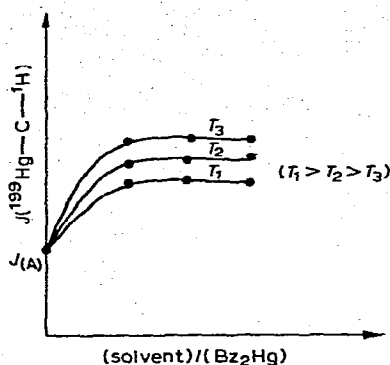
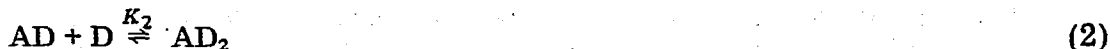


Fig. 1 The general pattern of concentration and temperature dependence for  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  constants for solutions of dibenzylmercury in various solvents.

$\text{CH}_2\text{Cl}_2$  and sharply in acetone, pyridine, DMF and DMSO. In all the systems studied the  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  constants increase with a decrease of concentration and temperature. It is also clear that there is a saturation of the increase of  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  in all systems, and at any one temperature a plateau of values of  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  (Fig. 1) may be observed. We believe that the data in Table 1 may be rationalized if the simultaneous equilibria (1) and (2) are assumed. Then



there are three types of organomercury molecules in the solution: free molecules of  $\text{Bz}_2\text{Hg}$ , and 1/1 and 1/2 complexes. Hence, under conditions of fast exchange between the free and complexed molecules of  $\text{Bz}_2\text{Hg}$ , the  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  constant observed can be represented by eqn. (3). In our case the solvent concentra-

$$J_{\text{obs}} = p(\text{A}) \cdot J(\text{A}) + p(\text{AD}) \cdot J(\text{AD}) + p(\text{AD}_2) \cdot J(\text{AD}_2) \quad (3)$$

where

$$p(\text{A}) + p(\text{AD}) + p(\text{AD}_2) = 1 \quad (4)$$

tion is considerably higher than the dibenzylmercury concentration, i.e.  $[\text{D}_0] \gg [\text{A}_0]$  and  $[\text{D}_0] \approx [\text{D}]$ . Then, combining eqns. (1)-(4),  $J_{\text{obs}}$  may be represented as in eqn. (5).

$$J_{\text{obs}} = \frac{J(\text{A}) + K_1[\text{D}_0] \cdot J(\text{AD}) + K_1 \cdot K_2 \cdot [\text{D}_0]^2 \cdot J(\text{AD}_2)}{1 + K_1 \cdot [\text{D}_0] + K_1 \cdot K_2 \cdot [\text{D}_0]^2} \quad (5)$$

In this case

$$\frac{dJ_{\text{obs}}}{d[\text{D}_0]} = \frac{K_1 \cdot (J(\text{AD}) - J(\text{A})) + 2K_1 \cdot K_2 \cdot [\text{D}_0] \cdot (J(\text{AD}_2) - J(\text{A})) + K_1^2 \cdot K_2 \cdot [\text{D}_0]^2 \cdot (J(\text{AD}_2) - J(\text{A}))}{(1 + K_1[\text{D}_0] + K_1 \cdot K_2 \cdot [\text{D}_0]^2)^2} \quad (6)$$

The data of Table 1 demonstrate that there is a moment of time when

$$\frac{dJ_{\text{obs}}}{d[\text{D}_0]} = 0 \quad (7)$$

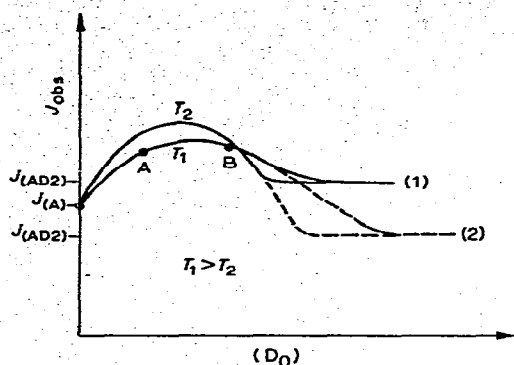


Fig. 2. The general type of function  $J_{\text{obs}}([D_0])$  for  $J(AD_2) > J(A)$  (1) and  $J(AD_2) < J(A)$  (2) (see text).

