Structure and Stability of Carboxylate Complexes. Part 17.[1] Stability Constants of some Mercury(I) Carboxylates

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Complex formation between mercury(I) ions and a series of unsubstituted and substituted monocarboxylates (including some potentially bidentate ligands) has been studied by precise potentiometric titration at 25.00 °C in 3 mol dm^{-3} sodium perchlorate medium. A linear-free-energy plot indicates that unidentate complexes are formed in all the systems studied.

OUR recently described work[1] on the complexes of mercury(II) with some substituted and unsubstituted alkanoate ligands containing one or more oxygen-donor atoms has been followed by a study of the complexes of mercury(I) ions with many of the same ligands. Mercury(I) ions form stable complexes with fewer ligands than do mercury(II) ions, owing to the disproportionation reaction (i) which occurs slowly in aqueous solutions. A typical value[2] of $K_d = [Hg_2{}^{2+}][Hg^{2+}]^{-1} = 132.4$ (in 0.5 mol dm^{-3} sodium perchlorate at 25 °C) shows that the equilibrium lies well to the right in perchlorate media, but the position of this equilibrium can be altered markedly in a complex system by preferential co-ordination of Hg^{II}.

$$Hg^{2+} + Hg \rightleftharpoons [Hg_2]^{2+} \qquad (i)$$

The well known compounds of Hg^{I}, such as the halides, therefore, tend to be those sparingly soluble in water. However, a number of stable complexes of Hg^{I} in solution

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[1] Part 16, preceding paper.

[2] W. Forsling, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, 1952, **6**, 901.

have been reported, including those with polyphosphates and dicarboxylates,[3] phthalate,[4] iminodiacetate,[5] and aniline.[6]

As with the complexes of Hg^{II}, linear co-ordination is well established for mercury(I) complexes. Thus *X*-ray studies of mercury(I) nitrate dihydrate[7] and of mercury(I) perchlorate[8] in crystals and in solution indicate linear H_2O–Hg–Hg–H_2O units, and dipole-moment studies[9] show the existence of collinear atoms –O–Hg–Hg–O– in mercury(I) trichloroacetate.

EXPERIMENTAL

A stock solution of mercury(I) perchlorate was prepared by shaking *ca.* 0.1 mol dm^{-3} mercury(II) perchlorate with mercury for 48 h. Working solutions [1×10^{-2} mol dm^{-3} mercury(I) perchlorate, 2×10^{-2} mol dm^{-3} perchloric acid, 2.98 mol dm^{-3} sodium perchlorate] were analysed potentiometrically for Hg^{I} with potassium dichromate in the presence of excess of iron(II) and thiocyanate ions.[10] The mercury(II) concentration was determined from the changes in the redox potential as the mercury(I) solution was titrated with acidic mercury(II) perchlorate of known concentration in a sodium perchlorate medium. A 1×10^{-2} mol dm^{-3} solution of Hg^{I} contained typically 5.5×10^{-5} mol dm^{-3} Hg^{II}. Analyses were checked frequently.[11]

The sources and preparation of other reagents are described elsewhere[1] together with details of the potentiometric apparatus, the glass-electrode calibration, and the titration procedure.

CALCULATIONS

The calculation of the standard potential of the electrode system is described in ref. 1, and the same symbols and strategy of calculation are followed here. Particularly, *M*, *B*, *A*, and *H* represent the total analytical concentrations of Hg^{I}, Hg^{II}, ligand, and proton, and *m*, *b*, *a* and *h* the concentrations of the respective free species. In the calculation, the free-ligand concentration (*a*) and the formation function

$$\bar{n} = (\sum^{N} n[MA_n])\,(m + \sum^{N}[MA_n])^{-1} \qquad (1)$$

($\bar{n}$) were obtained from the experimental data, and two stability constants, ${}^{I}\beta_n$, were fitted to the formation curve

$${}^{I}\beta_n = [MA_n]a^{-n}m^{-1} \qquad (2)$$

using normalised curves and the LINEFITTING[1,12] procedure of our program MERCURY.

Determination of the Formation Curve.—The treatment of the proton complexes of the carboxylate ligands described in ref. 1 includes a simple protonation constant K_1^{H} (= $[HA]h^{-1}a^{-1}$) together with two stability constants β_{12}^{H} and β_{22}^{H} ($\beta_{j2}^{H} = [H_jA_2]h^{-j}a^{-2}$) quantifying the apparent formation of associated species in solution. In view of the very low concentration of mercury(II) ions relative to mercury(I), it is possible to neglect the hydrolysis of Hg^{II} in the mass-balance equations at hydrogen-ion concentrations above $10^{-2.3}$ mol dm^{-3} and to obtain from the proton mass

$$0 = (h - H) + ahK_1^{H} + a^2h(\beta_{12}^{H} + 2h\beta_{22}^{H}) \qquad (3)$$

balance equation (3) [compare ref. 1, equation (8)] which is readily solved for *a* by Newton's iterative method, using as an initial value $a = (H - h)(hK_1^{H})^{-1}$. From the remaining

$$\bar{n} = [(A - a) - (H - h) - a^2h\beta_{12}^{H} - B\bar{n}_2]M^{-1} \qquad (4)$$

mass balances we obtain (4) [compare ref. 1, equation (11)] where $\bar{n}_2$ is the degree of formation of mercury(II) complexes calculated from *a* and the known β_n of the mercury(II) complex system.

