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

VII. A ^{19}F NMR STUDY OF COMPLEXATION OF CF_3HgX ($X = Cl, I, OCOCF_3$)

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Summary

The concentration and temperature dependence of $J(^{199}Hg—C—^{19}F)$ for solutions of CF_3HgX ($X = Cl, I, OCOCF_3$) in various solvents shows that in inert solvents these molecules exist mainly as non-solvated dimers (X = I or $OCOCF_3$) or as monomers (X = Cl). In strongly coordinated solvents 1/2 complexes are largely formed from CF_3HgX and the electron-donating solvent molecules. In pyridine solutions an equilibrium exists between the 1/1 and 1/2 complexes. Complexes of the type $CF_3HgX \cdot D$ are T-shaped and have a higher relative content of *s*-electrons in the Hg—C—F group compared with tetrahedral $CF_3HgX \cdot 2D$ complexes.

Introduction

In compliance with the conclusions of the first paper of this series [1] we have studied the effect of solvents upon the rates and mechanism of the reaction (1). Some of the kinetic data for this reaction in various solvents have already

$$Bz_2Hg + CF_3HgX \xrightarrow{\text{Solvent}} BzHgCF_3 + BzHgX \qquad (1)$$

(where X = Cl, I, $COOCF_3$ [2].)

been presented [3] and more detail will be given in a later paper. The behaviour of dibenzylmercury in various solvents has been studied by means of PMR spectroscopy [4]. In the present work we have applied ^{19}F NMR spectroscopy to CF_3HgX ($X = Cl, I, OCOCF_3$) molecules in the same solvents.

Results and discussions

Recently [5], the spin—spin coupling constants $J(^{199}Hg—C—^{19}F)$ were analysed for compounds of the type CF_3HgX and from there it was concluded that increase of electron-withdrawing power of X led to an increase of the relative content of s-electrons in Hg—C bonds, and an increase of p-electrons in Hg—X bonds. In particular it has been shown in the present work that for such molecules $J(^{199}Hg—C—^{19}F)$ increases in the series $I < Cl < OCOCF_3$. These changes of $J(^{199}Hg—C—^{19}F)$ are analogous to the respective changes of $J(^{199}Hg—C—^{1}H)$ for similar CH_3HgX molecules. We therefore concluded that the regularities of changes in $J(^{199}Hg—C—^{1}H)$ and $J(^{199}Hg—C—^{19}F)$ for RHgX molecules when X is altered are similar and are applicable to a study of complexation of such molecules.

It was shown primarily that for fused $CF_3HgOCOCF_3$ and CF_3HgCl $J(^{199}Hg—C—^{19}F)$ values are considerably higher than for their solutions and are 2268 and 2034 Hz respectively. Unfortunately it was not possible to carry out the experiment with CF_3HgI, owing to the volatility and instability of this compound [6]. Decreasing the temperature of the fused compound to an increase of $J(^{199}Hg—C—^{19}F)$, so we conclude that for monomeric CF_3HgX molecules these constants are lower than for associated $(CF_3HgX)_n$ molecules. Bearing in mind that in crystals RHgX molecules are associated through X···Hg bridging bonds [7] one may assume that intermolecular coordination of electron-donating atoms (oxygen in $CF_3HgOCOCF_3$ or halogen in CF_3HgHal) leads to an increase of $J(^{199}Hg—C—^{19}F)$ values. On the other hand, the rupture of these intermolecular coordination bonds on dilution by an inert solvent decreases these spin—spin coupling constants; a feature which was observed for the compounds under investigation on going from the melts to solutions in tetrachloroethylene, methylene chloride and benzene (Tables 1-3). It is important to note that even in strongly coordinated solvents such as dimethyl sulphoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), pyridine and acetone $J(^{199}Hg—C—^{19}F)$ values are considerably lower than in the melts. Our data suggest that in inert solvents an important equilibrium exists between the associated and monomeric molecules of CF_3HgX (eqn. 2). In strongly coordinated solvents there are various

$$(CF_3HgX)_n \rightleftharpoons nCF_3HgX \tag{2}$$

equilibria between associated molecules, monomers, and 1/1 and 1/2 complexes of CF_3HgX with the solvents [8-10]. Therefore, the $J(^{199}Hg—C—^{19}F)$ constant observed for a solution of a given concentration at a given temperature could be presented in the form (3).

