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On the Ligand Exchange Equilibrium in the Propylene-Mercury(II) Complex

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The equilibrium between the propylene-mercuric complex and either Cl⁻, Br⁻, I⁻, or EDTA, and their dependences on the pH were investigated manometrically. The propylene-mercuric complexes present in the above equilibrium were found to be $(HO^-)_n$-Hg^{2+}-Propylene ($n=0$, 1 and 2) and $(HO^-)_n$-$Hg^{2+}(X^-)$-Propylene ($n=0$ and 1), and their equilibrium equations were:

$$(HO^-)_n\text{-}Hg^{2+} + \text{Propylene} \xrightleftharpoons{K_{p1}} (HO^-)\text{-}Hg^{2+}\text{-Propylene}$$

$$X^-\text{-}Hg^{2+}\text{-}(HO^-)_n + \text{Propylene} \xrightleftharpoons{K_{p2}} (HO^-)_n\text{-}Hg^{2+}(X^-)\text{-Propylene.}$$

By introducing $K_{p1}=K'_{p1}$ and $K_{p2}=K'_{p2}$ when $n=0$, the dependences on the pH were shown by:

$$\log K_{p1} = \log K'_{p1} + 2\cdot\text{pH}, \quad \log K_{p2} = \log K'_{p2} + \text{pH}$$

where $K'_{p1}=2.2\times10^5$, $K'_{p2(Cl)}=4.1\times10^5$, and $K'_{p2(Br)}=2.7\times10^6$ at 25°C and $\mu=0.8$. As was to be expected from the above equilibrium, K'_{p1} was idependent of the presence of Cl⁻, Br⁻, I⁻, and EDTA, while K'_{p1} varied in the presence of Cl⁻, Br⁻, and I⁻. The above relationships were also derived theoretically.

It has been well known that the mercuric ion in an aqueous solution can be made to react with olefin to form a stable complex[1] and that the complex can be decomposed by adding a chloride ion to an olefin and mercuric complex.[2]

Though the mercuric chloride-olefin system has been studied by many people, no satisfactory explanation of the equilibrium has been given. The equilibrium constant for the mercuric chloride-ethylene system was estimated by Allen *et al.*,[2] but they could not explain the effect of sodium chloride and perchloric acid on the equilibrium. The equilibrium between *cis*- or *trans*-butene-2 and mercuric chloride was also investigated by Kreevoy *et al.*,[3] but their study was limited to the range in which $HgCl_3^-$ and $HgCl_4^{2-}$ can be neglected.

The present study was carried out in order to make clear the species present in an aqueous solution and to calculate the equilibrium constants. On the basis of the species and the equilibrium constants thus obtained, the ligand-exchange reactions between the propylene-mercury(II) complex and chloride, bromide, iodide, and ethylenediaminetetraacetate were satisfactorily explained.

It has been reported in a preceding paper[4] that the mercury(II) in an aqueous solution can be determined indirectly by adding such ligand as chloride, bromide, iodide, and ethylenediaminetetraacetate to the propylene-mercury(II) complex and by then measuring the amount of propylene evolved.

The amount of propylene evolved in these ligand-exchange reactions decreased with an increase in the pH in the pH range of >0.15 for chloride, >2.10 for bromide, and >4.00 for iodide, while it decreased with a decrease in the pH in the range of pH<4.90 for ethylenediaminetetraacetate. These phenomena seemed to be very interesting from the standpoint of understanding the mechanism of oxymetallation, they could be explained satisfactorily using the species and the equilibrium con-

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[1] J. Sand and F. Breest, *Z. Phys. Chem.*, **59**, 424 (1907).

[2] E. R. Allen, J. Cartlidge, M. M. Taylor and C. F. H. Tipper, *J. Phys. Chem.*, **63**, 1437 (1959).

[3] M. M. Kreevoy, L. L. Schaleger and J. C. Ware, *Trans. Faraday Soc.*, **58**, 2433 (1962).

[4] I. Kawai and T. Hara, This Bulletin, **42**, 3466 (1969).

stants, as has been mentioned above.

No discussion including oxymetallation has been given for an equilibrium in the propylene-mercury(II) system in which the formation constants of mercuric halide are taken into consideration. In the present paper, all the species, such as $HgX_i^{(2-i)+}$ (i=1—4), $(HO^-)_n$-Hg^{2+}-Propylene (n=0, 1 and 2), $(HO^-)_n$-$Hg^{2+}(X^-)$-Propylene (n=0 and 1), and $Hg(OH)_i^{(2-i)+}$ (i=0, 1 and 2), were taken into consideration in an equilibrium. The above-mentioned phenomena were attributed to the difference in the formation constants of mercuric halide complexes and to the affinity between the α-carbon in propylene and the hydroxyl groups produced by the hydrolysis of the hydrated propylene-mercury(II) complex.

