NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (7), 2165—2166 (1978)

Chemical Equilibria of Methyl-, Ethyl-, and Propylmercury(II) Chlorides and Their Complexes with L-Cysteine in Liquid-Liquid Distribution Systems

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(Received August 11, 1977)

Synopsis. The distribution constants for methyl-, ethyl-, and propylmercury(II) chlorides (RHgCl) between aqueous 1 mol dm^{-3} (H, Na)Cl and benzene were determined to be $10^{1.04}$, $10^{1.60}$, and $10^{2.20}$ respectively. The formation constants for the complexes of these organomercury(II) chlorides with L-cysteine (R′SH), K=[RHgSR′][H$^+$][Cl$^-$][RHgCl]$^{-1}$[R′SH]$^{-1}$, were determined to be $10^{1.71}$ $10^{1.55}$, and $10^{1.49}$ respectively.

The formation of highly stable complex with L-cysteine has been employed in analytical procedures for methylmercury(II),[1,2] on the basis that organomercury(II) is highly extractable into organic solvents as halides but the extractability disappears in an exchange of the halide ion with L-cysteine.[3,4]

In the present study, the distribution equilibria of methyl-, ethyl-, and propylmercury(II) chlorides and the exchange equilibria of the chloride ion in these compounds with L-cysteine in the aqueous phase were studied in systems containing two liquid-phases, aqueous 1 mol dm^{-3} (H, Na)Cl and benzene.

Experimental

The methyl-, ethyl-, and propylmercury(II) chlorides were obtained from Mitsuwa Chemical Co. and Soekawa Rikagaku Co., and the L-cysteine from Wako-Pure Chemical Co. The other reagents were of an analytical grade.

All the procedures were carried out at 25 °C. Benzene containing a certain amount of an organomercury(II) chloride was washed with 0.1 mol dm^{-3} hydrochloric acid and used. A portion of the benzene solution and the same volume of an aqueous 1 mol dm^{-3} (H, Na)Cl solution containing none or 1×10^{-3} mol dm^{-3} of L-cysteine were placed in a stoppered glass tube, agitated vigorously for 2 min and centrifuged. The organomercury(II) in the aqueous phase was extracted into carbon tetrachloride containing diphenyl thiocarbazone and the absorption of the organic phase at 620 nm was measured.[5]

Results and Discussion

For the analysis of the distribution data, the following equations were employed:

$$D = [\mathrm{RHgCl}]_{\mathrm{org}}([\mathrm{RHgCl}]+[\mathrm{RHgSR'}])^{-1} \quad (1)$$

$$\mathrm{RHgCl} \rightleftharpoons \mathrm{RHgCl(org)}$$

$$K_\mathrm{d} = [\mathrm{RHgCl}]_{\mathrm{org}}[\mathrm{RHgCl}]^{-1} \quad (2)$$

$$\mathrm{RHgCl} + \mathrm{R'SH} \rightleftharpoons \mathrm{RHgSR'} + \mathrm{H^+} + \mathrm{Cl^-}$$

$$K = [\mathrm{RHgSR'}][\mathrm{H^+}][\mathrm{Cl^-}][\mathrm{RHgCl}]^{-1}[\mathrm{R'SH}]^{-1} \quad (3)$$

where R denotes an alkyl group, and R′SH denotes L-cysteine. The subscript "org" and the lack of subscript denote the chemical species in the organic and aqueous phases respectively. The formation constant K was calculated by introducing Eqs. 1 and 2 into the following equations:

$$[\mathrm{RHgSR'}] = [\mathrm{RHg(II)}]_{\mathrm{total}} - [\mathrm{RHgCl}] \quad (4)$$

$$[\mathrm{R'SH}] = [\mathrm{R'SH}]_{\mathrm{total}} - [\mathrm{RHgSR'}] \quad (5)$$

In the preliminary experiments, it was found that the distribution ratios of these organomercury(II) chlorides were independent of both the hydrogen-ion concentration in the aqueous phase and their own concentration in the organic phase in ranges of 3×10^{-3} to 1 mol dm^{-3} and 3×10^{-4} to 2×10^{-2} mol dm^{-3} respectively. The effect of the chloride ion on the distribution of methyl-, ethyl-, and propylmercury(II) chlorides was also measured when the aqueous phase was 1 mol dm^{-3} (H, Na)(Cl, ClO_4) containing 0.1 mol dm^{-3} of hydrogen-ion and the initial concentration of methyl-, ethyl-, and propylmercury(II) chlorides was 5.0×10^{-4}, 1.1×10^{-3}, and 5.7×10^{-3} mol dm^{-3} respectively. It was found that the distribution ratio was independent of the chloride ion concentration in the range 10^{-3} to 1 mol dm^{-3}. The distribution constants, K_d, between 1 mol dm^{-3} (H, Na)Cl and benzene were thus determined to be $10^{1.04}$, $10^{1.60}$, and $10^{2.20}$ respectively for methyl-, ethyl-, and propylmercury(II) chlorides.

