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A ^{199}Hg NMR Study of Redistribution Reactions Involving bis(trichloroethenyl)-mercury

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The redistribution equilibria $Hg(C_2Cl_3)_2 + HgY_2 \rightleftharpoons 2Cl_3C_2HgY$ *(Y = Cl, Br, I, CN, SCN,* SC_2H_5, SC_6H_5, *OAc,* O_3SCF_3, C_6H_5 *and bis(2-chlorophenyl)-1-triazenato-N*^{1}*,N*^{3}*) were investigated by means of* ^{199}*Hg NMR. Starting from the symmetric compounds the time necessary for equilibration varies between minutes and months and correlates with the polarity of the Hg–Y bond. The equilibrium constants* $K = [HgXY]^2/([HgX_2][HgY_2])$ *increase in the order X = CN <* C_2Cl_3 *<* C_6H_5*.* $C_6H_5HgC_2Cl_3$ *decomposes in DMSO at 100 °C to yield* C_6H_5HgCl*. The solvent effects upon* $\delta(^{199}Hg)$ *of* $Hg(C_2Cl_3)_2$ *disagree considerably with that upon non-coordinating* $HgMe_2$ *indicating different mechanisms to be effective.*

Introduction

Redistribution equilibria [1, 2] (eqn. 1) in solution can be studied in favorable cases using

$$HgX_2 + HgY_2 \rightleftharpoons 2\,HgXY \qquad (1)$$

vibrational [3] or electronic absorption [4] spectroscopy or ^{1}H NMR [5], ^{199}Hg NMR on the other hand provides a generally applicable technique: (*i*) If one or both of the Hg–X and Hg–Y bonds are stable on the NMR time scale, the various species being present in solution according to eqn. 1 display distinct absorptions, this allowing straightforward inspection of the equilibrium. (ii) If both the Hg–X and the Hg–Y bonds are kinetically labile on the NMR time scale evaluation of eqn. 2 for different concentrations readily yields ν_{HgXY} and $K = [HgXY]^2/([HgX_2]\,[HgY_2])$.

$$\nu = \nu_{HgX_2}\,p_{HgX_2} + \nu_{HgY_2}\,p_{HgY_2} + \nu_{HgXY}\,p_{HgXY} \qquad (2)$$

This work dealing with trichloroethenylmercury compounds is an example of type (i) in view of the kinetic stability of the Hg–C bond on the NMR time scale usually observed.

Results and Discussion

The ^{199}Hg NMR spectra of equimolar mixtures of bis(trichloroethenyl)-mercury and one of HgY_2 (Y = Cl, Br, I, CN, SCN, SC_2H_5, SC_6H_5, OAc, O_3SCF_3, C_6H_5 and bis(2-chlorophenyl)-1-triazenato-N^1, N^3), being in equilibrium according to the redistribution reaction eqn. 1, consist of three signals attributable to the respective symmetric and the asymmetric (mixed) species. This proves that even the mixed compounds being not capable of existence in the solid state (Y = I, SCN) [6] are present in solution. Equimolar equilibrated mixtures of $Hg(C_2Cl_3)_2/Hg(OAc)_2$ and $Hg(C_2Cl_3)_2/Hg(O_3SCF_3)_2$ in methanol on the other hand display only the signal of the mixed species. The redistribution equilibrium (eqn. 1) thus lies completely on the (right) side of the asymmetric species for Y = OAc and O_3SCF_3. The absence of rapid exchange reactions according to eqns. 2 and 3, which would also give rise to only one absorption was assured by the observation of two resonances in

$$\underline{Hg}(C_2Cl_3)_2 + Cl_3C_2HgY \rightleftharpoons Cl_3C_2\underline{Hg}Y + Hg(C_2Cl_3)_2 \qquad (2)$$

$$Cl_3C_2\underline{Hg}Y + HgY_2 \rightleftharpoons \underline{Hg}Y_2 + Cl_3C_2HgY \qquad (3)$$

$$Y = OAc,\ O_3SCF_3$$

suitably nonequimolar mixtures. This was also noted for $NCHgO_3SCF_3$ [7]. The kinetic stability of the Hg–C bond in $Cl_3C_2HgO_3SCF_3$ towards 'one alkyl exchange' (eqn. 3) is in contrast to $C_6H_5HgO_3SCF_3$ [8] where C_6H_5 exchange occurs on the Hg NMR time scale. Electron withdrawing substitution of the organo groups thus appears to increase the kinetic stability of the Hg–C bond in keeping with the electrophilic substitution mechanism proposed [9].

The equilibrium constants of the redistribution reaction (eqn. 1) were estimated by integration of the

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TABLE I. Equilibrium Constants.