Experimental

The amount of propylene evolved or absorbed was measured by the same apparatus and procedure as in the preceding paper.[4] With the objective of examining the hydrolysis of the aquo mercuric complex, the absorption spectra of 8×10^{-4}M Hg(II) solutions (pH: 0, 1, 2, 3, 5 and 7; ionic strength with sodium perchlorate : 1) were obtained over 210—300 mμ at 25°C by means of a Shimadzu QR-50 spectrophotometer, using 1-cm cells. The acidity was regulated with a 10^{-3}M sodium hydroxide solution after a preliminary run had been made. With the same objective as above, 5×10^{-2}M Hg(II) solutions (0.7N in perchloric acid concentration) in the presence and in the absence of 0.15M chloride or bromide or iodide were titrated with 0.97N NaOH, and the pH during titration was measured by means of a Horiba M-5 pH-meter.

Results

The amounts of propylene absorbed into mercuric solutions at various concentrations are shown in Table 1, along with the apparent formation constant, which was directly estimated from the experimental data. Since the mole ratio of propylene to mercury is 1 : 1, the composition of the propylene-mercury(II) complex can also be expected to be 1 : 1.

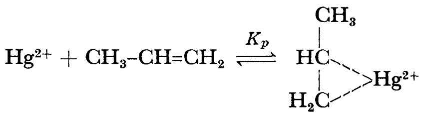
Table 1. Apparent formation constant (K_p) between mercuric ion and propylene

t=25°C, P_{tot}=total pressure of propylene=1 atm, μ=0.85, $[HClO_4]$=0.7N, Total volume=7.00 ml

$[\sum Hg]$ mol/l	Propylene absorbed sample ml (mol/l)	Formation constants (K_p) l/mol
2.867×10^{-2}	5.70 (3.340×10^{-2})	3.0×10^4
3.584×10^{-2}	6.88 (4.029×10^{-2})	1.5×10^4
4.301×10^{-2}	8.12 (4.756×10^{-2})	2.3×10^4
5.017×10^{-2}	9.30 (5.445×10^{-2})	1.5×10^4
		Av.=2.1×10^4

Blank 0.84 ml (4.92×10^{-3} mol/l)

The reaction is thus given by Eq. (1):



$$Hg^{2+} + CH_3\text{-}CH{=}CH_2 \overset{K_p}{\rightleftharpoons} \begin{matrix} CH_3 \\ | \\ HC \\ | \\ H_2C \end{matrix} {>} Hg^{2+} \quad (1)$$

The equilibrium constant is, therefore, shown by Eq. (2), and the values of K_p are as shown in Table 1.

$$K_p = \frac{[\text{Hg}^{2+}\text{-Propylene}]}{[\text{Hg}^{2+}]\cdot[\text{Propylene}]} = \frac{[\text{Total amount of propylene absorbed}] - [\text{Blank}]}{\{[\sum\text{Hg}] - [\text{Total amount of propylene absorbed}] + [\text{Blank}]\}\cdot[\text{Blank}]} \quad (2)$$

Where [Blank] indicates the amount of propylene absorbed into the solution containing no mercuric ion, and [Total amount of propylene absorbed] corresponds to the propylene absorbed into the Sample as shown in Table 1. Hereafter, [Propylene] and [Hg^{2+}-Propylene] will be abbreviated as [P] and [Hg^{2+}-P] respectively.

Though the values of K_p were obtained directly from the experimental data, they are not very accurate since the value of [Blank] contains something of an experimental error. Therefoer, the value of K_p was estimated indirectly by means of Eq. (9), using the equilibrium data concerning the Hg(II)-EDTA and propylene-Hg(II)-EDTA systems. For the former system, Eqs. (3), (4), (5) and (6) are given:

$$Hg^{2+} + L^{4-} \overset{K_{EDTA}}{\rightleftharpoons} Hg\text{-}L^{2-} \quad (3)$$

$$K_{EDTA} = \frac{[HgL^{2-}]}{[Hg^{2+}]\cdot[L^{4-}]} \quad (4)$$

$$H_{5-i}L^{1-i} \overset{K_{ai}}{\rightleftharpoons} H_{4-i}L^{-i} + H^+ \quad (5)$$

$$K_{ai} = \frac{[H_{4-i}L^{-i}]\cdot[H^+]}{[H_{5-i}L^{1-i}]} \quad (i=1\text{—}4) \quad (6)$$

