

ORGANOMERCURY ANIONIC COMPLEXES IN ACETONITRILE*

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(Received December 21st, 1970)

SUMMARY

Coordination properties of organomercury compounds RHgCl ($\text{R} = \text{Me, Et, Pr}$ and Ph) have been studied spectrophotometrically in acetonitrile. The stability constants of the halocomplexes RHgCl_2^- have been determined, and are discussed.

INTRODUCTION

The coordinating ability of organomercury acceptors as RHgX , R_FHgX , RHg^+ and R_FHg^+ ($\text{R} = \text{alkyl or aryl group}$, $\text{R}_F = \text{perfluoroalkyl or aryl group}$, $\text{X} = \text{halide ion}$) are markedly affected by the nature of organic substituents. The ability to form complexes has been extensively investigated for the cationic species¹, but few data are reported in literature for the anionic species $(\text{RHgX}_{n+1})^{n-}$ and $(\text{R}_F\text{HgX}_{n+1})^{n-}$ ($n = 1, 2$)^{2,3,4}. In order to determine the coordination number of mercury in such anionic complexes and the influence of R on their stability we have studied the interaction between RHgCl ($\text{R} = \text{Me, Et, Pr, Ph}$) and Ph_3CCl as a Cl^- donor in acetonitrile; this solvent provides a suitable medium for the formation of anionic complexes^{5,6}.

EXPERIMENTAL

Materials

MeHgCl , EtHgCl , PrHgCl and PhHgCl supplied by K and K Labs (U.S.A.) were further purified by crystallization⁷. Ph_3CCl (K and K) was recrystallized from petroleum ether (b.p. $40-70^\circ$) and dried under vacuum at 60° (m.p. $110-111^\circ$ uncorrected). Acetonitrile RP (C. Erba, Italy) was purified by a published method reported⁸. The specific conductance of acetonitrile was below $1 \times 10^{-7} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$.

Molecular weight measurements

These were determined in acetonitrile at 37° using a Mechrolab vapour phase Osmometer Model 301 A.

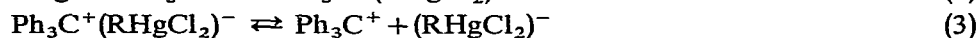
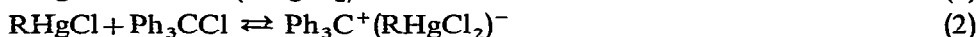
* Support of this work by N.A.T.O. Research Grant N. 374, is gratefully acknowledged.

** Ricercatore qualificato C.N.R. Laboratorio di Chimica e Tecnologia dei Radioelementi del CNR, Padova.

Spectrophotometric measurements and results

It is known that ionization of Ph_3CCl in appropriate non-aqueous media is greatly increased in presence of Cl^- acceptors; this furnishes a useful method for quantitative determination of the stability of chloro-complexes^{9,10,11}. Using this technique the absorbance of solution containing RHgCl (conc. range 5×10^{-2} – 5×10^{-3} M) and Ph_3CCl (1×10^{-3} – 2×10^{-2} M) was measured at 35° with a Unicam SP 800 Spectrophotometer.

The total concentrations of Ph_3C^+ ions and that of the ion pairs Ph_3C^+ - RHgCl_2^- , involved in the Cl^- exchange equilibria in each solution, were obtained directly from the absorbance at $\lambda = 402$ nm ($\epsilon = 4 \times 10^4$)⁹. The spectra of the solutions used are very similar to those of Ph_3COH in 98% sulphuric acid, and for the $\text{Ph}_3\text{CCl}/\text{HgCl}_2$ system in nitromethane we have assumed, as have other authors^{10,11}, that the extinction coefficients of the Ph_3C^+ ions and the $\text{Ph}_3\text{C}^+(\text{RHgCl}_2)^-$ ion pairs are also the same in acetonitrile. The following equilibria between RHgCl and Ph_3CCl in acetonitrile must be taken into account:



The stability constant K_1 may be calculated by using the values of the product K_4K_5

$$K_1 = \frac{K_2 \cdot K_3}{K_4 \cdot K_5} \quad (6)$$

(7×10^{-10}) previously⁹ found and those of the product K_2K_3 which may be evaluated graphically. Under our experimental conditions (see Table 1) it can be assumed that $[\text{Ph}_3\text{C}^+] \approx [(\text{RHgCl}_2)^-]$, since the concentrations of Ph_3C^+ and Cl^- ions produced by self-dissociation of Ph_3CCl is negligible. A rearrangement of the above equilibrium equations gives the following relation:

$$\frac{[\text{Ph}_3\text{C}^+] + [\text{Ph}_3\text{C}^+(\text{RHgCl}_2)^-]}{[\text{Ph}_3\text{CCl}] \cdot [\text{RHgCl}]} = K_2 + \left(\frac{K_2 \cdot K_3}{[\text{Ph}_3\text{CCl}] \cdot [\text{RHgCl}]} \right)^{\frac{1}{2}} \quad (7)$$

Plotting the left side of (7) against $([\text{Ph}_3\text{CCl}] \cdot [\text{RHgCl}])^{-\frac{1}{2}}$ should give a straight line of slope $(K_2 \cdot K_3)^{\frac{1}{2}}$ and intercept K_2 .

