[CONTRIBUTION FROM THE INSTITUTE FOR CHEMICAL RESEARCH, KYOTO UNIVERSITY, JAPAN]

The Kinetics of the Demercuration Reaction of Benzyl- and β-(*p*-Methoxyphenyl)-ethylmercuric Acetate with Perchloric Acid

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To clarify the reaction mechanism of the final steps involved in the reactions of olefin–mercuric acetate addition compounds with aromatics to form β-arylethyl acetates, the kinetics of the demercuration reactions of benzyl- and β-(*p*-methoxyphenyl)-ethylmercuric acetate (one of the intermediate mercurials) have been studied. In aqueous acetic acid solutions containing perchloric acid, rate expressions were established for the second-order reaction 1 and first-order reaction 2 (where Z = OAc). Perchloric acid concentrations affected the rates of both reactions remarkably. Possible mechanisms are discussed.

In previous papers, it was reported that the organic mercurials which are formed by the reaction of olefin–mercuric salt addition compounds with aromatics or acetoacetic ester are demercurated to give the corresponding esters or alcohols in the presence of strong acids.[2,3] Two types of reactions were observed.

$$ArCH_2HgZ + HgZ_2 \xrightarrow{H^+} ArCH_2Z + Hg_2Z_2 \qquad (1)$$

$$ArCH_2HgZ \xrightarrow{H^+} ArCH_2Z + Hg \qquad (2)$$

$$Ar = C_6H_5\text{– or } CH_3OC_6H_4CH_2\text{–},\ Z = \text{acid radicals}$$

The literature contains little information on these reactions of simple alkyl or aralkyl mercuric salts.[4–6] Many examples of similar results, however, can be found in the oxidation of olefins (for example, terpenes) with mercuric acetate. Since this oxidation proceeds through addition compounds between the mercuric salt and olefins ($-\overset{|}{\underset{|}{C}}(OR)-\overset{|}{\underset{|}{C}}-HgZ$, where R = H, alkyl or acyl and Z = acid radicals), this is a special case of reaction 1 or 2.[7] This oxidation, however, is carried out at higher temperatures in acetic acid or by allowing the reaction mixture to stand for long periods of time at lower temperatures. In no report except that mentioned below, is the catalytic effect of strong acids on these oxidations reported. Shearer and Wright studied the kinetics of the reactions between mercuric salt and olefin–mercuric salt addition compounds in the presence of strong acids (reaction 1) and suggested a radical mechanism on the basis of their rather qualitative results.[6] Further investigation, however, appears to be required to determine the mechanism. In addition, it is doubtful that the reactions of an alkyl or aralkyl mercuric salt would proceed through the same mechanism as that for olefin–mercuric acetate addition compounds which belong to a special type of mercurials and show peculiar reactivities.[8] Therefore, we have studied the kinetics of the reactions of benzyl- and β-(*p*-methoxyphenyl)-ethylmercuric acetate by equation 1 or 2.

Results and Discussion

Two possible side reactions must be considered in the kinetic study of reaction 1. First is the decomposition of mercuric acetate itself in acetic acid.[9] Blank tests, however, showed that this reaction was too slow to affect the results under the conditions studied. Second is the mercuration of the benzene ring with mercuric acetate. This reaction is reversible and the mercurated compounds are decomposed to the original aromatics and mercuric salt in concentrated solutions of strong acids. Although slight mercuration was observed with benzylmercuric acetate under conditions where reaction 1 proceeds with moderate rates, no substantial effect on the reaction order was produced. In the case of β-(*p*-methoxyphenyl)-ethylmercuric acetate, however, the mercuration was so great that the rate study was impossible.

The rates of reaction of benzylmercuric acetate in water–acetic acid mixtures containing perchloric and nitric acid were followed by determining both decreases of benzylmercuric acetate and increases of Hg(I). Despite the possible side reactions mentioned above, fairly good second-order constants were obtained (see, for example, Fig. 1) and are shown in Table I.