For the latter system, Eqs. (7), (8) and (9) are given:

$$Hg^{2+}\text{-Propylene} + L^{4-} \overset{K_{p3}}{\rightleftharpoons} Hg\text{-}L^{2-} + \text{Propylene} \quad (7)$$

$$K_{p3} = \frac{[HgL^{2-}]\cdot[P]}{[Hg^{2+}\text{–}P]\cdot[L^{4-}]} \quad (8)$$

$$K_{p1} = \frac{K_{EDTA}}{K_{p3}} \quad (9)$$

where K_{p1} is theoretically equal to K_p, but it is differentiated from K_p since K_{p1} is indirectly calculated. Table 2 shows the experimental data obtained in the preceding paper; these data show the residual amount of the propylene mercuric complex on the addition of chloride, bromide, iodide, and ethylenediaminetetraacetate. The values of K_{p3} were estimated from the data (Table 2) obtained at pH 5 and at varying mole ratios of EDTA to Hg(II); they are shown in Table 3.

TABLE 2. THE RESIDUAL AMOUNT OF PROPYLENE MERCURIC COMPLEX IN AN ADDITION OF SODIUM CHLORIDE, SODIUM BROMIDE, SODIUM IODIDE AND EDTA

$t=25°C$, $P_{tot}=1$ atm, $\mu=0.8$, $[HClO_4]=0.7$N for halide, pH=5 for EDTA

Mole ratio $[\sum L]$**/$[\sum Hg]$	Propylene mercuric complex (mol/l)			
	Cl^-	Br^-	I^-	EDTA
1.0	1.1×10^{-2}	9.6×10^{-3}	7.4×10^{-3}	3.1×10^{-3}
1.5	6.9×10^{-3}	5.3×10^{-3}	3.9×10^{-3}	1.7×10^{-3}
2.0	3.5×10^{-3}	2.0×10^{-3}	—*	1.0×10^{-3}
2.5	1.2×10^{-3}	—*	—*	4.4×10^{-4}
3.0	—*	—*	—*	—*

* less than 2.8×10^{-5} mol/l

** stand for $[\sum Cl]$, $[\sum Br]$, $[\sum I]$, and $[\sum EDTA]$

TABLE 3. FORMATION CONSTANT (K_{p3}) BETWEEN MERCURIC EDTA COMPLEX AND PROPYLENE

$t=25°C$, $P_{tot}=1$ atm, $\mu=0.8$, pH=5

Mole ratio $[\sum EDTA]/[\sum Hg]$	Formation constant K_{p3}
1.25	1.2×10^7
1.50	1.2×10^7
1.75	1.2×10^7
2.00	1.2×10^7
2.25	1.2×10^7
	Av.$=1.2\times10^7$

Formation constant (K_{p3}) were calculated using Schwarzenbach's[5] stability constants; $K_{a1}=1.02\times10^{-2}$, $K_{a2}=2.14\times10^{-3}$, $K_{a3}=6.92\times10^{-7}$, $K_{a4}=5.49\times10^{-11}$, $K_{EDTA}=6.31\times10^{21}$

TABLE 4. THE RESIDUAL AMOUNT OF PRORYLENE MERCURIC COMPLEX IN AN ADDITION OF SODIUM CHLORIDE, SODIUM BROMIDE, SODIUM IODIDE AND EDTA

$t=25°C$, $P_{tot}=1$ atm, $\mu=0.8$, mole ratio: $[\sum L]/[\sum Hg]=3$

pH	Propylene mercuric complex (mol/l)			
	Cl^-	Br^-	I^-	EDTA
0.15	—*	—*	—*	—*
1.00	3.2×10^{-3}	—*	—*	—*
2.10	7.6×10^{-3}	—*	—*	2.0×10^{-3}
3.00	1.1×10^{-2}	3.9×10^{-3}	—*	1.6×10^{-3}
4.00	1.3×10^{-2}	7.8×10^{-3}	—*	1.0×10^{-3}
5.00	—*	9.9×10^{-3}	4.7×10^{-3}	—*
6.10	—*	—*	7.9×10^{-3}	—*

* less than 2.8×10^{-5} mol/l

The values of K_{p1} were calculated by Eq. (9) using the values of K_{p3} calculated from the data (Table 4) obtained at various pH values and at the mole ratio of EDTA to Hg(II) of 3; they are shown in Table 5 and in Fig. 1. On the basis of Fig. 1, the relationship between K_{p1} and pH can be expressed by Eq. (10):