DISCUSSION

Hydroxomercury(I) *Complexes.*—Previous measurements[2] of the hydroxomercury(I) system give $\log {}^{I}\beta_1{}^{*} = \log \{[M(OH)]hm^{-1}\} = -5 \pm 0.3$ in 0.5 mol dm^{-3} $Na[ClO_4]$. Such species are therefore justifiably neglected in the calculation of our mercury(I) alkanoate stability constants, and further it is expected that any hydroxo-complex will be relatively unstable to disproportionation. Our titrations of the hydroxide system indeed gave permanent black precipitates, and in view of this the mercury(I) alkanoate titrations were carried out at low (1×10^{-3}—3×10^{-3} mol dm^{-3}) concentrations of Hg^{I} to prevent precipitation during the electrode-calibration titrations.

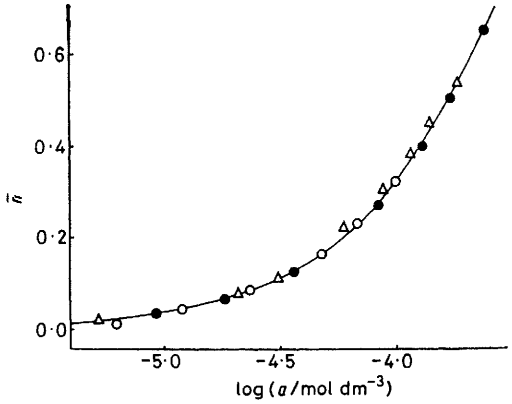

FIGURE 1 Formation curve for mercury(I) acetate; initial mercury(I)-ion concentrations 1.6×10^{-3} mol dm^{-3} (○ and △) and 3.0×10^{-3} mol dm^{-3} (●). The curve was calculated from $\log {}^{I}\beta_2 = 3.57$, $\log {}^{I}\beta_2 = 6.63$

Mercury(I) *Alkanoates.*—At least two titrations were

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[3] T. Yamane and N. Davidson, *J. Amer. Chem. Soc.*, 1960, **82**, 2123.

[4] Z. Gregorowicz and J. Ciba, *Roczniki Chem.*, 1966, **40**, 1377.

[5] N. A. Skorik and V. N. Kumok, *Zhur. obshchei Khim.*, 1967, **37**, 1722.

[6] T. H. Wirth and N. Davidson, *J. Amer. Chem. Soc.*, 1964, **86**, 4314.

[7] D. Grdenic, *J. Chem. Soc.*, 1956, 312.

[8] G. Johansson, *Acta Chem. Scand.*, 1966, **20**, 553.

[9] N. R. Davidson and L. E. Sutton, *J. Chem. Soc.*, 1942, 565.

[10] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961.

[11] R. J. Merrer and J. T. Stock, *Analyst*, 1971, **96**, 359.

[12] G. L. Cumming, J. S. Rollett, F. J. C. Rossotti, and R. J. Whewell, *J.C.S. Dalton*, 1972, 2652.

carried out for each ligand system, using different concentrations of Hg^I. No precipitate was formed during these titrations, and close examination of the solutions after titration failed to reveal any trace of mercury deposits even after 24 h. We therefore conclude that stable complexes were formed. The formation curves for the two titrations were in each case superimposable, so that the stepwise formation of complex species MA_n was demonstrated. The formation curves extended to maximum values of $\bar{n}$ between 0.5 and 1.3, and the use of only two stability constants ${}^I\beta_n$ [equation (2)] gave excellent reproduction of the formation curves (see, for example, Figure 1). The values of the constants obtained are shown in the Table, together with the protonation constants K_1^H from ref. 1. The value for 3-hydroxybutanoate should be regarded as tentative since $\bar{n}$ did not exceed 0.2 in these titrations.

Stability constants of mercury(I) complexes at 25.00 °C in a 3 mol dm^{-3} sodium perchlorate medium

Ligand	log K_1^H	log ${}^I\beta_1$	log ${}^I\beta_2$	log (K_1/K_2)
(1) Formate	3.907	2.94 ± 0.02	5.45 ± 0.02	0.43
(2) Acetate	5.011	3.57 ± 0.03	6.63 ± 0.03	0.51
(3) Propanoate	5.161	3.72 ± 0.02	6.99 ± 0.01	0.45
(4) Chloroacetate	3.028	2.40 ± 0.05	4.4 ± 0.1	0.4
(6) Hydroxyacetate	3.923	3.01 ± 0.02	5.71 ± 0.05	0.31
(7) 3-Hydroxybutanoate	4.757	3.3 ± 0.1		
(9) Methoxyacetate	3.743	2.98 ± 0.01	5.41 ± 0.01	0.55
(10) 3-Methoxypropanoate	4.707	3.50 ± 0.01	6.63 ± 0.06	0.37

