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PROTODEMERCURATION OF SOME MERCURY DERIVATIVES OF FERROCENE AND CYCLOPENTADIENYLMANGANESE TRICARBONYL

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SUMMARY

The protolysis of some symmetrical and asymmetrical mercury derivatives of ferrocene and cyclopentadienylmanganese tricarbonyl in 90% dioxane has been described. In this reaction the ferrocenyl radical was found to be more electron-attracting than the *p*-anisyl radical, while the cyclopentadienylmanganese-tricarbonyl radical behaved as a weak acceptor with respect to the phenyl radical. The protodemercuration of diferrocenylmercury proceeds about 130 times more rapidly than that of ferrocenylmercury chloride, and the protolysis of bis(cyclopentadienylmanganese-tricarbonyl)mercury is 30 times faster than the protolysis of cyclopentadienylmanganese-tricarbonylmercury chloride. The protodemercuration of diferrocenylmercury with perchloric acid is about half that with hydrochloric acid As in the case of diphenylmercury, the addition of potassium chloride increases the reaction rate in the protolysis with both perchloric and hydrochloric acids. It was shown that the sensitivities of the mercury atoms in diferrocenylmercury and in diphenylmercury to nucleophilic assistance are approximately equivalent. The effect of the water content of dioxane on the rate of protodemercuration of diferrocenylmercury, bis(cyclopentadienylmanganese-tricarbonyl)mercury and diphenylmercury has been studied. The rates of decompositions of all three compounds were found to decrease with increase in the water content of dioxane. It was also shown that the mechanisms of protodemercuration of diferrocenylmercury and bis(cyclopentadienylmanganese-tricarbonyl)mercury do not differ in principle from that of diphenylmercury and the explanation does not require the participation of the metal atom in any form in the stage determining the reaction rate.

INTRODUCTION

The protodemercuration of arylmercury derivatives provides a possibility of elucidating the mechanism of electrophilic substitution. Noteworthy features of this reaction are the revealing of the reaction centre; the simplicity of the attacking reagent and the easy availability of information on its course. However, the reaction of protolysis is characterized by certain specific catalysis such as the nucleophilic assistance described in detail by Reutov and Beletskaya[1].

Dessy and his coworkers have established the mechanism of protodemercuration of some arylmercury derivatives[2-5]. According to their study, hydrogen chloride or the ionic pair, H^+Cl^-, attacks the mercury–carbon bond and the reaction proceeds through the four-centre transition state. Their main reasons for postulating this mechanism are as follows: (a) a decrease in the reaction rate caused by an increase in water content of a solvent; (b) the replacement of hydrochloric acids by strong acids containing no anions, able to coordinate with mercury, also decreases the rate; (c) the addition of both halide ions and protons increases the reaction rate.

Three factors suggest another mechanism for the protodemercuration of diferrocenylmercury and bis(cyclopentadienylmanganese-tricarbonyl)mercury: (a) the alternative sensitivity of the mercury atom to nucleophilic assistance; (b) the tendency of ferrocene to protonate[6] (establishing pre kinetic equilibrium); (c) the steric conditions for the reaction differ from those for planar aryl nuclei.

In the present paper we describe the protodemercuration of some mercury derivatives of ferrocene and cyclopentadienylmanganese tricarbonyl by hydrochloric acid in aqueous dioxane. We have also studied under the same conditions the protolysis of diphenylmercury and the effect of the water content of the dioxane, anion concentration, and addition of potassium chloride on the rates of protolysis of these substances.

EXPERIMENTAL

The organomercury compounds studied in this paper have been prepared and purified by the method previously described. Commercial dioxane ("chemically pure") was refluxed with KOH for 10–12 h, distilled, refluxed with hydrochloric acid in a stream of nitrogen for 10–12 h, distilled over KOH, refluxed for 6–10 h over metallic sodium and distilled. The fraction within 101–101.5°/760 mm was collected. Only freshly distilled dioxane was used in all the kinetic measurements. Sodium hydroxide solution in 60% (vol.) dioxane was prepared by mixing the aqueous alkali solution (carbonate free) with dioxane. The concentration of sodium hydroxide in this solution was accurately determined by potentiometric titration with aqueous standard hydrochloric acid.

In a previous study we have shown that the reactions of mercury derivatives of ferrocene[7] and cyclopentadienylmanganese tricarbonyl with hydrochloric acid in aqueous dioxane follow the same path as analogous reactions of aryl derivatives of mercury:

$$RHgX + HCl \rightarrow RH + HgXCl$$

where $X = R$ or Cl, $R = C_5H_4FeC_5H_5$ or $C_5H_4Mn(CO)_3$.