Y	solvent		$\delta(^{199}Hg)^a$			K^b
			$Hg(C_2Cl_3)_2$	Cl_3C_2HgY	HgY_2	
Cl	DMSO*	c	1158.0	1049.3	889.7	130
Br	DMSO	c	1159.9	889.4	320.8	8.0
Br	pyridine	c	1243.7	1097.4	763.3	1.4
I	DMSO	c	1163.3	586.5	−735.1	0.2
CN	DMSO	c	1157.1	1102.4	1034.3	2.8
SCN	DMSO	c	1157.8	1156.9	1152.2	1.4
SCN	DMSO pyridine 1:1	d	1205.5	1198.0	1426.4	0.72
SC_2H_5	DMSO pyridine 1:1	d	1212.4	1398.6	1495.5	2.0
SC_6H_5	DMSO	c	1166.2	1240.3	1276.6	2.0
SC_6H_5	DMSO pyridine 1:1	d	1206.1	1292.2	1360.3	1.9
OAc	methyl alcohol	c		712.0		>10000
OAc	DMSO	c	1154.6	764.5		2700
O_3SCF_3	methyl alcohol	c		730.8		>10000
O_3SCF_3	DMSO	c	1157.0	789.5	62.2	8.3
C_6H_5	toluene	c	1189.2	1409.2	1639.4	87
C_6H_5	DMSO	c	1157.6	1355.2	1578.5	83
C_6H_5	pyridine	c	1239.4	1395.0	1601.8	59
$2Cl\text{-}T^e$	DMSO pyridine 1:1	d	1203.9	999.4	600.0	390

*DMSO = methylsulfoxide. [a] In ppm to high frequency of aqueous $Hg(ClO_4)_2$ (2 mmol HgO/ml 60% $HClO_4$), 308 K. [b] $K = [Cl_3C_2HgY]^2/([Hg(C_2Cl_3)_2][HgY_2])$. [c] Equilibrated mixtures of 0.5 mmol $Hg(C_2Cl_3)_2$ and 0.5 mmol HgY_2/ml solvent. [d] Equilibrated mixtures of 0.25 mmol $Hg(C_2Cl_3)_2$ and 0.25 mmol HgY_2/ml solvent. [e] bis(2-chlorophenyl)-1-triazenato-N^1, N^3.

signals and are listed in Table I. As has been presumed earlier [6] the greater the difference in electronegativity between X and Y (eqn. 1), the more stable is the respective mixed species XHgY. Equilibria of the corresponding systems involving diphenyl-mercury instead of $Hg(C_2Cl_3)_2$ are well over to the side of the asymmetric species [10].

For $Hg(CN)_2$ [7] the equilibria lie even more on the side of the symmetric species than for $Hg(C_2Cl_3)_2$. The acceptor behaviour (in keeping with the electronegativity of the organo groups) of $Hg(C_2Cl_3)_2$ has recently been estimated to be between $Hg(C_6H_5)_2$ and $Hg(C_6F_5)_2$ [11]. Surprisingly the respective symmetric compounds could not be detected for mixed trifluoromethyl-mercury compounds [12] although the existence of solid coordination of $Hg(CF_3)_2$ demonstrates the electronegativity of the CF_3 group.

It is interesting to note that the position of the redistribution equilibrium in solution may differ from that in the solid state or, expressed in another way, that solid mixed compounds may be isolated in quantitative yield despite the presence of the respective symmetric compounds in solution. A corresponding situation has also been observed for some mixed triazenato-mercury compounds [13]. As can be seen from Table I there is only a gradual difference in K for Y = Br and I but Cl_3C_2HgBr is capable of existence in the solid state whilst Cl_3C_2HgI is not. Besides the stability of the mixed compound in solution, crystal forces seem thus to be responsible for the existence of a mixed mercury compound in the solid state.

Stronger donor solvents, *e.g.* pyridine, decrease the equilibrium constants (Table I) *i.e.* partially symmetrisize the mixed species, this reflecting the relative strength of donor acceptor complexes of the symmetric or the asymmetric compounds with the solvent.

Large differences in the time necessary for equilibration according to eqn. 1 were noted: Equilibration of bis(trichloroethenyl)-mercury with $Hg(OAc)_2$ or $Hg(O_3SCF_3)_2$ is attained within minutes, and with $Hg(SC_2H_5)_2$, $Hg(SC_6H_5)_2$ or HgY_2 (Y = Cl, Br, I) within hours. The reaction of $HgCl_2$ proceeds faster than of HgI_2. For the triazenato-mercury compounds equilibrium is reached within a day whilst the reaction of $Hg(C_2Cl_3)_2$ and $Hg(C_6H_5)_2$ takes several months in DMSO at room temperature. The latter reaction speeds up at 100 °C to a few days and proceeds faster in pyridine than in DMSO and even slower in toluene. The reaction

TABLE II. Chemical Shifts[a] of $HgMe_2$ [b], $Hg(C_2Cl_3)_2$[c] and $Hg(CN)_2$[d] in Different Media.