TABLE 5. FORMATION CONSTANT (K_{p1}) BETWEEN MERCURIC ION AND PROPYLENE

$t=25°C$, $P_{tot}=1$ atm, $\mu=0.8$, mole ratio: $[\sum EDTA]/[\sum Hg]=3$

pH	Formation constant (K_{p1})
2	2.4×10^8
3	9.1×10^{10}
4	1.1×10^{12}
5	5.4×10^{14}

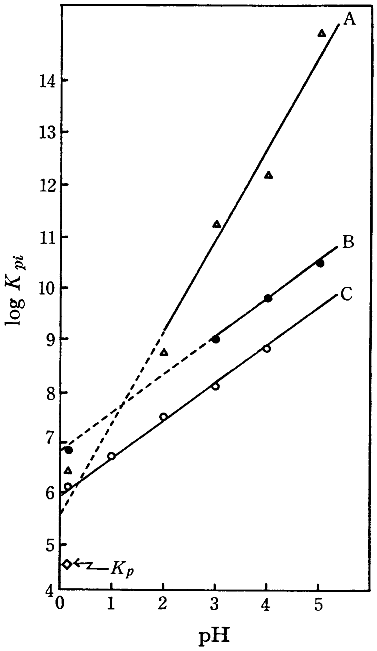


Fig. 1. Relationship among log K_{p1}, log K_{p2} and pH; $t=25°C$, $\mu=0.8$
$i=1$: A
$i=2$: B(Br), C(Cl)

$$\log K_{p1} = \log K'_{p1} + 2\text{pH} \tag{10}$$

where $K'_{p1} = 2.2 \times 10^5$

In the propylene-Hg(II)-halide system, Eqs. (11) and (12), in addition to Eqs. (1) and (2), were taken into consideration:

$$HgX_{i-1}^{(3-i)+} + X^- \overset{K_i}{\rightleftharpoons} HgX_i^{(2-i)+} \tag{11}$$

$$K_i = \frac{[HgX_i^{(2-i)+}]}{[HgX_{i-1}^{(3-i)+}]\cdot[X^-]} \quad (i=1\text{—}4,\ X\text{: Cl, Br}) \tag{12}$$

Under the experimental conditions shown in

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[5] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

TABLE 6. FORMATION CONSTANTS (K_{p1} and K_{p2}) IN THE PROPYLENE-MERCURY(II)-HALIDE SYSTEM

$t=25°\text{C}$, $P_{\text{tot}}=1$ atm, $\mu=0.8$, $[\text{HClO}_4]=0.7\text{N}$

Mole ratio $[\sum X]/[\sum \text{Hg}]$	K_{p2}		K_{p1}	
	Cl^-	Br^-	Cl^-	Br^-
1.00	7.5×10^5	3.3×10^6	1.4×10^6	1.5×10^6
1.25	6.8×10^5	3.1×10^6	1.3×10^6	1.6×10^6
1.50	6.7×10^5	2.9×10^6	1.3×10^6	1.4×10^6
1.75	6.3×10^5	3.1×10^6	1.3×10^6	1.4×10^6
2.00	6.4×10^5	3.7×10^6		
2.25	6.4×10^5	3.8×10^6		
Av	6.9×10^5	3.3×10^6	1.3×10^6	1.5×10^6

X: Cl, Br

Formation constants (K_{p1} and K_{p2}) were calculated using Sillén's[6] stability constants;

Cl: $K_1=5.49\times10^6$, $K_2=3.02\times10^6$, $K_3=7.08$, $K_4=1.26\times10$

Br: $K_1=1.12\times10^9$, $K_2=1.91\times10^8$, $K_3=2.57\times10^2$, $K_4=1.82\times10$

Table 6, Eqs. (13) and (14) held:

$$[\sum X] = \sum_{i=1}^{4}(i\cdot[\text{HgX}_i^{(2-i)+}]) + [\text{X}^-] \tag{13}$$

$$[\sum \text{Hg}] = \sum_{i=1}^{4}[\text{HgX}_i^{(2-i)+}] + [\text{Hg}^{2+}] + [\text{Hg}^{2+}\text{-P}] \tag{14}$$

By combining Eqs. (11)—(14), Eq. (15) was obtained:

$$\begin{aligned}&(\prod_{i=1}^{4}\text{K}_i)\cdot[\text{X}^-]^5 + (\prod_{i=1}^{3}\text{K}_i\cdot(1-K_4\cdot[\sum X]-4[\sum \text{Hg}]))\\ &\times[\text{X}^-]^4 + (\prod_{i=1}^{2}\text{K}_i\cdot(1-K_3([\sum X]+3[\sum \text{Hg}])))\cdot[\text{X}^-]^3\\ &\quad + (K_1\,(1-K_2([\sum X]-2[\sum \text{Hg}])))\cdot[\text{X}^-]^2\\ &\quad + (1+K_1\cdot([\sum \text{Hg}]-[\sum X]))\cdot[\text{X}^-]\\ &\quad - [\sum X] = 0\end{aligned} \tag{15}$$