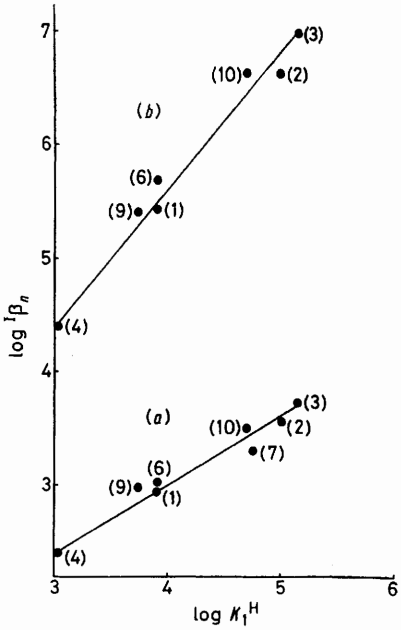

FIGURE 2 Linear-free-energy plots for complexes of mercury(I) ions with oxygen-donor ligands. The identification numbers correspond to those in the Table. Line (*a*) is log ${}^I\beta_1 = 0.6 + 0.6 \log K_1^H$; (*b*) is log ${}^I\beta_2 = 0.8 + 1.2 \log K_1^H$

Figure 2 shows linear-free-energy plots [13] in which log ${}^I\beta_1$ and log ${}^I\beta_2$ are plotted against log K_1^H. The straight line drawn, log ${}^I\beta_1 = 0.6 + 0.6 \log K_1^H$, fits all the log ${}^I\beta_1$ values satisfactorily, and the value of log ${}^I\beta_1$ when log K_1^H = log K_w (=14.22 in 3 mol dm^{-3} Na[ClO$_4$] [14]) is close to log K_w + log ${}^I\beta_1{}^*$ for the hydroxide system.[2] The existence of these straight lines demonstrates that all of the ligands complex similarly with Hg^I, and that chelated complexes are not formed.

A major difference between the mercury(I) and mercury(II) systems is shown in the values of log(K_1/K_2) of the successive stepwise formation constants, expected statistically to be 0.6 for a two-co-ordinate system. While the values for Hg^I vary from 0.31 to 0.55 (Table), those for Hg^{II} are closer to zero and are in some cases negative. In mercury(II) systems an abnormal release of water caused by a change in co-ordination number [equation (5)] could give rise to entropic stabilisation of

$$[HgA(OH_2)_x]^+ + A^- \rightleftharpoons [HgA_2] + xH_2O \quad (5)$$

the second complex. There is no reason to suppose that the same release should occur in these mercury(I) systems, in which the central group is already dimeric.

The values of log ${}^I\beta_1$ are uniformly lower than the

$$[HgA]^+ + Hg \rightleftharpoons [Hg_2A]^+ \quad (6)$$

values of log β_1 for the corresponding mercury(II) complexes by between 0.55 and 0.72 log units. For the disproportion reaction (6) it is clear that these oxygen-donor

$$K_d' = [Hg_2A^+][HgA^+]^{-1} = K_d{}^I\beta_1\beta_1^{-1} \quad (7)$$

ligands reduce the stability of Hg^I with respect to Hg^{II}, but to an extent quite insufficient to cause significant disproportionation to occur. The analogous reaction (8)

$$[HgA_2] + Hg \rightleftharpoons [Hg_2A_2] \quad (8)$$

is affected similarly, and the particular stabilisation of the second mercury(II) alkanoate complexes results in the ordering $K_d'' < K_d' < K_d$. When this stabilisation

$$K_d'' = [Hg_2A_2][HgA_2]^{-1} = K_d{}^I\beta_2\beta_2^{-1} \quad (9)$$

is very marked, as in the case of the hydroxide, the mercury(I) complexes undergo considerable disproportionation, and the precipitation of mercury from the solutions becomes visible.

Recent ^1H nuclear magnetic resonance work [15] on the

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[13] H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904, 2910; *Acta Chem. Scand.*, 1956, **10**, 72.

[14] N. Ingri, G. Lagerström, M. Frydman, and L. G. Sillén, *Acta Chem. Scand.*, 1957, **11**, 1034.

[15] S. Libich and D. L. Rabenstein, *Analyt. Chem.*, 1973, **45**, 118.

carboxylate complexes of the methylmercury ion shows that the stability constants ${}^{M}\beta_1$ (at 25 °C and *ca.* 0.4 mol dm^{-3} ionic strength) are well described by the relation $\log {}^{M}\beta_1 = 0.61 + 0.58 \log K_1{}^{H}$. This line is virtually coincident with the lower line of Figure 2, and a remarkable similarity between the first stability constants of Hg^{I} and methylmercury is demonstrated.

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