In all cases the overall reaction was second order (of the first order in respect of each reactant). Experiments (one is described below) have shown that the amounts of reaction products at any time, calculated from the kinetic equation, agree within 10–15% with those determined experimentally.

To a solution of 0.4211 g of chloromercuryferrocene in 90 ml of dioxane at 30°, was added 10 ml of a 0.100 *M* solution of hydrochloric acid at 30°. After the mixture had been stirred rigorously for 10 sec, it was allowed to stand for 150 min at 30°, then poured into 1 l of water and extracted with ether. The ether layer was separated and the solvent removed *in vacuo*. The residue was washed with water, dried and extracted with petroleum ether; 0.1502 g of ferrocenylmercury chloride remained undissolved (92% of the amount calculated from the kinetic equation). 0.1053 g of ferrocene was isolated from the petroleum ether solution (89 % of theory). There was no depression in melting points after mixing with a pure specimen.

Kinetic measurements

A standard flask containing the solution of an organomercury compound in dioxane and a flask with hydrochloric acid of known concentration were thermostatted for 30 min. The 10 ml of the hydrochloric acid was pipetted and added quickly to the organomercury solution and the mixture again thermostatted. Dioxane was added to the mark. After 5–10 sec vigorous stirring the flask was again thermostatted. The reaction was timed from when half the addition of hydrochloric acid had been added to the organomercury solution. The first test was made one minute after the reaction was started when the reaction was stopped by pouring an aliquot (10 ml) of the reaction mixture into a volume of alkaline solution sufficient to neutralise 80–90 % of the unreacted acid. The time was recorded when half of the reaction mixture aliquot had been added to the alkaline solution. The excess acid was titrated potentiometrically with a standard solution of sodium hydroxide in 60 % dioxane. The measurements were made with a LP-58 potentiometer using saturated aqueous calomel and glass electrodes and the millivolt scale. Control tests with specially prepared mixtures have shown that the presence of the reaction products does not affect the accuracy of the potentiometric determination of hydrochloric acid. The reaction order was calculated by the integral method as well as from the kinetic curve[8]. The reaction rates in all

TABLE 1

RATE CONSTANTS OF PROTODEMERCURATION OF DIFERROCENYLMERCURY AND FERROCENYLMERCURY CHLORIDE

Compound	Dioxane/water (vol. %)	T (°C)	K_2 (mole^{-1} min^{-1} l)	E^* (kcal mole)	ΔS^* (entr. unit)
$(C_5H_5FeC_5H_4)_2Hg$	80	20	10.2	16.9	−6.2
		25	18.2		
		30	31.2		
		35	43.8		
	85	15	10.5	18.0	−1.3
		20	19.0		
		25	34.0		
		30	48.4		
	90	10[a]	14.3	18.7	+2.7
		15[a]	25.0		
		20[a]	44.0		
		25	75.9		
	92.5	10	26.1	19.5	+6.6
		15	48.9		
		20	92.5		
		25	146.2		
$C_5H_5FeC_5H_4HgCl$	90	20[a]	$34\cdot10^{-2}$	19.1	−5.6
		25[a]	$63\cdot10^{-2}$		
		30[a]	$10.4\cdot10^{-1}$		
		35	$15.7\cdot10^{-1}$		

[a] Since in the present study, E^* and ΔS^* were calculated for four temperatures, these values for 90 % dioxane differ somewhat from those described in our previous work[9] but these deviations are within the expected accuracy of the experiment.