The value of $[\text{X}^-]$ in Eq. (15) was obtained by the method of halving by a computor, followed by the calculation of the constituent concentration and of K_{p1}. Though the value of K_{p1} was expected to be constant, it varied with the kind and with the concentration of the halide. This seemed to be attributable to the fact that Hg^{2+}-P alone was adopted as the propylene-mercury(II) complex in the above equilibrium. However, those data are not shown since they are not useful in explaining the equilibrium. Paul and Brandt[7] took the monohalogeno propylene mercuric complex alone into consideration in examining an equilibrium of the propylene-Hg(II)-halide system, but the present authors took both the monohalogeno-propylene mercuric complex and the propylene mercuric complex into consideration. Therefore, Eqs. (16) and (17), in addition to Eqs. (1) and (11), were considered:

$$\text{HgX}^+ + \text{Propylene} \overset{K_{p2}}{\rightleftharpoons} \text{X–Hg}^+\text{-Propylene} \tag{16}$$

$$K_{p2} = \frac{[\text{X-Hg}^+\text{-P}]}{[\text{HgX}^+]\cdot[\text{P}]} \tag{17}$$

Eqs. (13) and (14) were rewritten as Eqs. (18) and (19):

$$[\sum X] = \sum_{i=1}^{4}(i\cdot[\text{HgX}_i^{(2-i)+}]) + [\text{X}^-] + [\text{X-Hg}^+\text{-P}] \tag{18}$$

$$\begin{aligned}[\sum \text{Hg}] = \sum_{i=1}^{4}[\text{HgX}_i^{(2-i)+}] + [\text{Hg}^{2+}] + [\text{Hg}^{2+}\text{-P}]\\ + [\text{X-Hg}^+\text{-P}]\end{aligned} \tag{19}$$

By combining Eqs. (12), (17), (18), and (19), the equation corresponding to Eq. (15) was derived; here $[\text{Hg}^{2+}\text{-P}]$ and $[\text{X-Hg}^+\text{-P}]$ were included, while K_{p1} and K_{p2} were calculated by the method of trial and error after having assigned arbitrary values to $[\text{Hg}^{2+}\text{-P}]$ and $[\text{X-Hg}^+\text{-P}]$. The results obtained are shown in Table 6, while the mole fraction of the complexes is plotted against the mole ratio of halide to mercury in Fig. 2. Thus, the value of K_{p1} became independent of the kind and of the concentration of the halide. The value of K_{p1} obtained at pH 0.15 from Eq. (10) agreed approximately with those in Table 6; therefore, the values of K_{p2} for chloride and bromide were calculated using the values of K_{p1} at various pH values. The results obtained are shown in Table 7, while the mole fractions of the complexes are shown in Fig. 3. The data concerning K_{p2} and pH in Table 7 are shown as B and C in Fig. 1. From Fig. 1, the relationship between K_{p2} and pH is given by Eq. (20):

$$\log K_{p2} = \log K'_{p2} + \text{pH} \tag{20}$$

where the K'_{p2} values for chloride and bromide are 4.1×10^5 and 2.7×10^6 respectively.

The absorption spectra of mercuric perchlorate solutions are shown in Fig. 4; there are two isosbestic points among the curves (2), (3), (4), and (5).

The titration curves of mercuric perchlorate solutions in the presence and in the absence of chloride, bromide, and iodide are shown in Fig. 5.

Discussion

Since there were two isosbestic points in Fig. 4, the aquo complex seems to be more or less subject to hydrolysis at pH 2—7. The process of hydrolysis can be understood more precisely from the titration curves in Fig. 5. The amount of sodium hydroxide corresponding to $\overline{\text{AB}}$ in Fig. 5 is exactly equivalent to the amount of mercury(II) used in the experiment, and the hydrolysis of the aquo complex begins and ends at approximately pH 2. On the other

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6) P. Brandt and O. Plum, *Acta Chem. Scand.*, **7**, 97 (1957).

7) L. G. Sillén, *ibid.*, **3**, 539 (1949).