$$J_{obs} = p(A) \cdot J(A) + p(A_n) \cdot J(A_n) + p(AD) \cdot J(AD) + p(AD_2) \cdot J(AD_2) + p(A_nD_n) \cdot J(A_nD_n) \tag{3}$$

[where A is CF_3HgX, D is solvent, p is molar fraction and J is $J(^{199}Hg—C—^{19}F)$].

A study of the complexation of methyltin halides [11] and dibenzylmercury [4] carried out in our laboratory showed that the concentration and temperature dependence of $J(^{119}Sn—C—^{1}H)$ and $J(^{199}Hg—C—^{1}H)$ are very indicative of the behaviour of these molecules in solution. We therefore studied the concentration and temperature dependence of $J(^{199}Hg—C—^{19}F)$ for the CF_3HgX solutions mentioned above; data obtained are given in Tables 1-3. Analysis of these data shows that for solutions of CF_3HgCl or CF_3HgI in C_2Cl_4 and for solutions of CF_3HgCl in CH_2Cl_2 or benzene an increase of temperature and of the D/A ratio (the de-

TABLE 1

CONCENTRATION AND TEMPERATURE DEPENDENCE OF $J(^{199}Hg—C—^{19}F)$ CONSTANTS FOR SOLUTIONS OF CF_3HgI

Solvent	D/A	$J(^{199}Hg—C—^{19}F)$ (Hz)						
		—10°	+18°	+30°	+42°	+50°	+60°	+70°
DMSO	28		1768	1768	1768		1768	
	40		1768	1768	1768		1768	
	60		1768	1768	1768		1768	
DMF	25		1768	1768	1768		1768	
	42		1768	1768	1768		1768	
	63		1768	1768	1768		1768	
Acetone	25		1758	1758	1760			
	41		1758	1758	1760			
	67		1758	1758	1760			
THF	28		1752	1752	1754		1756	
	45		1752	1752	1754		1756	
	61		1752	1752	1754		1756	
Pyridine	23		1694	1694	1700		1710	
	32		1694	1694	1700		1710	
	50		1694	1694	1700		1710	
$CCl_2=CCl_2$	19					1734		1720
	23					1728		1715
	45					1720		1708
CH_2Cl_2	30	1722	1722	1722				
	45	1716	1716	1716				
	73	1710	1710	1710				
Benzene	21		1708	1708	1708		1708	
	35		1698	1698	1698		1698	
	49		1690	1690	1690		1690	

TABLE 2

CONCENTRATION AND TEMPERATURE DEPENDENCE OF $J(^{199}Hg—C—^{19}F)$ CONSTANTS FOR SOLUTIONS OF CF_3HgCl

Solvent	D/A	$J(^{199}Hg—C—^{19}F)$ (Hz)						
		—20°	—10°	+18°	+30°	+40°	+60°	+70°
DMSO	20			1944	1944	1942	1942	1942
	25			1944	1944	1942	1942	1942
	33			1944	1944	1942	1942	1942
	71			1944	1944	1942	1942	1942
DMF	18		1934	1934	1934	1932	1932	1932
	23		1934	1934	1934	1932	1932	1932
	43		1934	1934	1934	1932	1932	1932
	67		1934	1934	1934	1932	1932	1932
Acetone	16		1924	1924	1922	1922		
	24		1924	1924	1922	1922		
	35		1924	1924	1922	1922		
	60		1924	1924	1922	1922		
THF	18		1914	1914	1914	1912	1910	
	24		1914	1914	1914	1912	1910	
	34		1914	1914	1912	1912	1910	
	61		1914	1914	1912	1912	1910	

TABLE 2 (Continued)