TABLE 2

RATE CONSTANTS OF PROTODEMERCURATION OF DIPHENYLMERCURY AND BIS(p-CHLOROPHENYL)MERCURY

Compound	Dioxane/water (vol. %)	T (°C)	K_2 (mole^{-1} min^{-1} l)	$E^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ (entr. unit)
$(C_6H_5)_2Hg$	80	25	$4.58 \cdot 10^{-2}$	22.2	−0.3
		30	$8.56 \cdot 10^{-2}$		
		35	$15.1 \cdot 10^{-2}$		
		40	$27.8 \cdot 10^{-2}$		
	85	25	$8.33 \cdot 10^{-2}$	23.6	+5.6
		30	$15.5 \cdot 10^{-2}$		
		35	$28.4 \cdot 10^{-2}$		
		40	$57.0 \cdot 10^{-2}$		
	90	25	$2.00 \cdot 10^{-1}$	24.2	+9.3
		30[a]	$3.99 \cdot 10^{-1}$		
		40[a]	$14.2 \cdot 10^{-1}$		
	92.5	25	$3.88 \cdot 10^{-1}$	25.2	+14.0
		30	$7.49 \cdot 10^{-1}$		
		35	$14.6 \cdot 10^{-1}$		
		40	$29.9 \cdot 10^{-1}$		
$(p\text{-}ClC_6H_4)_2Hg$	90	30[a]	$6.78 \cdot 10^{-2}$	24.6	+7.1
		50[a]	$8.52 \cdot 10^{-1}$		
		60[a]	$27.8 \cdot 10^{-1}$		

[a] From ref. 10.

cases were in accordance with the second-order kinetic equation:

$$K = \frac{2.303}{(a-b)t} \cdot \log \frac{b(a-x)}{a(b-x)}$$

where a and b are the initial concentrations of acid and organomercury compound, respectively, x is the change in reactant concentration during time, t, from the beginning of the reaction.

The degree of conversion was usually 40–60% and a linear dependency of $\log b(a-x)/a(b-x)$ on the time, t, was observed in all cases. The rate constants (mean values of at least three measurements), and the activation energies, calculated by the method of least squares, are given in Tables 1–3. The rate constants were measured with an accuracy of ±5% and the activation energies with an accuracy of ±6%. The entropies of activation were calculated from the equation:

$$K = \frac{ekT}{h} \cdot e^{-E^{\neq}/RT} \cdot e^{S^{\neq}/R}$$

RESULTS AND DISCUSSION

Rates of protodemercuration of some mercury derivatives of ferrocene and cyclopentadienylmanganese tricarbonyl

In protolysis reactions of mercury derivatives (as well as in some other reactions) ferrocenyl exhibits electron-donating properties, while the cyclopentadienylmanganese-tricarbonyl radical shows weak electron-attracting properties with

TABLE 3

RATE CONSTANTS OF PROTODEMERCURATION OF SOME MERCURY DERIVATIVES OF CYCLOPENTADIENYLMANGANESE TRICARBONYL

The activation entropies were calculated for 25°.

The rate constants for these compounds in 90% dioxane have already been reported[11].

Compound	Dioxane/water (vol. %)	T (°C)	K_2 (mole^{-1} min^{-1} l)	E^* (kcal/mole)	ΔS^* (entr. unit)
$[C_5H_4Mn(CO)_3]_2Hg$	85	40	$10.3 \cdot 10^{-2}$	23.0	0.3
		45	$18.5 \cdot 10^{-2}$		
		50	$34.0 \cdot 10^{-2}$		
		55	$55.0 \cdot 10^{-2}$		
	90	40	$28.0 \cdot 10^{-2}$	22.9	1.9
		45	$48.0 \cdot 10^{-2}$		
		50	$85.0 \cdot 10^{-2}$		
		55	$15.1 \cdot 10^{-1}$		
	92.5	40	$47.4 \cdot 10^{-2}$	22.4	1.4
		45	$84.0 \cdot 10^{-2}$		
		50	$15.4 \cdot 10^{-1}$		
		55	$21.7 \cdot 10^{-1}$		
$C_5H_4Mn(CO)_3HgCl$	90	60	$8.1 \cdot 10^{-2}$	20.6	−13.2
		65	$12.2 \cdot 10^{-2}$		
		70	$19.7 \cdot 10^{-2}$		
		75	$30.3 \cdot 10^{-2}$		

respect to the phenyl group. If for comparison purposes we take the rate of protodemercuration of diphenylmercury[10] as unity then the rates for other compounds are as follows (*cf.* Tables 1–3): bis(cyclopentadienylmanganese-tricarbonyl)mercury, 0.20; bis(*p*-chlorophenyl)mercury[10], 0.18; di-*p*-anisylmercury[10], 71 and diferrocenylmercury, 380.

A comparison of the reactivities of symmetrical mercury compounds with some organomercury salts of ferrocene and cyclopentadienylmanganese tricarbonyl shows that the dependency observed for arylmercury compounds also obtains here; *viz.*, the symmetrical compounds react more quickly than asymmetric compounds: the rate of protodemercuration of diferrocenylmercury is almost 130 times that of ferrocenylmercury chloride. The protolysis of bis(cyclopentadienylmanganese-tricarbonyl)mercury also proceeds more rapidly (about 30 times) than that of the asymmetrical compound.