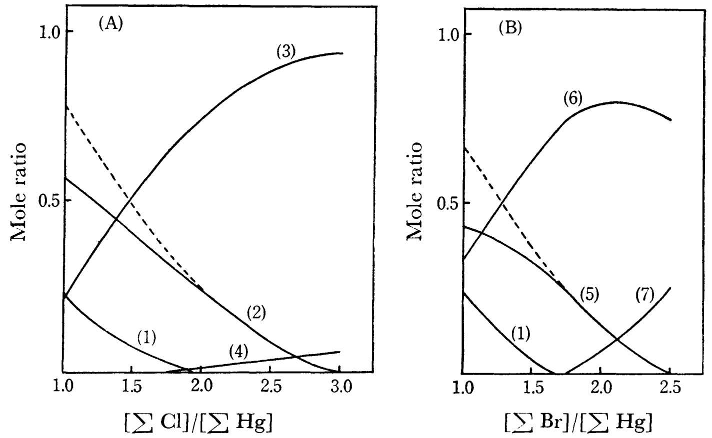


Fig. 2. Composition of the propylene-mercury system containing various amounts of halide; t=25°C, μ=0.8, $[HClO_4]$=0.7N
(A) Propylene-mercury-chloride system
(B) Propylene-mercury-bromide system
(1): $[Hg^{2+}\text{-}P]$, (2): $[Cl\text{-}Hg^{+}\text{-}P]$, (3): $[HgCl_2]$, (4): $[HgCl_3^{-}]$, (5): $[Br\text{-}Hg^{+}\text{-}P]$, (6): $[HgBr_2]$, (7): $[HgBr_3^{-}]$

Table 7. Formation constant (K_{p2}) in the propylene-mercury(II)-halide system

t=25°C, P_{tot}=1 atm, μ=0.8, mole ratio: $[\Sigma X]/[\Sigma Hg]=3$

pH	K_{p2}	
	Cl^-	Br^-
1	3.1×10^{6}	
2	1.6×10^{7}	
3	5.9×10^{7}	5.0×10^{8}
4	3.0×10^{7}	4.2×10^{9}
5		1.3×10^{10}

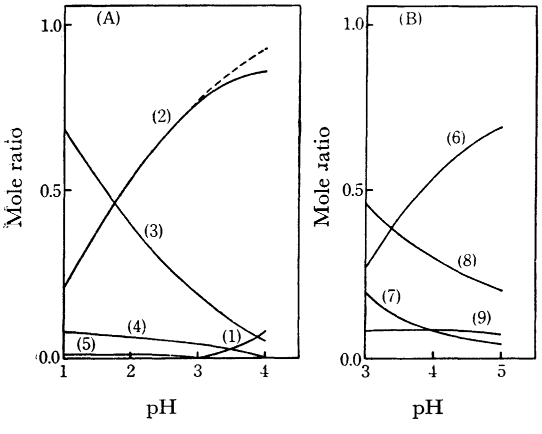


Fig. 3. Compostion of the proyplene-mercury system containing a definite amount of halide; t=25°C, μ=0.8, $[\Sigma X]/[\Sigma Hg]=3$, X^-: Cl^-, Br^-
(A) Propylene-mercury-chloride system
(B) Propylene-mercury-bromide system
(1): $[Hg^{2+}\text{-}P]$, (2): $[Cl\text{-}Hg^{+}\text{-}P]$, (3): $[HgCl_2]$, (4): $[Hg\text{-}Cl_3^{-}]$, (5): $[HgCl_4^{2-}]$, (6): $[Br\text{-}Hg^{+}\text{-}P]$, (7): $[HgBr_2]$, (8): $[HgBr_3^{-}]$, (9): $[HgBr_4^{2-}]$

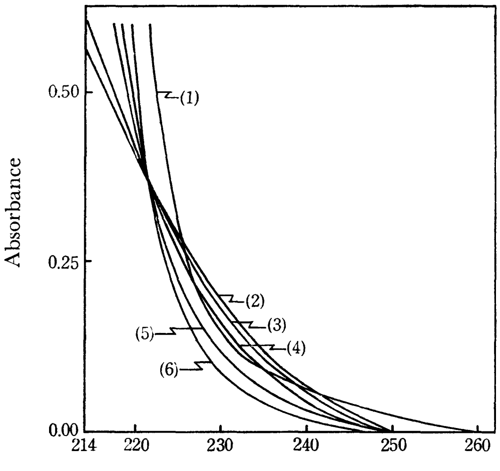


Fig. 4. Absorption spectra of mercuric perchlorate soltuions; t=25°C, μ=1, $[\Sigma Hg]=8\times10^{-4}$ mol/l (1): 1 normal solution, (2): pH=7, (3): pH=5, (4): pH=3, (5): pH=2, (6): pH=1

hand, the hydrolysis of the aquo complex in the presence of halide begins at pH>7, judging from the titration curves (2), (3), and (4). Since a precipitate was produced in the presence of iodide, no further analysis was carried out.