Solvent	$HgMe_2$	$Hg(C_2Cl_3)_2$	$Hg(CN)_2$
carbon disulfide		1251.5	
pyridine	2292.3	1240.8	1312.0
bromoform		1238.5	
carbon tetrachloride	2375.1	1225.2	
chloroform	2358.1	1216.4	
dichloromethane	2344.2	1208.0	
toluene	2336.2	1187.2	
diethyl ether	2357.5	1177.3	
methyl sulfoxide	2278.1	1158.0	1033.7
methyl alcohol		1148.0	1020.6
acetonitrile	2308.0	1148.0	973.3
tetrahydrofuran	2310.4	1127.8	1001.6
p-dioxane	2295.3	1122.0	
acetone	2315.1	1121.7	933.4

[a] In ppm to high frequency of aqueous $Hg(ClO_4)_2$ (2 mmol/ml 60% $HClO_4$), 308 K. [b] Taken from Ref. [18], 1.0 *M* converted to $Hg(ClO_4)_2$ reference: 1.0 *M* $Hg(C_6H_5)_2$ in DMSO: 1577.8 ppm (reference $Hg(ClO_4)_2$) and −808.5 ppm (reference $HgMe_2$ neat, [18]). [c] 0.5 *M*. [d] Taken from Ref. [7], 0.5 *M*.

rates correlate thus with the polarity of the Hg–Y bond.

In DMSO at 100 °C almost quantitative decomposition of phenyl(trichloroethenyl)-mercury to chlorophenyl-mercury occurs within 5 days. Divalent carbon transfer [14] to DMSO seems indicated in view of the reactivity of DMSO towards carbenes [15]. The nature of the 'divalent carbon acceptor' seems to play an important role in the transfer reaction since $|C = CCl_2$ transfer to some other acceptors could not be induced thermally but only photochemically [16].

The ^{199}Hg chemical shifts (see Table I) of the mixed species were found within the range of the respective symmetric compounds with the exception of Cl_3C_2HgSCN (this was also noted to apply for $C_2H_5SHgSCN$ and $C_6H_5SHgSCN$ [17]). The position of $\delta(^{199}Hg)$ of the asymmetric compound relative to the symmetric ones is quite characteristic [7, 12], although more experimental data seem to be necessary for a comprehensive explanation. The variation in $\delta(^{199}Hg)$ of $Hg(C_2Cl_3)_2$ in Table I includes the effects of concentration, solvents and the different other Hg-species in solution. Thus $\delta(^{199}Hg)$ increases in the presence of HgY_2 and Cl_3C_2HgY in the order Y = Cl < Br < I. The presence of SC_2H_5 and SC_6H_5 groups shifts $\delta(^{199}Hg)$ of $Hg(C_2Cl_3)$ to the highest frequencies observed.

The effects of the solvents alone upon $\delta(^{199}Hg)$ of bis(trichloroethenyl)-mercury were examined and are presented in Table II and compared with dimethyl-mercury [18] and mercuric cyanide [7]. There is a considerable disagreement between the solvent series of $Hg(C_2Cl_3)_2$ and $HgMe_2$. On the other hand data of $Hg(C_2Cl_3)_2$ and $Hg(CN)_2$ look qualitatively similar. Non-coordinating organo-mercury compounds exhibit appreciable solvent effects upon $\delta(^{199}Hg)$ which are unlikely to be due to solvent coordination to mercury [19]. For dimethyl-mercury interactions of the quadrupolar $HgMe_2$ with the fields produced by the polar solvents in a solvation shell were presumed [19]. Whilst in general the more polar solvents cause $\delta(^{199}Hg)$ of relatively inert organo-mercurials to be shifted to low frequencies, coordination should shift $\delta(^{199}Hg)$ towards high frequencies [19]. In this context it is interesting to note the relative position of pyridine, the solvent most likely to coordinate, in the solvent series of $HgMe_2$, $Hg(C_2Cl_3)_2$ and $Hg(CN)_2$. Increasing $\delta(^{199}Hg)$ values with increasing acceptor qualities in the order $HgMe_2 < Hg(C_2Cl_3)_2 < Hg(CN)_2$ indicate thus coordination to play an increasing role as mechanism for solvent effects.

Experimental

The NMR spectra were recorded on a Bruker WP-80 multinuclear instrument in the FT mode, mass spectra were obtained on a Varian Mat CH 7, elemental analysis on a Heraeus EA 415. Bis(trichloroethenyl)-mercury [6], bis[bis(2-chlorophenyl)-1-triazenato-N^1, N^3]-mercury [13], $[Hg(DMSO)_6](O_3SCF_3)_2$ [20], $Hg(SC_2H_5)_2$ and $Hg(SC_6H_5)_2$ [21] were prepared according to the literature, the other mercuric compounds were commercial.

(Ethanethiolato-S)trichloroethenyl-mercury was obtained in quantitative yield by slow evaporation of an equilibrated solution of equimolar amounts of the respective symmetric compounds in DMSO/pyridine 1:1; colorless needles, m.p. 126 °C. *Anal.* Calcd. for $C_4H_5Cl_3HgS$, C, 12;3; H, 1.3. Found C, 12.5; H, 1.3%. MW: m/e 390 (M^+ for ^{35}Cl and ^{200}Hg).

[Bis(2-chlorophenyl)-1-triazenato-N^1, N^3] trichloroethenyl-mercury was obtained as described above; orange-yellow crystals, m.p. 177 °C. *Anal.* Calcd. for $C_{14}H_8Cl_5N_3Hg$, C, 28.2; H, 1.4; N, 7.0. Found C, 28.3; H, 1.2; N, 7.1%. MW: m/e 593 (M^+ for ^{35}Cl and ^{200}Hg).

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