The replacement of a radical markedly changes the thermodynamic parameters. The reactions of mercury derivatives of ferrocene and cyclopentadienylmanganese tricarbonyl differ mostly in their activation energies (*cf.* Tables 1–3) while their entropies of activation are nearly the same. This indicates that the transition states in the reactions of these compounds are equivalent and the latter differ only in the polarizability of the C–Hg bonds. The entropies of activation for the reactions of mercury derivatives of ferrocene and cyclopentadienylmanganese tricarbonyl are smaller than those for arylmercury derivatives[10]. The lower entropies of activation for the symmetrical mercury derivatives of ferrocene and cyclopentadienylmanganese tricarbonyl are probably associated with steric hindrance preventing the attack of a reagent (for any possible configuration of these compounds) compared with mercury derivatives of the aryl series.

Protodemercuration of diferrocenylmercury with perchloric acid in 90% (vol.) aqueous dioxane

The rates of protolysis of diferrocenylmercury and diphenylmercury[12,13] with perchloric acid are approximately half that with hydrochloric acid under the same conditions. This equal deviation in reactivity when one acid is replaced by another means that the acid anion has the same function in the protodemercuration of both diphenylmercury and diferrocenylmercury.

As with protolysis with hydrochloric acid, this reaction is of the second order. We have determined the temperature-dependency of the rate constants and calculated the energies and entropies of activation (*cf.* Table 4). The activation energies and entropies of protodemercuration of diferrocenylmercury with perchloric acid are smaller than those with hydrochloric acid. In protolysis with perchloric acid, the solvated proton is the reacting species*. The increase in solvation of the charged transition state compared to the uncharged state in protolysis with hydrochloric acid, is evidenced by the decrease of both the activation energy and activation entropy.

TABLE 4

KINETIC DATA ON PROTODEMERCURATION OF DIFERROCENYLMERCURY WITH PERCHLORIC ACID ($C_{HClO_4} = C_{(C_5H_5FeC_5H_4)_2Hg} = 10^{-3}$ mole)

No.	T(°C)	K_2(mole^{-1} min^{-1} l)	E^* (kcal/mole)	ΔS^* (entr. unit)
1	10	6.75	17.7	−2.3
2	15	13.67		
3	20	22.46		
4	25	33.16		

The effect of potassium chloride in the rate of protodemercuration of diferrocenylmercury with perchloric and hydrochloric acids

We have shown above that the rate of protolysis of diferrocenylmercury with perchloric acid is half that with hydrochloric acid of the same concentration. This increase in rate is mainly due to the nucleophilic assistance of the chloride ion. This was most evident when the effect of addition of KCl in the rate of protodemercuration of diferrocenylmercury with both hydrochloric and perchloric acids was investigated. It can be seen from Table 5, that the addition of KCl increases the reaction rate in both cases although the magnitude was not the same: a 4-fold increase in the concentration of KCl causes the rate of decomposition with perchloric acid to be increased 1.7 times, whereas protolysis with hydrochloric acid proceeds only 10% more quickly. The addition of KCl probably has the same effect as in the aromatic series[2,12] and causes the dissociation equilibrium of hydrochloric acid to be shifted to give higher concentrations of the undissociated form. A 2-fold increase in concentration of KCl results in

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* Ferrocene is known to behave as a base in strong acidic media[6]. The measurements of the strength of conjugated acid for ferrocene ($pK_a = -6.6$) and for some of its derivatives has shown[14] that the protonation of the ferrocene nucleus is of significance only in media of acidity approximating that of concentrated H_2SO_4 or CF_3COOH.

TABLE 5

THE EFFECT OF ADDITION OF POTASSIUM CHLORIDE ON PROTODEMERCURATION OF DIFERROCENYLMERCURY WITH HYDROCHLORIC AND PERCHLORIC ACIDS IN 90% (VOL.) AQUEOUS DIOXANE AT 20° ±0.1°

Acid	C_{KCl} (mole·10^4)	C_{acid}[a] (mole·10^4)	K_2 (mole^{-1} min^{-1} l)
$HClO_4$	0	8.57	22.5
	4.28	8.57	23.3
	8.57	8.57	30.9
	17.14	8.57	40.5
HCl	0	10.0	44.0
	5.00	10.0	43.8
	10.0	10.0	45.1
	20.0	10.0	50.0

[a] In all experiments the concentration of diferrocenylmercury was the same as that of the corresponding acid.

a 1.32-fold increase in the protolysis rate of diferrocenylmercury with perchloric acid. For diphenylmercury this value is 1.26[12]. Therefore, the sensitivity of the mercury atom in diferrocenyl- and diphenyl-mercury to nucleophilic assistance is nearly the same.

