

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

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The redistribution equilibria $\text{Hg}(\text{C}_2\text{Cl}_3)_2 + \text{HgY}_2 \rightleftharpoons 2\text{Cl}_3\text{C}_2\text{HgY}$ ($\text{Y} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{SCN}, \text{SC}_2\text{H}_5, \text{SC}_6\text{H}_5, \text{OAc}, \text{O}_3\text{SCF}_3, \text{C}_6\text{H}_5$ and bis(2-chlorophenyl)-1-triazenato- N^1, N^3) were investigated by means of ¹⁹⁹Hg 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 $K = [\text{HgXY}]^2/([\text{HgX}_2][\text{HgY}_2])$ increase in the order $\text{X} = \text{CN} < \text{C}_2\text{Cl}_3 < \text{C}_6\text{H}_5$. $\text{C}_6\text{H}_5\text{HgC}_2\text{Cl}_3$ decomposes in DMSO at 100 °C to yield $\text{C}_6\text{H}_5\text{HgCl}$. The solvent effects upon $\delta(^{199}\text{Hg})$ of $\text{Hg}(\text{C}_2\text{Cl}_3)_2$ 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



vibrational [3] or electronic absorption [4] spectroscopy or ¹H NMR [5], ¹⁹⁹Hg 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 concentra-

$$\nu = \nu_{\text{HgX}_2} \text{P}_{\text{HgX}_2} + \nu_{\text{HgY}_2} \text{P}_{\text{HgY}_2} + \nu_{\text{HgXY}} \text{P}_{\text{HgXY}} \quad (2)$$

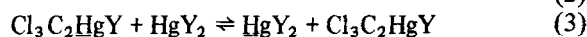
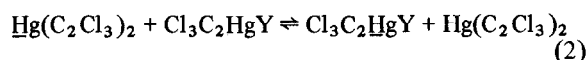
tions readily yields ν_{HgXY} and $K = [\text{HgXY}]^2/([\text{HgX}_2][\text{HgY}_2])$.

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 ¹⁹⁹Hg NMR spectra of equimolar mixtures of bis(trichloroethenyl)-mercury and one of HgY_2 ($\text{Y} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{SCN}, \text{SC}_2\text{H}_5, \text{SC}_6\text{H}_5, \text{OAc}, \text{O}_3\text{SCF}_3, \text{C}_6\text{H}_5$ 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 ($\text{Y} = \text{I}, \text{SCN}$) [6] are present in solution. Equimolar equilibrated mixtures of $\text{Hg}(\text{C}_2\text{Cl}_3)_2/\text{Hg}(\text{OAc})_2$ and $\text{Hg}(\text{C}_2\text{Cl}_3)_2/\text{Hg}(\text{O}_3\text{SCF}_3)_2$ 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 $\text{Y} = \text{OAc}$ 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



$\text{Y} = \text{OAc}, \text{O}_3\text{SCF}_3$

suitably nonequimolar mixtures. This was also noted for $\text{NCHgO}_3\text{SCF}_3$ [7]. The kinetic stability of the Hg–C bond in $\text{Cl}_3\text{C}_2\text{HgO}_3\text{SCF}_3$ towards ‘one alkyl exchange’ (eqn. 3) is in contrast to $\text{C}_6\text{H}_5\text{HgO}_3\text{SCF}_3$ [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		$\delta(^{199}\text{Hg})^a$			K^b
			$\text{Hg}(\text{C}_2\text{Cl}_3)_2$	$\text{Cl}_3\text{C}_2\text{HgY}$	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-T^e	DMSO pyridine 1:1	d	1203.9	999.4	600.0	390

*DMSO = methylsulfoxide. ^aIn ppm to high frequency of aqueous $\text{Hg}(\text{ClO}_4)_2$ (2 mmol HgO/ml 60% HClO_4), 308 K. ^b $K = [\text{Cl}_3\text{C}_2\text{HgY}]^2 / ([\text{Hg}(\text{C}_2\text{Cl}_3)_2][\text{HgY}_2])$. ^cEquilibrated mixtures of 0.5 mmol $\text{Hg}(\text{C}_2\text{Cl}_3)_2$ and 0.5 mmol HgY_2/ml solvent. ^dEquilibrated mixtures of 0.25 mmol $\text{Hg}(\text{C}_2\text{Cl}_3)_2$ and 0.25 mmol HgY_2/ml solvent. ^ebis(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 $\text{Hg}(\text{C}_2\text{Cl}_3)_2$ are well over to the side of the asymmetric species [10].