This is the behaviour we found for RHgCl ($R = \text{Me}, \text{Et}$) and Ph_3CCl systems (Fig. 1); the K_1 values are given in Table 2. The linear relationship further indicates that these acceptors do not form anionic complexes of type $(\text{RHgCl}_{n+1})^{n-}$, having $n > 1$.

In contrast, the absorbance of Ph_3CCl solutions (0.05 M) is not appreciably increased by adding PhHgCl or PrHgCl (0.05 M), and in these cases we can only obtain an indication of the highest possible values of the stability constants (Table 2).

Our results clearly reveal the ability of monoorganomercury to extend its

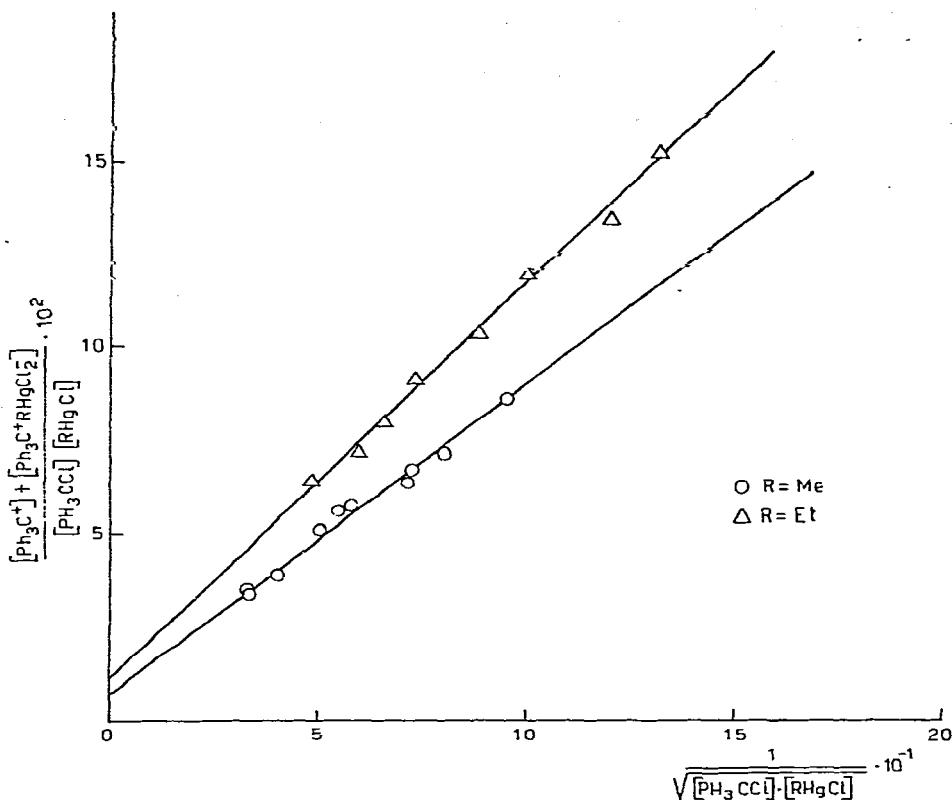
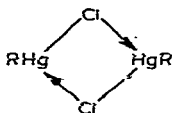


Fig. 1. Plot of $\frac{[\text{Ph}_3\text{C}^+] + [\text{Ph}_3\text{C}^+(\text{RHgCl}_2)^-]}{[\text{Ph}_3\text{CCl}] \cdot [\text{RHgCl}]}$ against $([\text{Ph}_3\text{CCl}] \cdot [\text{RHgCl}])^{-\frac{1}{2}}$.

coordination number from two to three under appropriate conditions. No evidence for $(\text{RHgX}_3)^{2-}$ species was found, although for inorganic mercury $(\text{HgX}_3)^-$ and $(\text{HgX}_4)^{2-}$ species are known. The $(\text{HgX}_3)^-$ species are considerably more stable^{1,2} than the corresponding $(\text{RHgX}_2)^-$, and this indicates a reluctance of organomercury acceptors to reach a coordination number higher than two. This behaviour may be explained by taking into account the easy distortion of the d^{10} charge cloud on the mercury atom in the linear arrangement $\text{R}-\text{Hg}-\text{X}$. The increased charge density in the plane perpendicular to $\text{C}-\text{Hg}-\text{X}$ axis reduces the possibility of attachment of other ligands¹³.