The effect of the water content of dioxane on the rate of protodemercuration of diphenylmercury, diferrocenylmercury and bis(cyclopentadienylmanganese-tricarbonyl)mercury

When Dessy *et al.*[2] established the mechanism of protodemercuration of diphenylmercury they studied the effect of dioxane or water addition on the rate of this protolysis in dimethyl sulfoxide. The rate increased with increase in dioxane concentration and decreased with increase in water concentration. Since the additions of dioxane or water were insignificant, they have associated the notable change in the rate constants, not with the change in dielectric constant of the medium, but with the shift of the dissociation equilibrium of hydrochloric acid. We have studied the effect of water content of dioxane on the protolysis rate of diferrocenylmercury and bis(cyclopentadienylmanganese-tricarbonyl)mercury and, for a comparison, the comparable reaction of diphenylmercury with hydrochloric acid. The measurements were carried out using 80, 85, 90 and 92.5% (vol.) aqueous dioxane. Activation energies and entropies were calculated from the temperature-dependencies of the rate constants. The results obtained are shown in Tables 1–3. The decrease in water content of dioxane

TABLE 6

THE DEPENDENCE OF COMPARATIVE PROTODEMERCURATION RATE CONSTANTS ON THE WATER CONTENT OF DIOXANE

Compound	Content of dioxane (%)			
	80	85	90	92.5
$(C_5H_5FeC_5H_4)_2Hg$	0.53	1	2.2	4.3
$(C_6H_5)_2Hg$	0.55	1	2.4	4.6
$[C_5H_4Mn(CO)_3]_2Hg$	—	1	2.7	4.6

increases the rate of protodemercuration of diferrocenylmercury as well as the rate of protolysis of both bis(cyclopentadienylmanganese-tricarbonyl)mercury and diphenylmercury. If the reaction rate in 85% dioxane is taken as unity, an increase in the rate constants with decrease in water content could be expressed by the comparative values tabulated in Table 6.

In spite of some differences in the absolute values of the rate constants, they all increase with decrease in solvent water content. This is clearly seen from Fig. 1. For diferrocenylmercury and diphenylmercury, analogous decreases in activation energy and entropy were observed when the water content of dioxane increased*. This can be explained by the high solvation in the transition state when dioxane contains much water, causing a decrease in the activation energy which in turn leads to a restriction in the vibrations and rotations of the solvent molecules and hence to a loss in the activation entropy.

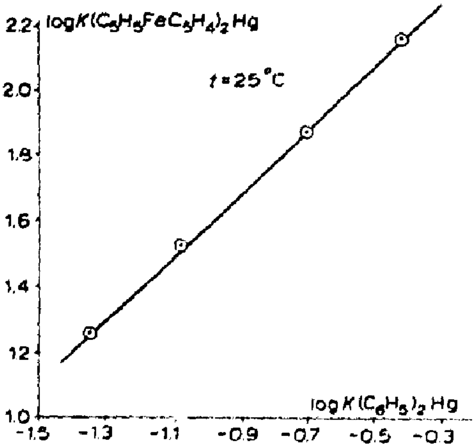

Fig. 1. The dependency of log $K(C_5H_5FeC_5H_4)_2Hg$/log $K(C_6H_5)_2Hg$ on the percentage water content of dioxane.

Relations between certain values are applied for identifying reaction mechanisms when the rate constants are known. In particular, the existence of a linear dependency between activation energy and activation entropy, called the isokinetic relation, is considered by many authors as a good criterion for coincidence of reaction mechanisms. On the other hand, the absence of such a dependency is usually regarded as an indication of some specific interactions in the transition state.

Exner[15] has pointed out, however, that the correlation of the logarithms of the rate constants for various temperatures is more accurate and, hence, more reliable than the correlation of energy parameters. The former is directly associated with the energy and entropy of activation. We have investigated the dependency between the rate constants for diphenylmercury and diferrocenylmercury for two different temperatures (25 and 30°) and for various water contents of dioxane, and found that the points for diferrocenylmercury lie in the same line as those for diphenylmercury

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* We have failed to obtain such a dependency for bis(cyclopentadienylmanganese-tricarbonyl)mercury probably because of a less accurate experiment.