Differences between the two second-order constants obtained appear to show the effects of benzene ring mercuration. These differences are small at higher concentrations of perchloric acid and at smaller initial concentrations of mercuric acetate. No metallic mercury which might be produced by disproportionation of mercurous salt was observed. Increases of perchloric acid concentrations resulted in marked increases in rate.

The reaction of ethylmeruric acetate with mercuric acetate was too slow to allow a determination of the rate.

Contrary to the radical mechanism proposed by Shearer and Wright,[6] these results suggest strongly an ionic mechanism and are consistent with the mechanism shown in equations 3 and 4.

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[1] Department of Chemical Engineering, University of Osaka Prefecture.

[2] (a) K. Ichikawa, S. Fukushima, H. Ouchi and M. Tsuchida, THIS JOURNAL, **80**, 6005 (1958); (b) **81**, 3401 (1959).

[3] K. Ichikawa, H. Ouchi and S. Fukushima, *J. Org. Chem.*, **24**, 1129 (1959).

[4] L. W. Jones and L. Werner, THIS JOURNAL, **40**, 1257 (1918).

[5] P. R. Jefferies, A. K. Macbeth and B. Milligan, *J. Chem. Soc.*, 705 (1954).

[6] D. A. Shearer and G. F. Wright, *Can. J. Chem.*, **33**, 1002 (1955).

[7] For equation 1, see, for example, D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 2381 (1951); W. Treibs, G. Lucius, H. Kögler and H. Breslauer, *Ann.*, **581**, 59 (1953); A. Kregomand, *Ann. chim.* (*Paris*), **8**, 172 (1953). For equation 2, see, for example, W. Treibs and H. Bast, *Ann.*, **561**, 165 (1949); L. Balbiano and V. Paolini, *Ber.*, **35**, 2994 (1902).

[8] J. Chatt, *Chem. Revs.*, **48**, 7 (1951).

[9] H. C. Brown and C. W. McGary, THIS JOURNAL, **77**, 2300 (1955).

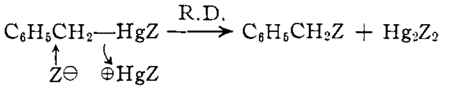
TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF BENZYLMERCURIC ACETATE WITH MERCURIC ACETATE IN ACETIC ACID–WATER MIXTURES IN THE PRESENCE OF PERCHLORIC ACID

Solvent HOAc, vol. %	Reacn. temp., °C.	Perchloric acid, moles/l.	Initial concn. of $C_6H_5CH_2$-HgOAc, mole/l.	Initial concn. of Hg-$(OAc)_2$, mole/l.	$k_2 \times 10^3$, l./mole sec. I[a]	$k_2 \times 10^3$, l./mole sec. 11[b]
50	25.0	2.38	0.0250	0.0500	8.36	9.01
			.0500	.0500	8.26	8.26
			.0509	.1000	8.20	8.05
			.0500	.2000	8.40	7.17
	25.0	0.79	.0509	.1000	0.606	0.399
		1.58	.0509	.1000	2.06	2.01
		2.38	.0509	.1000	8.20	8.05
		2.78	.0500	.1000	13.7	13.2
65	25.0	1.58	.0500	.1000	4.13	3.47
50	25.0	1.58	.0509	.1000	2.06	2.01
	35.0	1.58	.0500	.1000	6.37	6.20 [c]
	45.0	1.58	.0500	.1000	19.2	18.7
		Nitric acid				
50	25.0	0.56	0.0500	0.1000	0.95	0.77
		1.13	.0500	.1000	3.3	4.2
		1.58	.0500	.1000	7.6	8.5
65	25.0	1.13	.0500	.1000		6.2

[a] I, obtained by following the increase of Hg(I) concentration. [b] II, obtained by following the decrease of C_6H_5-CH_2HgOAc concentration. [c] E_{act} = 21.0 kcal./mole, log PZ = 12.7.

$$HgZ_2 + H^{\oplus} \underset{}{\overset{\text{fast}}{\rightleftarrows}} {}^{\oplus}HgZ + HZ \tag{3}$$



$$\underset{\underset{Z^{\ominus}}{\uparrow}}{C_6H_5CH_2}—\underset{\underset{{}^{\oplus}HgZ}{\searrow}}{HgZ} \xrightarrow{\text{R.D.}} C_6H_5CH_2Z + Hg_2Z_2 \tag{4}$$

In this mechanism the rate-determining step is electrophilic attack of ${}^{\oplus}HgZ$ on the mercury (not on the carbon).