The absence of detectable formation of anionic complexes from PrHgCl and PhHgCl is very surprising; in other series of organometallic acceptors⁹, phenyl groups enhance the complexes stability. Formation of dimeric species such as



in which the central atom reach coordination number three via chloro-bridges, is

TABLE 1

EQUILIBRIUM CONCENTRATIONS OF REACTANTS IN ACETONITRILE AT 35°

Compound	$10^3 \times ([\text{Ph}_3\text{C}^+] + [\text{Ph}_3\text{C}^+(\text{RHgCl}_2)^-])$ (mole/l)	$10^3 \times [\text{Ph}_3\text{CCl}]$ (mole/l)	$10^3 \times [\text{MeHgCl}]$ (mole/l)
MeHgCl	1.25	8.56	22.88
	1.80	14.23	21.40
	0.95	6.42	17.16
	1.95	12.00	32.10
	3.12	14.23	64.40
	2.40	14.23	42.80
	3.20	13.96	64.40
	1.12	7.11	21.40
	1.27	10.68	17.82
	1.70	6.97	42.80
	EtHgCl	0.88	7.82
1.85		9.08	25.40
2.72		12.10	34.80
2.02		21.15	13.00
1.70		17.92	10.40
1.17		12.70	7.80
0.92		10.60	6.50
1.32		12.70	10.03

TABLE 2

STABILITY CONSTANTS OF THE HALOCOMPLEXES $(\text{RHgCl}_2)^-$ IN ACETONITRILE AT 35°

Complexes	Stability constants
MeHgCl_2^-	1.00×10^3
EtHgCl_2^-	1.63×10^3
PrHgCl_2^-	$< 2.5 \times 10^{-2}$
PhHgCl_2^-	$< 2.5 \times 10^{-2}$

excluded by the observed molecular weights (Found: mol.wt., 278. PrHgCl calcd.: 278; Found: mol.wt., 308. PhHgCl calcd.: 313.10.) We suggest that the difficulty of obtaining the anionic complexes $(\text{PrHgCl}_2)^-$ can be ascribed to the steric hindrance between the chlorine and hydrogen atoms bonded to the γ -carbon atom of the propyl group. In the case of $(\text{PhHgCl}_2)^-$ the delocalization of the charge from the central atom into the phenyl group is probably too small to stabilize the anionic complex. This hypothesis is supported by NMR studies on phenylmercurials¹⁴ which show that there are only feeble electronic interactions between the mercury and the aromatic organic groups.

ACKNOWLEDGEMENTS

The authors wish to thank Professor G. Tagliavini for helpful discussions.

REFERENCES

- 1 P. ZANELLA, G. PLAZZOGNA AND G. TAGLIAVINI, *Inorg. Chim. Acta*, 2 (1968) 340 and references therein.
- 2 V. F. TOROPOVA, M. K. SAIKINA, M. G. KHAKIMOV, *J. Gen. Chem. USSR*, (1967) 41.
- 3 H. J. EMELEUS AND J. J. LAGOWSKI, *J. Chem. Soc.*, (1959) 1497.
- 4 G. C. STOCCO, E. RIVAROLA, R. ROMEO AND R. BARBIERI, *J. Inorg. Nucl. Chem.*, 30 (1968) 2409 and references therein.
- 5 G. CHARLOT AND B. TRÉMILLON, *Les réactions chimiques dans les solvants et les sels fondus*, Gauthier-Villars, Editeur, Paris, 1963.
- 6 V. GUTMAN, *Coordination Chemistry in Non-Aqueous Solutions*, Springer, New York, 1968.
- 7 K. H. SLOTTA AND K. R. JACOBI, *J. Prakt. Chem.*, 120 (1928-29) 273.
- 8 J. K. KUCHARSKI AND L. SAFARIK, *Titration in non aqueous solvents*, Elsevier, Amsterdam, (1965) 53.
- 9 P. ZANELLA AND G. TAGLIAVINI, *J. Organometal. Chem.*, 12 (1968) 355.
- 10 J. W. BAYLES, A. G. EVANS AND J. R. JONES, *J. Chem. Soc.*, (1955) 206.
- 11 M. BAAZ, V. GUTMAN AND O. KUNZE, *Monatsh. Chem.*, 93 (1962) 1142.
- 12 M. BAAZ, V. GUTMAN AND O. KUNZE, *Monatsh. Chem.*, 93 (1962) 1162.
- 13 E. CARTMELL AND G. W. A. FOWLES, *Valency and molecular structure*, 3rd ed., Butterworth, London, (1966), p. 242.
- 14 W. ADCOCK, B. F. HEGARTY, W. KITCHING AND A. J. SMITH, *J. Organometal. Chem.*, 12 (1968) 21.

J. Organometal. Chem., 29 (1971) 169-173