(*cf.* Fig. 2). The relationships between the logarithms of protodemercuration rate constants for diphenylmercury and bis(cyclopentadienylmanganese-tricarbonyl)-mercury observed with various concentrations of dioxane are also rectilinear. (Fig. 3). The existence of these rectilinear relationships indicates an identical protodemercuration mechanism for the compounds investigated.

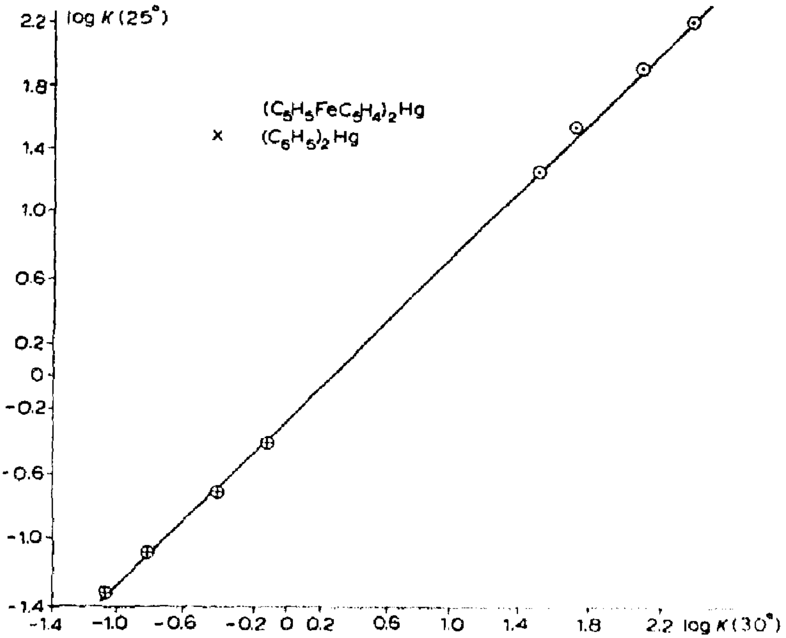

Fig. 2. The dependency of log $K(25°)$/log $K(30°)$ for protodemercuration of diphenylmercury and diferrocenylmercury in dioxane containing various amounts of water. (log $K(30°)(C_5H_5FeC_5H_4)_2Hg$ for 90 and 92.5% dioxane were calculated from temperature dependency).

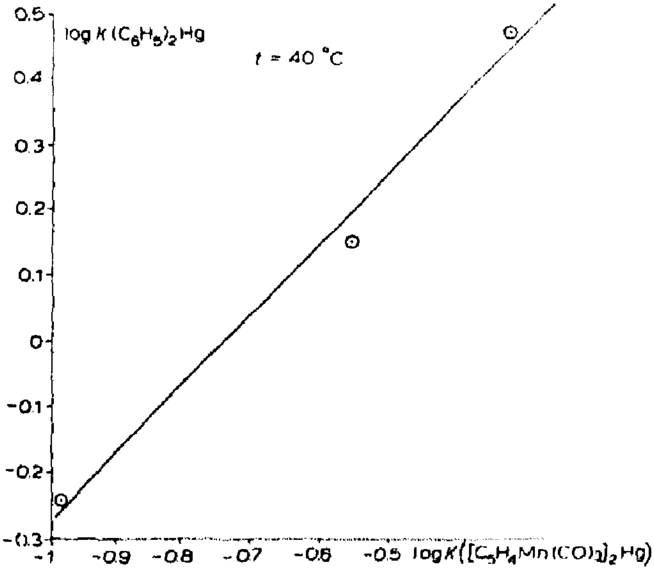

Fig. 3. The dependency of log $K(C_6H_5)_2Hg$/log $K[C_5H_4Mn(CO)_3]_2Hg$ on the percentage water content of dioxane.

Thus the conclusion to be drawn from the acid anion effect, the effect of addition of potassium chloride, and water content of dioxane effect on the protodemercuration rate of diphenylmercury, diferrocenylmercury and bis(cyclopentadienylmanganese-tricarbonyl)mercury is that the mechanism of protodemercuration of diferrocenylmercury and bis(cyclopentadienylmanganese-tricarbonyl)mercury does not differ essentially from that for diphenylmercury and this explanation does not require the participation of the metal atom in any form[16] in the stage determining the reaction rate.

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