It is not clear whether the benzylmercuric acetate added reacts in the form of acetate or whether it reacts in the form of benzylmercuric perchlorate. The general electrolytic behavior of RHgZ suggests that since the dissociation constant of RHgOAc is much smaller than that of $RHgNO_3$ or $RHgClO_4$,[10] the reacting species are probably the acetate. It is difficult to decide what the reacting form of the other reagent, $Hg(OAc)_2$, is. An equilibrium between $Hg(OAc)_2$ and $Hg(NO_3)_2$ or between Hg-$(OAc)_2$ and $Hg(ClO_4)_2$ may exist in the reaction mixture. For example, the solubility of mercuric acetate in acetic acid is increased considerably by adding nitric or perchloric acids. The fact that the rates are faster in the presence of nitric acid than in the case of perchloric acid appears to show differences of electrophilicity of ${}^{\oplus}HgOAc$, ${}^{\oplus}Hg$-ClO_4 and ${}^{\oplus}HgNO_3$ on the mercury atom of benzylmercuric acetate.

In the case of nitric acid catalyst, however, clean-cut constants were not obtained, probably because of air oxidation of mercurous nitrate during the course of the analysis. These values, therefore, are much more inaccurate than those obtained by perchloric acid catalysis.

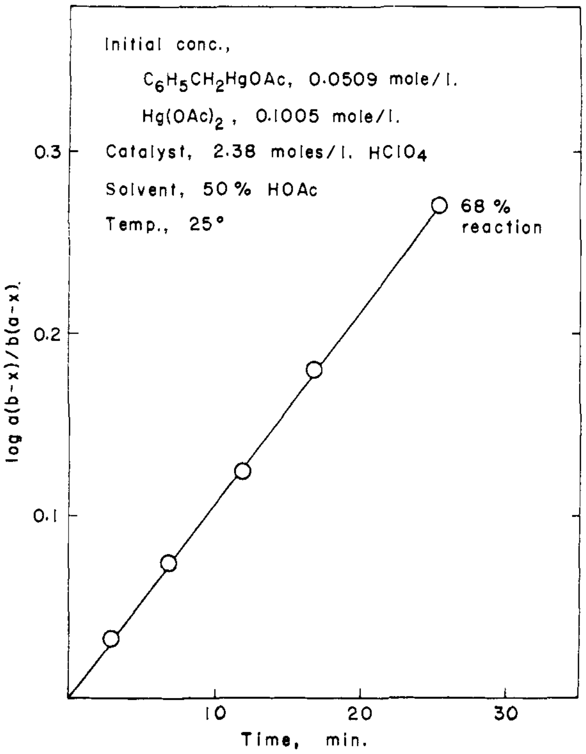


Fig. 1.—Typical example of the second-order plot for the reaction between benzylmercuric acetate and mercuric acetate.

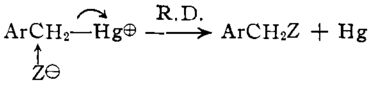
It is difficult to estimate whether equation 4 involves formation of a carbonium ion or whether it is a concerted type. The mechanism depicted formally in equation 4 is not meant to imply that the reaction is concerted.

The demercuration rates of benzyl- and β-(*p*-methoxyphenyl)-ethylmercuric acetate in the absence of mercuric acetate (reaction 2) have been studied under conditions similar to those mentioned above. The rates followed first-order kinetics. Despite the fact that considerable amounts of mercurous salt (12–18 mole per cent. of the reacted substrate) were formed besides metallic mercury in the case of benzylmercuric acetate, clean-cut first-order constants were obtained (see, for example, Fig. 2.). Results obtained are shown in Tables II and III.

The rates are much smaller than in the second-order reaction mentioned above under the corresponding conditions. Here again, an increase in perchloric acid concentration results in a marked increase in rate. Plots of log k_1 against perchloric acid concentration gave straight lines (Fig. 4).