For $\text{Hg}(\text{CN})_2$ [7] the equilibria lie even more on the side of the symmetric species than for $\text{Hg}(\text{C}_2\text{Cl}_3)_2$. The acceptor behaviour (in keeping with the electronegativity of the organo groups) of $\text{Hg}(\text{C}_2\text{Cl}_3)_2$ has recently been estimated to be between $\text{Hg}(\text{C}_6\text{H}_5)_2$ and $\text{Hg}(\text{C}_6\text{F}_5)_2$ [11]. Surprisingly the respective symmetric compounds could not be detected for mixed trifluoromethyl-mercury compounds [12] although the existence of solid coordination of $\text{Hg}(\text{CF}_3)_2$ 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 $\text{Cl}_3\text{C}_2\text{HgBr}$ is capable of existence in the solid state whilst $\text{Cl}_3\text{C}_2\text{HgI}$ 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 symmetrize 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 $\text{Hg}(\text{OAc})_2$ or $\text{Hg}(\text{O}_3\text{SCF}_3)_2$ is attained within minutes, and with $\text{Hg}(\text{SC}_2\text{H}_5)_2$, $\text{Hg}(\text{SC}_6\text{H}_5)_2$ 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 $\text{Hg}(\text{C}_2\text{Cl}_3)_2$ and $\text{Hg}(\text{C}_6\text{H}_5)_2$ 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 HgMe₂, Hg(C₂Cl₃)₂^c and Hg(CN)₂^d in Different Media.

Solvent	HgMe ₂	Hg(C ₂ Cl 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

^aIn ppm to high frequency of aqueous Hg(ClO₄)₂ (2 mmol/ml 60% HClO₄), 308 K. ^bTaken from Ref. [18], 1.0 M converted to Hg(ClO₄)₂ reference: 1.0 M Hg(C₆H₅)₂ in DMSO: 1577.8 ppm (reference Hg(ClO₄)₂) and -808.5 ppm (reference HgMe₂ neat, [18]). ^c0.5 M. ^dTaken 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 = CCl₂ transfer to some other acceptors could not be induced thermally but only photochemically [16].

The ¹⁹⁹Hg chemical shifts (see Table I) of the mixed species were found within the range of the respective symmetric compounds with the exception of Cl₃C₂HgSCN (this was also noted to apply for C₂H₅SHgSCN and C₆H₅SHgSCN [17]). The position of δ(¹⁹⁹Hg) 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 δ(¹⁹⁹Hg) of Hg(C₂Cl₃)₂ in Table I includes the effects of concentration, solvents and the different other Hg-species in solution. Thus δ(¹⁹⁹Hg) increases in the presence of HgY₂ and Cl₃C₂HgY in the order Y = Cl < Br < I. The presence of SC₂H₅ and SC₆H₅ groups shifts δ(¹⁹⁹Hg) of Hg(C₂Cl₃)₂ to the highest frequencies observed.

The effects of the solvents alone upon δ(¹⁹⁹Hg) 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(C₂Cl₃)₂ and HgMe₂. On the other hand data of Hg(C₂Cl₃)₂ and Hg(CN)₂ look qualitatively similar. Non-coordinating organo-mercury compounds exhibit appreciable solvent effects upon δ(¹⁹⁹Hg) which are unlikely to be due to solvent coordination to mercury [19]. For dimethyl-mercury interactions of the quadrupolar HgMe₂ with the fields produced by the polar solvents in a solvation shell were presumed [19]. Whilst in general the more polar solvents cause δ(¹⁹⁹Hg) of relatively inert organo-mercurials to be shifted to low frequencies, coordination should shift δ(¹⁹⁹Hg) 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 HgMe₂, Hg(C₂Cl₃)₂ and Hg(CN)₂. Increasing δ(¹⁹⁹Hg) values with increasing acceptor qualities in the order HgMe₂ < Hg(C₂Cl₃)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-N¹, N³]-mercury [13], [Hg(DMSO)₆](O₃SCF₃)₂ [20], Hg(SC₂H₅)₂ and Hg(SC₆H₅)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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