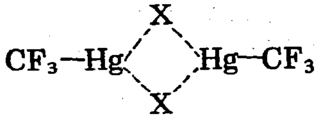
Solvent	D/A	$J(^{199}Hg{-}C{-}^{19}F)$ (Hz)						
		−20°	−10°	+18°	+30°	+40°	+60°	+70°
Pyridine	18		1888	1888	1888	1886	1886	
	23		1888	1888	1888	1886	1886	
	32		1888	1888	1888	1886	1886	
	62		1888	1888	1888	1886	1886	
CH_2Cl_2	23	1942	1936	1922				
	42	1934	1924	1908				
	74	1926	1910	1898				
$CCl_2{=}CCl_2$	14						1944	1912
	24						1924	1898
	40						1906	1884
Benzene	16			1906		1900	1892	
	31			1890		1882	1878	
	56			1880		1874	1870	

TABLE 3

CONCENTRATION AND TEMPERATURE DEPENDENCE OF $J(^{199}Hg{-}C{-}^{19}F)$CONSTANTS FOR SOLUTIONS OF $CF_3HgOCOCF_3$

Solvent	D/A	$J(^{199}Hg{-}C{-}^{19}F)$ (Hz)						
		−10°	+18°	+30°	+40°	+50°	+60°	+70°
DMSO	22		2198	2200	2200	2200	2202	2208
	31		2198	2200	2200	2200	2202	2206
	49		2198	2200	2200	2200	2202	2204
	84		2198	2200	2200	2200	2202	2202
Acetone	20	2198	2198	2198	2198			
	34	2198	2198	2198	2198			
	51	2198	2198	2198	2198			
	70	2198	2198	2198	2198			
DMF	20	2194	2194	2194	2196	2196	2196	2200
	38	2194	2194	2194	2196	2196	2196	2198
	49	2194	2194	2194	2196	2196	2196	2196
	75	2194	2194	2194	2196	2196	2196	2196
THF	20	2192	2192	2192	2192			
	35	2192	2192	2192	2192			
	48	2192	2192	2192	2192			
	66	2192	2192	2192	2192			
Pyridine	21	2038	2054			2082		
	40	2038	2054			2082		
	50	2038	2054			2082		
	65	2038	2054			2082		
CH_2Cl_2	27		2190	2190				
	51		2182	2182				
	76	2176	2176					
Benzene	23		2158	2158	2158	2158		
	40		2150	2150	2150	2150		
	63		2144	2144	2144	2144		

crease of the CF_3HgX concentration) leads to a decrease of $J(^{199}Hg—C—^{19}F)$, i.e. it displaces equilibrium (2) towards the monomers. It is very interesting that for solutions of CF_3HgI or $CF_3HgOCOCF_3$ in CH_2Cl_2 or benzene the $J(^{199}Hg—C—^{19}F)$ constants depend on concentration but not on temperature. To explain this, we note that the half-widths of the satellites due to the mercury—fluorine coupling in CF_3HgX molecules depend considerably on the nature of X, the solvent, and the temperature of the sample. The values of half-widths (Hz) increase in the series $Cl < OCOCF_3 \ll I$, and with an increase of temperature. A similar pattern was observed earlier for CH_3HgX molecules [12, 13] and was rationalized in terms of anion exchange in these compounds. Consequently, association of CF_3HgX molecules decreases in the series $I \gg OCOCF_3 > Cl$. Therefore, in the case of the chloride it is much easier to displace equilibrium (2) towards the monomers by dilution with inert solvents than in the case of the trifluoroacetate or the iodide. As for the influence of temperature on solutions of CF_3HgI or $CF_3HgOCOCF_3$ in CH_2Cl_2 or benzene we may assume that these strongly associated molecules exist mainly in the form of dimers (I) in the solutions under investigation.