A possible mechanism (A) which appears to be consistent with the results obtained is proposed in equations 5 and 6.

$$\text{A.}\quad ArCH_2—HgOAc + H^{\oplus} \overset{\text{fast}}{\rightleftarrows} ArCH_2—Hg^{\oplus} + HOAc \tag{5}$$



$$\underset{\underset{Z^{\ominus}}{\uparrow}}{ArCH_2}\overset{\curvearrowright}{—}Hg^{\oplus} \xrightarrow{\text{R.D.}} ArCH_2Z + Hg \tag{6}$$

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[10] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. 1, Oxford University Press, Amen House, London, 1950, p. 310.

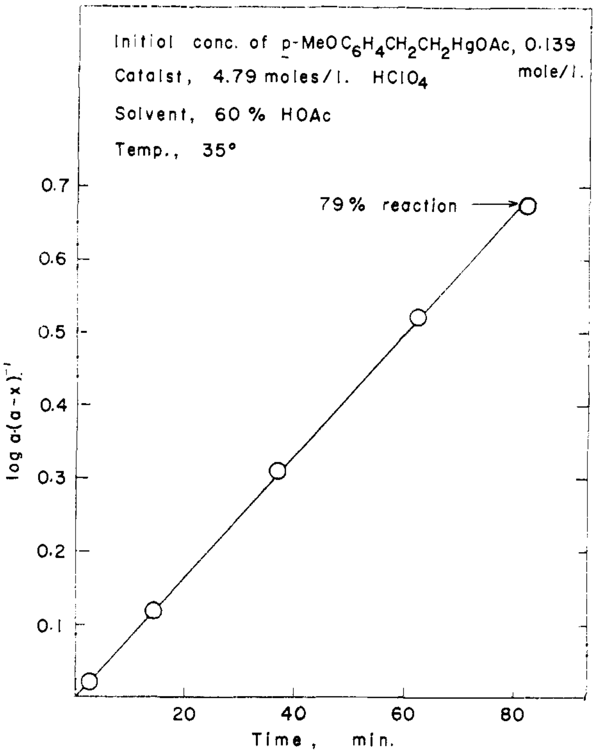


Fig. 2.—Typical example of the first-order plot for the reaction of benzylmercuric acetate.

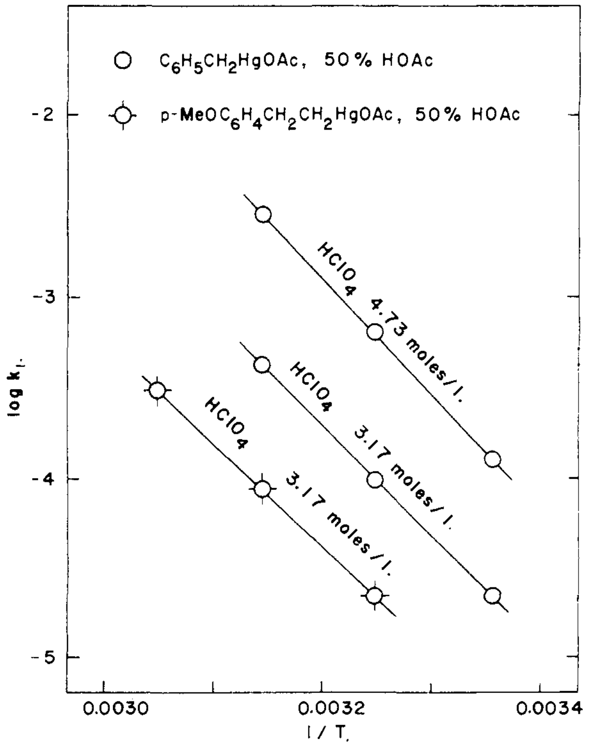


Fig. 3.—Arrhenius plots of the reactions of benzyl- and β-(p-methoxyphenyl)-ethylmercuric acetate.