The values of the formation constant (at pH 0.15) shown in Table 1 are smaller than those of K_{p1} in Table 6 and the value of K_{p1} (4.4×10^{5}) at pH 0.15 as calculated by Eq. (10). This is probably because of the experimental error in the direct method, since the propylene-mercury complex was quite stable and the equilibrium was shifted remarkedly to the right-hand side of Eq. (1).

Eqation (10) is derived as follows. The propyl-

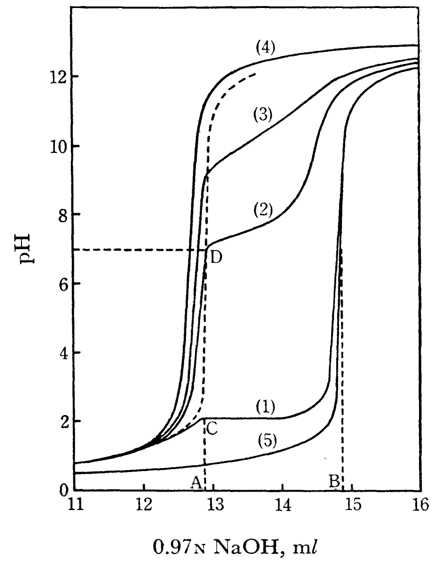


Fig. 5. Titration of mercuric perchlorate solutions; $t=25°C$, $\mu=1$, $[\sum Hg]=5\times10^{-2}$ mol/l, $[\sum X]/[\sum Hg]=3$, X^-: Cl^-, Br^-, I^-
(1): Mercuric perchlorate solution
(2): Solution containing chloride
(3): Solution containing bromide
(4): Solution containing iodide
(5): Perchloric acid solution

enemercury complex seems to undergo hydrolysis at pH 2—5 in accordance with Eq. (21):

$$Hg(OH_2)_2{}^{2+}\text{-}P \overset{k_1}{\rightleftharpoons} Hg(OH)_2\text{-}P + 2H^+ \tag{21}$$

$$k_1 = \frac{[Hg(OH)_2\text{-}P]\cdot[H^+]}{[Hg(OH_2)_2{}^{2+}\text{-}P]} \tag{22}$$

$$[Hg(OH)_2\text{-}P] = k_1\cdot[Hg(OH_2)_2{}^{2+}\text{-}P]\cdot[H^+]^{-2} \tag{23}$$

Since the Hg^{2+}-P in Eq. (8) is actually present as $Hg(OH)_2$-P, the K_{p3} in Eq. (8) is given by K_{p4}:

$$\begin{aligned} K_{p4} &= \frac{[Hg\text{-}L^{2-}]\cdot[P]}{[Hg(OH)_2\text{-}P]\cdot[L^{4-}]} \\ &= \frac{[Hg\text{-}L^{2}]\cdot[P]\cdot[H^+]^2}{k_1\cdot[Hg(OH_2)_2{}^{2+}\text{-}P]\cdot[L^{4-}]} \end{aligned} \tag{24}$$

Hence, Eq. (25) is obtained instead of Eq. (9):

$$\begin{aligned} K_{p1} &= \frac{K_{EDTA}}{K_{p4}} = \frac{[Hg(OH_2)_2{}^{2+}\text{-}P]\cdot k_1}{[Hg^{2+}]\cdot[P]\cdot[H^+]^2} \\ &= K_{p1E}\cdot k_1\cdot[H^+]^{-2} \end{aligned} \tag{25}$$

where $K_{p1E}=[Hg(OH_2)_2{}^{2+}\text{–}P]\cdot[Hg^{2+}]^{-1}\cdot[P]^{-1}$
Eqation (25) is then rewritten as Eq. (26);

$$\log K_{p1} = \log K_{p1E} + 2\cdot pH + \log k_1 \tag{26}$$

The K_{p1E} in Eq. (26) indicates the formation constant of the propylene-mercury(II) complex at very low pH values. On the other hand, the K'_{p1} in Eq. (10) indicates the intercept ($pH=0$) on the ordinate in Fig. 1. Therefore, the values of K_{p1E} and K'_{p1} may be expected to be approximately equal, and $\log k_1$, to be approximately zero. Therefore, Eqs. (10) and (26) become indentical.