To solve eq. (6) with respect to  $[D_0]$  it should be remembered that  $J_{\text{obs}}$  increases with  $[D_0]$  before it reaches the plateau, whence  $J(AD) > J(A)$  and that  $[D_0]$  is positive. It may be shown that the function  $J_{\text{obs}}([D_0])$  has a maximum value only when  $J(AD_2) < J(AD)$  or  $J(AD_2) < J(A)$ . In both the cases  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  in the 1/2 complex is lower than in the 1/1 complex. Consequently, the function (5) may be represented as in Fig. 2.

By assuming that the  $K_1$  and  $K_2$  values are small and bearing in mind the limited accuracy of spin-spin coupling constant measurements, one may represent the AB section of the curve (Fig. 2) as a straight line, and this is the case in our experiments. Our results gave us to assume that the plateau values of  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  show that equilibrium (1) and even more so equilibrium (2) were never totally displaced to the complexed molecules. It was also assumed that  $J(AD_2)$  was lower than  $J(AD)$ . It was then necessary to observe, at least for one system, the decrease of  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  with further decrease of concentration or temperature. Such a decrease was observed for a 0.05 mole/l solution of  $\text{Bz}_2\text{Hg}$  in pyridine while the temperature was decreased to  $-50^\circ$  (Fig. 3). Unfortunately, the limited so-

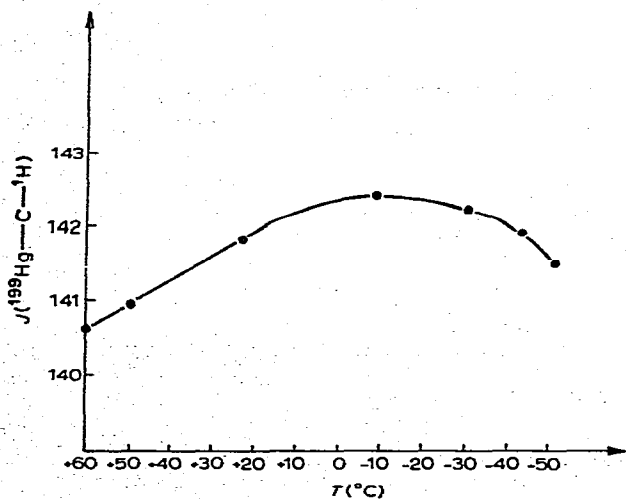
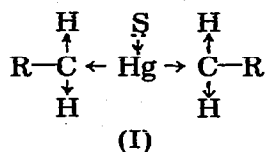


Fig. 3. Temperature dependence of  $J(^{199}\text{Hg}-\text{C}-^1\text{H})$  for a 0.05 mole/l solution of dibenzylmercury in pyridine.

lubility of  $\text{Bz}_2\text{Hg}$  and the freezing of the solutions prevented us from studying the other systems. Nevertheless, we believe that the data for the  $\text{Bz}_2\text{Hg-Py}$  system show that the assumptions made above are correct.