Ar = C_6H_5– or $CH_3OC_6H_4CH_2$–, Z = acid radicals

$ArCH_2$–$Hg^{\oplus}$ might exist in the form of $ArCH_2$–$HgHO^{\oplus}Ac$. The mechanism (B) which was pro-

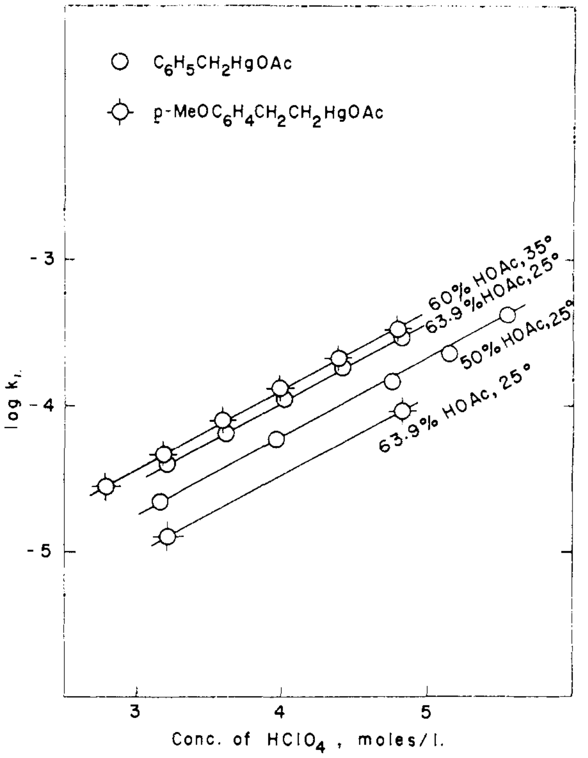


Fig. 4.—Relationship between log k_1 and perchloric acid concentrations.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF BENZYLMERCURIC ACETATE

Solvent HOAc, vol. %	Reacn. temp., °C.	Perchloric acid, moles/l.	Initial concn. of $C_6H_5CH_2$-HgOAc, mole/l.	$k_1 \times 10^5$, sec.$^{-1}$	NaClO$_4$ added, moles/l.
78.1	25.0	3.22	0.0241	11.9	
			.0483	10.8	
			.0965	11.1	
63.9	25.0	3.22	.0511	3.93	
		3.62	.0508	6.23	
		4.02	.0511	10.9	
		4.42	.0508	17.3	
		4.83	.0511	28.2	
50.0	25.0	3.18	.1000	2.24	
		3.97	.0508	5.73	
		4.76	.0511	14.6	
		5.15	.0508	22.5	
		5.55	.0511	42.2	
50.0	25.0	3.17	.0511	2.22[a]	
	35.0	3.17	.0508	9.87	
	45.0	3.17	.0508	41.8	
	45.0	3.19	.0508	42.7	
	60.0	3.19	.0508	313	
	25.0	4.73	.0509	12.7[b]	
	35.0	4.73	.0509	64.5	
	45.0	4.73	.0509	284	
50.0	25.0	3.19	0.0508	2.25	0.00
			.0508	3.97	0.80
			.0508	6.67	1.60
			.0508	8.40	2.00

[a] E_{act} = 27.7 kcal./mole, log PZ = 15.7. [b] E_{act} = 29.3 kcal./mole, log PZ = 17.6 (see Fig. 3).

TABLE III

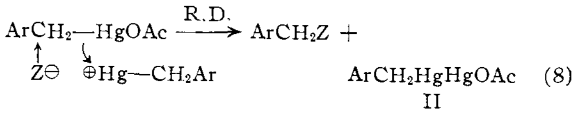
FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF β-(*p*-METHOXYPHENYL)-ETHYLMERCURIC ACETATE