(I)

The dimers are weakly solvated by CH_2Cl_2 or benzene and there are three equilibria in these solutions (4-6). An increase of the temperature of the solu-

$$(CF_3HgX)_2 \rightleftharpoons 2\ CF_3HgX \qquad (4)$$

$$(CF_3HgX)_2 + 2D \rightleftharpoons (CF_3HgX\cdot D)_2 \qquad (5)$$

$$CF_3HgX + 2D \rightleftharpoons CF_3HgX\cdot 2D \qquad (6)$$

tion will displace equilibrium (4) towards the monomers and at the same time equilibria (5) and (6) towards the nonsolvated dimers and monomers, respectively.

In the preceding paper, we made some conclusions about the 1/1 and 1/2 complexes of Bz_2Hg with various solvents [4]. We found that for a tetracoordinated mercury atom the $J(^{199}Hg—C—^{1}H)$ constant is lower than for a tricoordinated one. We may assume that $J(^{199}Hg—C—^{19}F)$ for $(CF_3HgX\cdot D)_2$ is lower than for dimer (I) and so the constancy of J_{obs} at various temperature is apparent. For solutions of CF_3HgX molecules in such solvents as DMSO, DMF, THF, acetone and pyridine, it is important to note primarily that for CF_3HgCl the J_{obs} values do not depend either on the concentration, or on the temperature but decrease in the series (see Table 2):

$$\text{DMSO} > \text{DMF} > \text{Acetone} > \text{THF} > \text{Pyridine} \qquad (7)$$

This observation may be rationalized if we assume that only complexes of the type $CF_3HgCl\cdot 2D$ exist for all concentrations and at all temperatures and that the $J(^{199}Hg—C—^{19}F)$ values observed reflect a redistribution of electron density in these complexes. In compliance with former conclusions [5], these $J(^{199}Hg—C—^{19}F)$ constants for complexes with various solvents reflect the electro-donor power of the solvents, and therefore the sequence (7) is the order of electron-donor ability of the solvents under investigation.

The picture changes slightly on going from CF_3HgCl to CF_3HgI (Table 1) or $CF_3HgOCOCF_3$ (Table 3). For CF_3HgI the J_{obs} values for solutions in DMSO or DMF are the same and, although we have the same order of electron-donor ability for the rest of solvents, there is a temperature dependence of J_{obs} for pyridine. This may be rationalized if we assume that equilibrium (8) is the most important in these solutions. An increase of temperature displaces equilibrium

$$CF_3HgI\cdot D + D \rightleftharpoons CF_3HgI\cdot 2D \qquad (8)$$

(8) to complexes of the type $CF_3HgI\cdot D$ and J_{obs} increases in accord with the conclusions derived in the preceding paper [4] on the complexes such as $Bz_2Hg\cdot D$ and $Bz_2Hg\cdot 2D$. So we conclude that $CF_3HgI\cdot D$ complexes are T-shaped, and the donor-acceptor bond in the complexes is of the *p—d*-type while the relative content of *s*-electrons in the F—C—Hg group is higher than in the CF_3HgI molecule and in the $CF_3HgI\cdot 2D$ complex. The latter complex is a distorted tetragonal pyramid in which the bonds of mercury with carbon, iodine, or donor atoms of the solvents are sp^3-hybrids.

The same conclusions have been derived for complexes of $CF_3HgOCOCF_3$ with pyridine (Table 3). For the electron-donor ability of solvents with respect to this organomercury molecule, we have obtained the sequence (9) in which the

$$\text{DMSO} > \text{Acetone} > \text{DMF} > \text{THF} \gg \text{Pyridine} \qquad (9)$$

differences between the J_{obs} for the various systems (except for pyridine) are very small.

Experimental

The synthesis of the compounds CF_3HgCl, CF_3HgI and $CF_3HgOCOCF_3$ was carried out as described elsewhere [6]. The method of purification of the solvents used is described elsewhere [14].

^{19}F NMR spectra were measured on a JEOL JNM 4H-100 spectrometer (94 MHz). Frequency sweep mode was employed and the ^{19}F CF_3HgX signal was used as the internal lock. Spin—spin coupling constants were measured accurately to ± 1.0 Hz. The temperature was adjusted by means of a JEOL T-3 probe and was measured accurately to ± 2°.

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