The qualitative analysis presented by Hatton and coworkers [14] showed that "spins of mercury and hydrogen nuclei in alkyl-mercuric compounds are coupled mainly through Fermi contact interaction". A recent semi-empirical molecular orbital study of  $J(^{199}\text{Hg-C-}^1\text{H})$  constants [15] also resulted in the conclusion that "all the major features of  $^{199}\text{Hg-}^1\text{H}$  spin coupling in saturated organomercurials can be accounted for in terms of a dominant Fermi contact term, and little use of mercury's  $5d$  orbitals in bonding". Bearing in mind that the Fermi contact coupling is proportional to the  $s$ -electron density at the coupled nuclei [14] one can assume that the increase of  $J(^{199}\text{Hg-C-}^1\text{H})$  observed for  $\text{Bz}_2\text{Hg}$  on going from solutions in  $\text{CCl}_4$  or  $\text{C}_2\text{Cl}_4$  to other solvents is due to changes in the  $s$ -electron density at the  $\text{Hg-C-H}$  site. It was assumed earlier [4, 5, 16, 17] that the increase of  $J(^{199}\text{Hg-C-}^1\text{H})$  is due to an increase of  $s$ -character of the  $sp$ -hybrid orbitals of mercury during the solvation of organomercurials. A study of the solvent effect upon  $J(^{199}\text{Hg-C-}^1\text{H})$  and  $J(^{199}\text{Hg-C-C-}^1\text{H})$  in diethylmercury [6] showed that on going from inert to solvating solvents  $J(^{199}\text{Hg-C-}^1\text{H})$  changes from 98.0 to 104.5 Hz, whereas  $J(^{199}\text{Hg-C-C-}^1\text{H})$  remains unaltered and equal to 127.5 Hz. It is therefore concluded that solvation raises the  $s$ -electron density on the geminal protons while not affecting the  $s$ -electron density on either the vicinal hydrogens or the mercury atom. This fits well the recent data by Fedin and his coworkers [18] who showed that  $J(^{199}\text{Hg-}^{13}\text{C})$  for solutions of  $\text{Et}_2\text{Hg}$  in various solvents increases from 642.0 to 688.0 Hz, whereas  $J(^{199}\text{Hg-C-}^{13}\text{C})$  does not change and is equal to 25.0 Hz.

It may not be very surprising that solvation does not alter the  $s$ -electron density at the mercury nucleus since this is a donor-acceptor process involving the  $p$ -electrons of donor atoms in the solvents and the highest unoccupied orbitals of mercury in the organomercurials. As for the geminal protons, the solvation increases the  $s$ -electron density at these by an inductive mechanism as is shown in structure (I).



Our experimental results therefore suggest that in solution dibenzylmercury molecules form very weak 1/1 complexes in which the relative content of  $s$ -electrons at the  $\text{Hg-C-H}$  site is higher than it is in the uncomplexed dibenzylmercury. The experimental data infer that 1/2 complexes of dibenzylmercury exist only at low temperatures. This conclusion is not very surprising because it is well known [19] that even diphenylmercury has very weak acceptor properties and that bis(trinitromethyl)mercury forms 1/1 complexes [20] with monodentate solvents. Nevertheless, it is important to shed more light on the electronic and spatial structures of 1/2 complexes of organomercurials because it has been shown experimentally that such complexes can exist in solutions and in the

crystalline phase, especially when the organomercurial contains a strong electron-accepting group such as  $\text{CF}_3$  [11, 24–28],  $\text{C}_6\text{F}_5$  [11, 12, 21–23], and  $\text{C}_6\text{Cl}_5$  [29]. We have already shown that  $J(\text{AD}) > J(\text{AD}_2)$  and so the relative content of *s*-electrons in the Hg–C–H site of the 1/1 complexes is higher than it is in the 1/2 complexes. This will be so if the 1/1 complexes have a planar T-shaped structure in which mercury has *sp*-hybridisation in its  $\sigma$ -bonds with carbon atoms and *pd*-hybridisation in its donor–acceptor bonds with the oxygen or nitrogen atom of the coordinating solvent and if the 1/2 complexes are distorted tetragonal pyramids in which mercury has *sp*<sup>3</sup>-hybridisation in its bonds with carbon atoms and with donor atoms in the solvents.

## Experimental

The synthesis of dibenzylmercury [30] and the purification of solvents [31] have been described elsewhere. Concentrations of dibenzylmercury used in this study were 0.05 to 0.70 mole/l. PMR spectra were measured on a JEOL JNM-C-60 HL spectrometer (60 MHz). Frequency sweep mode was employed with hexamethyldisiloxane as the internal lock. Spin–spin coupling constants were measured accurately to 0.2 Hz. The temperature was adjusted by means of a JEOL T-3 controller and was accurate to  $\pm 2^\circ$ .

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