Solvent HOAc, vol. %	Reacn. temp., °C.	Perchloric acid, moles/l.	Initial concn. of $CH_3OC_6H_4$-C_2H_4HgOAc, mole/l.	$k_1 \times 10^5$, sec.$^{-1}$	NaClO$_4$ added, moles/l.
60.0	35.0	4.79	0.0255	33.0	
			.0493	32.0	
			.139	32.0	
60.0	35.0	2.79	.0493	2.72	
		3.19	.0493	4.67	
		3.59	.0493	7.75	
		3.99	.0493	13.0	
		4.39	.0493	20.4	
		4.79	.0493	32.0	
50.0	35.0	3.17	.0456	2.19[a]	
	45.0	3.17	.0456	8.70	
	55.0	3.17	.0456	30.4	
63.9	25.0	3.22	.0491	1.23	
		4.83	.0491	9.10	
60.0	35.0	2.79	0.0510	2.72	0.00
			.0510	4.46	0.63
			.0510	7.02	1.26
			.0510	8.94	1.61

[a] E_{act} = 26.4 kcal./mole, log PZ = 14.1 (see Fig. 3).

posed by analogy to those for reaction 1 in the previous paper[2a] should result in second-order kinetics.

$$\text{B.}\quad \mathrm{ArCH_2{-}HgOAc} + \mathrm{H}^{\oplus} \overset{\text{fast}}{\rightleftarrows} \underset{\text{I}}{\mathrm{ArCH_2{-}Hg^{\oplus}}} + \mathrm{HOAc} \qquad (7)$$



$$\mathrm{ArCH_2{-}HgOAc} \xrightarrow{\text{R.D.}} \mathrm{ArCH_2Z} + \underset{\text{II}}{\mathrm{ArCH_2HgHgOAc}} \qquad (8)$$

$$\mathrm{Z^{\ominus}} \quad \mathrm{^{\oplus}Hg{-}CH_2Ar}$$

Compound II reacts further to form mercury and $ArCH_2Z$ or it is analyzed as mercurous salt when it remains unchanged. The assumption that the forward reaction in equation 7 is rate-determining and the subsequent reaction 8 proceeds rapidly would result in first-order kinetics. This, however, appears unlikely, since reaction 7 is an ionization of a mercuric salt. The fact that mercurous salt formation was observed in the case of benzylmercuric acetate and not in the case of β-(*p*-methoxyphenyl)-ethylmercuric acetate might suggest that the reaction of the former involves side reaction by mechanism B to such an extent that it cannot be detected by kinetics. This difference in the two compounds may be explained by considering the electrophilicity of mercury in I. There is no reason why the mercury ion in I cannot form the same type of π-complex as in the case of olefin and mercuric ion.[2a,11,12] This is possible for β-(*p*-methoxyphenyl)-ethylmercuric ion but not for benzylmercuric ion. The electrophilicity of the former, therefore, is reduced and this would be one of the reasons why the reaction by mechanism B does not proceed.

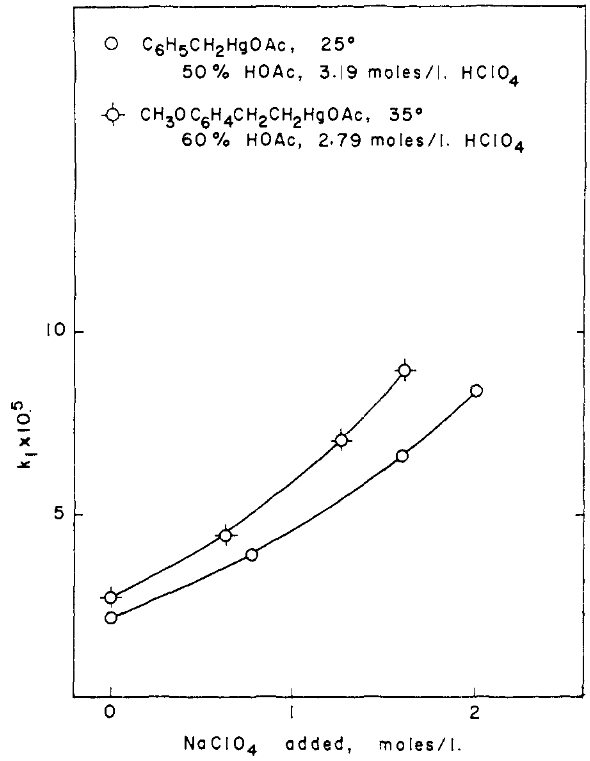


Fig. 5.—Effects of sodium perchlorate added on demercuration reactions.