The distribution ratio of these organomercury(II) as a function of the hydrogen-ion concentration was

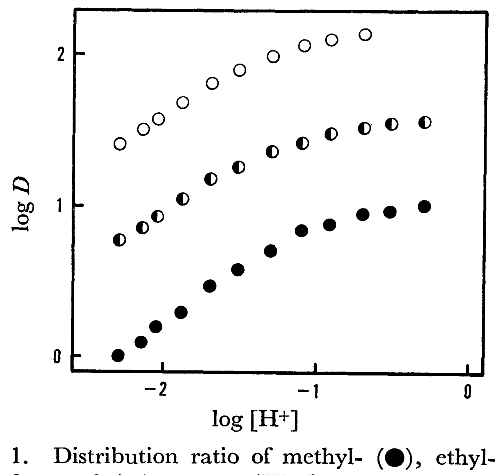

Fig. 1. Distribution ratio of methyl- (●), ethyl- (◐), and propyl (○) mercury(II) between benzene and 1 mol dm^{-3} (H, Na)Cl containing 10^{-3} mol dm^{-3} L-cysteine as a function of the hydrogen-ion concentration in the aqueous phase.

Table 1. The formation constants for the complexes of methyl-, ethyl-, and propylmercury(II) chlorides with L-cysteine in the 1 mol dm^{-3} (H,Na)Cl in Eq. 3

$[H^+]$	log K ($CH_3Hg(II)$)	log K ($C_2H_5Hg(II)$)	log K ($C_3H_7Hg(II)$)
5.0×10^{-1}	1.62	1.58	
3.0×10^{-1}	1.70	1.53	
2.0×10^{-1}	1.65	1.59	1.51
1.2×10^{-1}	1.72	1.57	1.48
8.0×10^{-2}	1.66	1.61	1.48
5.0×10^{-2}	1.77	1.56	1.49
3.0×10^{-2}	1.74	1.55	1.48
2.0×10^{-2}	1.73	1.51	1.48
1.3×10^{-2}	1.75	1.53	1.49
9.0×10^{-3}	1.70	1.54	1.49
7.0×10^{-3}	1.70	1.54	1.48
5.0×10^{-3}	1.72	1.51	1.47
mol dm^{-3}			
	Av 1.71	Av 1.55	Av 1.49

also measured in the presence of L-cysteine and illustrated in Fig. 1.

For the analysis of the data, no extraction of organomercury(II) as a L-cysteine complex was assumed.[1–4] The values of K calculated on this assumption in Table 1 were reasonably constant.

From these results, it can be concluded that K_d of these organomercury(II) chlorides increases by a factor of four by the addition of one $-CH_2-$ into the alkyl chain. This is an observation similar to that found among a series of organic compounds.[6] Simpson reported[4] a value of K_d of methylmercury(II) chloride between water and toluene to be $10^{1.04}$, and Budevsky, *et al.*[7] reported the value between 1 mol dm^{-3} (Na, H)ClO_4 and *o*-xylene to be $10^{1.07}$; they are similar to the present value.

The value of K is somewhat greater in the order of propylmercury(II) < ethylmercury(II) < methylmercury(II). This order may correspond with the basicity order of these organomercury(II).

It is readily seen that the electron density of the oxygen in the carboxyl group of L-cysteine (pK_a=1.96)[8] is affected by a change in the hydrogen-ion concentration but that of the sulfur in the thiol group (pK_a=10.28)[8] should remain constant. This seems to indicate coordination of the central mercury(II) in the complexes with the sulfur in the thiol group since the formation constant, K, was not affected by changes in the hydrogen-ion concentration. This agrees with the general tendency that mercury(II) is a soft acid which interacts with sulfur stronger than oxygen.

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