Equation (20) is derived as follows. As can be seen form Fig. 5, the aquo complex in the presence of three times as many moles of halide as those of mercury is not subject to hydrolysis up to pH 7. However, the monohalogeno propylene mercuric complex seems to be more or less subject to hydrolysis and to stabilize in accordance with Eq. (27):

$$X\text{-}Hg(OH_2)^+\text{-}P \overset{K_e}{\rightleftharpoons} X\text{-}Hg(OH)\text{-}P + H^+ \tag{27}$$

$$K_e = \frac{[X\text{-}Hg(OH)\text{-}P]\cdot[H^+]}{[X\text{-}Hg(OH_2)^+\text{-}P]} \tag{28}$$

$$[X\text{-}Hg(OH)\text{-}P] = K_e\cdot[X\text{-}Hg(OH_2)^+\text{-}P]/[H^+] \tag{29}$$

Hence, Eq. (17) may be rewritten as Eq. (30):

$$\begin{aligned} K_{p2} &= \frac{[X\text{-}Hg(OH)\text{-}P]}{[X\text{-}Hg^+]\cdot[P]} \\ &= \frac{[X\text{-}Hg(OH_2)^+\text{-}P]\cdot K_e}{[X\text{-}Hg^+]\cdot[P]\cdot[H^+]} = K'_{p2}\cdot K_e\cdot[H^+]^{-1} \end{aligned} \tag{30}$$

$$\log K_{p2} = \log K'_{p2} + pH = \log K_e \tag{31}$$

Since the K_{p2} values in Eqs. (20) and (31) are identical and since the K'_{p2} values in Eqs. (20) and (31) are approximately equal, log K_e may be expected to be around zero. Therefore, Eqs. (20) and (31) become identical.

In the practical experiment of the propylene-mercury(II)-halide system, a definite amount of halide is added to the $Hg(OH)_2$-P, and the X-Hg(OH)-P is formed by the replacement of the hydroxyl group with the halide ion. The formation of the X-Hg(OH)-P is considered to proceed with an increase in the stability of the halogeno mercuric complex. This makes K_{p2} in Eq. (30) large and locates the K_{p2}(Br) line over the K_{p2}(Cl) line, as is shown in Fig. 1.

The results obtained are summarized in the following schematic diagram:

EDTA-Mercury(II)-Propylene system, assumed species:

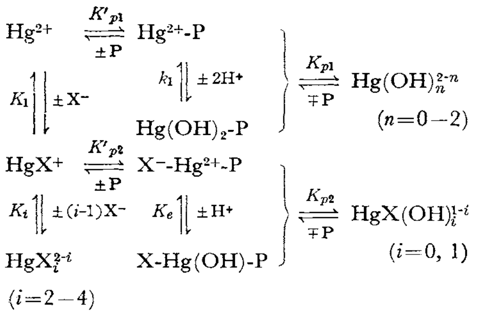
Hg^{2+}-P, $Hg(OH)_2$-P, $Hg(OH^-)_n$ ($n=0-2$),
$Hg\text{-}L^{2-}$, $H_{5-i}L^{1-i}$ ($i=1-4$), P, L^{4-}.

$$\left.\begin{array}{ccc} Hg^{2+} & \xrightleftharpoons[\pm P]{K'_{p1}} & Hg^{2+}\text{-}P \\ K_{EDTA}\,\upharpoonleft\!\downharpoonright\,L^{4-} & & k_1\,\upharpoonleft\!\downharpoonright\,\pm 2H^+ \\ HgL^{2-} & \xrightleftharpoons[\pm P]{K_{p4}} & Hg(OH)_2\text{-}P \end{array}\right\} \xrightleftharpoons[\pm P]{K_{p1}} \begin{array}{c} Hg(OH^-)_n \\ (n=0-2) \end{array}$$

$$H_{5-i}L^{1-i} \xrightleftharpoons[\pm H^+]{K_{ai}} H_{4-i}L^{i}$$

Halide-Mercury(II)-Propylene system, assumed species:

$Hg(OH^-)_n$ ($n=0-2$), Hg^{2+}-P, $Hg(OH)_2$-P, HgX_i^{2-i} ($i=1-4$), HgX(OH), X-Hg^+-P, X-Hg(OH)-P.



obtained equilibrium constants

$K_p = 2.2 \times 10^4$ (at pH 0.15)

$\log K_{p1} = \log K'_{p1} + 2 \cdot \mathrm{pH}$

$K'_{p1} = 2.2 \times 10^5$

$\log K_{p2} = \log K'_{p2} + \mathrm{pH}$

$K'_{p2} = 4.1 \times 10^5$ (for chloride)

$K'_{p2} = 2.7 \times 10^6$ (for bromide)