Whether reaction 6 involves formation of carbonium ion or is of the SN2 type is interesting. The activation energy for the reaction of benzylmercuric acetate is greater, despite the fact that rates are greater, with relative rates of 3.2–4.5 under the same conditions. This suggests that different types of mechanisms might exist for the two compounds as in the case of solvolysis of the corresponding halides. If this is the case, an SN1 type reaction would be more important in the benzyl derivative and an SN2 type in the β-(*p*-methoxyphenyl)-ethyl derivative. The fact that the increase of the rates by the addition of sodium perchlorate is greater in the case of the latter (see Fig. 5) appears to support this explanation.

Experimental

Materials.—Mercuric acetate and perchloric acid were C.P. grade and used without purification. Acetic acid was purified by distillation through a packed column.

Benzylmercuric Acetate.—Benzylmercuric chloride which was prepared by the reaction of mercuric chloride with benzylmagnesium chloride[13] was converted to the acetate by the silver acetate method.[14] Its melting point was 126.5–127° (reported[15] 128–128.8°) after recrystallizations from ethanol.

Ethylmercuric Acetate.—Ethylmercuric halide (a mixture of chloride and bromide) which was obtained by the reaction of mercuric chloride with ethylmagnesium bromide[16] was converted to the acetate by silver acetate method.[14] Its melting point was 69.5–69.7° after recrystallization from ethanol (reported[15] 69–69.8°).

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(11) K. Ichikawa, K. Fujita and H. Ouchi, THIS JOURNAL, **81**, 5316 (1959).

(12) H. Lucas, F. R. Hepner and S. Winstein, *ibid.*, **61**, 3102 (1939).

(13) S. Hilpert and G. Grüttner, *Ber.*, **48**, 913 (1915).

(14) M. C. Sneed and J. L. Maynard, THIS JOURNAL, **44**, 2946 (1922).

(15) G. H. Coleman, L. A. Weed and C. D. Myers, *ibid.*, **59**, 2703 (1937).

(16) P. Rumpf, *Bull. soc. chim.*, **9**, 935 (1942).

β-(p-Methoxyphenyl)-ethylmercuric acetate was prepared by the reaction of the ethylene-mercuric acetate addition compound with anisole.[2a]

Rate Measurements.—Solutions of benzylmercuric acetate in acetic acid were added to a solution of mercuric acetate and perchloric acid in aqueous acetic acid with good stirring. At proper intervals, aliquots (5 ml.) were withdrawn and added to 50 ml. of water in separatory funnels. Unreacted benzylmercuric acetate was extracted with 20 ml. of chloroform three times. To these chloroform extracts, 50 ml. of water and 2 ml. of concd. nitric acid were added and the benzylmercuric acetate remaining was titrated with 0.05 *N* ammonium thiocyanate solution. Water layers after the extractions were mixed with 40 ml. of 0.3 *N* potassium iodide and 5 or 10 ml. of 0.05 *N* iodine solution. After shaking for 10 min., excess iodine was titrated with 0.05 *N* sodium thiosulfate solution. Thus, decreases of benzylmercuric acetate and increases of mercurous salt were determined. The other rate measurements were carried out by the same method.

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[Contribution from the Institute for Chemical Research, Kyoto University, Japan]

The Kinetics of the Decompositions of Ethylene–Mercuric Salt Addition Compounds with Hydrochloric Acid

By Katsuhiko Ichikawa, Hajime Ouchi[1] and Shigemitsu Araki

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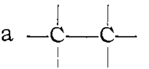
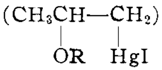
The kinetics of decompositions of ethylene–mercuric salt addition compounds ($ROCH_2CH_2HgCl$) with hydrochloric acid has been studied in water–ethanol mixtures and found to be third order (first order in addition compounds, hydronium ion and chloride ion, respectively). In the presence of perchloric acid, it has been demonstrated that R in the addition compound can be replaced by the solvent without decomposition. On the basis of these observations, the reaction mechanisms are discussed.

Since the first preparation of olefin–mercuric salt addition compounds,[2] the easy decomposition of these compounds with hydrochloric acid has proved puzzling. This decomposition gives the original olefins and mercuric salts, despite the fact that the usual reactions expected of the structural formula



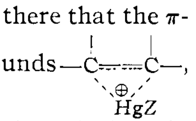
$$\underset{\textstyle OR}{\overset{|}{—C}}—\underset{\textstyle HgZ}{\overset{|}{C}}—$$

(where R = H, alkyl or acyl groups, and Z = inorganic or organic acid radicals) are reported. The addition compounds are also rather stable to non-halogen acids.[3] Recently, Kreevoy reported that the kinetics of the decomposition of propylene–mercuric salt addition compound



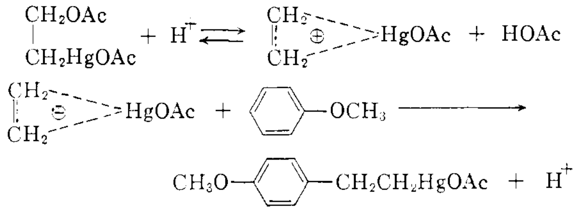
$$CH_3\underset{\textstyle OR}{\underset{|}{CH}}—\underset{\textstyle HgI}{\underset{|}{CH_2}}$$

in the presence of perchloric acid was a second-order reaction between the addition compound and hydronium ion and discussed the mechanism. It was concluded there that the π-complex form of the addition compounds



$$—\overset{|}{C}\overset{\oplus}{\underset{HgZ}{=\!=}}\overset{|}{C}—,$$

proposed by Lucas, Hepner and Winstein,[4] could not be the intermediate.[5] This complex, however, has been proposed as the intermediate in the reactions of the addition compounds with aromatics or acetoacetic ester in the presence of strong acids.[6-8] For example



To reconcile these two incompatible conclusions, the kinetics of decompositions of ethylene–mercuric salt addition compounds with hydrochloric acid have been studied.

There are several difficulties in this kinetic study. Mercuric chloride, one of the reaction products, may form complex compounds such as H_2HgCl_4 and $HHgCl_3$ with hydrochloric acid. These compounds are strong acids and therefore the proton concentrations are not affected, but chloride ion concentrations may change. Calculations on the basis of equilibrium constants reported by Damm and Weiss[9] show that mercuric chloride in hydrochloric acid exists largely in the form of the complexes. Despite these considerations, addition of aqueous sodium hydroxide to the mercuric chloride solutions in dilute hydrochloric acid (below 0.2 *M*) resulted in quantitative precipitations of mercuric oxide. On the other hand, sharp decreases of the yields of mercuric oxide in the range of more concentrated hydrochloric acid definitely indicate complex formation. It is doubtful, therefore, that the complexes are formed in dilute hydrochloric acid solution. As far as the determination of mercuric ion concentration by this method is applicable, however, the reaction order of chloride ion in this decomposition can be determined by checking the effects of initial concentrations of chloride

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[1] Department of Chemical Engineering, University of Osaka Prefecture.

[2] K. A. Hoffmann and J. Sand, *Ber.*, **33**, 1340, 2692 (1900).

[3] See, for example, J. Chatt, *Chem. Revs.*, **48**, 7 (1951).

[4] H. J. Lucas, F. R. Hepner and S. Winstein, This Journal, **61**, 3102 (1939).

[5] M. M. Kreevoy, *ibid.*, **81**, 1099 (1959).

[6] K. Ichikawa, S. Fukushima, H. Ouchi and M. Tsuchida, *ibid.*, **80**, 6005 (1958); **81**, 3401 (1959).

[7] K. Ichikawa, H. Ouchi and S. Fukushima, *J. Org. Chem.*, **24**, 1129 (1959).

[8] K. Ichikawa, K. Fujita and H. Ouchi, This Journal, **81**, 5316 (1959).

[9] K. Damm and A. Weiss, *Z. Naturforsch.*, **10b**, 534 (1955); *C. A.*, **50**, 9917 (1956).