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

Kinetics of the Reaction of the Ethylene–Mercuric Acetate Addition Compound with Anisole

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The kinetics of the reaction of the ethylene–mercuric acetate addition compound with anisole to form β-(*p*-methoxyphenyl)-ethyl mercuric acetate in acetic acid under perchloric acid catalysis has been found to be second order in both reactants. It is concluded that the essential role of the catalyst is not specific attack on the addition compound but its acidity.

The reactions of the ethylene–mercuric acetate addition compound (β-acetoxyethyl mercuric acetate) with aromatics to form β-arylethyl mercuric acetates were reported previously.[1] For example

$$\mathrm{AcOCH_2CH_2HgOAc + CH_3OC_6H_5 \longrightarrow CH_3OC_6H_4CH_2CH_2HgOAc + HOAc} \quad (1)$$

Since this is a new type of Friedel–Crafts reaction and proceeds under very mild conditions, it was desirable to study the kinetics in the hope of a quantitative approach to the reaction mechanism. This paper describes the results of a kinetic study of reaction 1 in acetic acid under perchloric acid catalysis. Under these conditions the reaction mixture is homogeneous.

It is well known that RHgZ can be titrated with thiocyanate. With the ethylene–mercuric acetate addition compound, however, these two reactions are possible

$$\mathrm{AcOCH_2CH_2HgZ + KSCN = AcOCH_2CH_2HgSCN + KZ} \quad (2)$$

$$\mathrm{AcOCH_2CH_2HgZ + 2KSCN = CH_2CH_2 + Hg(SCN)_2 + KOAc + KZ} \quad (3)$$

Reaction 2 cannot be used to follow the rate of reaction 1 because the thiocyanate consumption before and after the reaction is the same. Although the literature suggests that equation 3 could be used for analysis,[2] no quantitative data have been reported. To check this possibility, the ethylene–mercuric acetate addition compound solution in 75% acetic acid was titrated with 0.1 *N* potassium thiocyanate in the presence of nitric acid with the aid of ferric alum indicator. At room temperature, temporary appearance of the indicator color was observed, when an approximate equivalent amount of thiocyanate calculated by equation 2 was added. The reddish-orange color, however, soon disappeared and additional amounts of thiocyanate were added. This procedure was repeated until a permanent indicator color was observed. After about one hundred hours, the total amount of thiocyanate added was in accord with the calculated value (Fig. 1), and analysis is thus possible by reaction 3. To make this method practical for the purpose of the kinetic study, an excess of thiocyanate was allowed to react overnight, then a known amount of silver nitrate was added to react with the remaining thiocyanate and the excess silver nitrate was titrated again with thiocyanate. This modified method was shown to be satisfactory in the presence of perchloric acid. An attempt to shorten the reaction time by warming the reaction mixture resulted in erratic data, because of the decomposition of thiocyanate in the presence of perchloric acid.

Before the rate experiments, it was confirmed that the addition compound (0.5 *M* in 75% acetic acid) was stable in the presence of 1.5 *M* perchloric acid at 25° at least for ten hours, while this compound decomposes easily to give ethylene and mer-

TABLE I

SECOND-ORDER CONSTANTS FOR THE REACTION OF ETHYLENE–MERCURIC ACETATE ADDITION COMPOUND WITH ANISOLE AT 25.15°

Solvent acetic acid, wt. %	Perchloric acid, mole/l.	Initial concn. of anisole, mole/l.	Initial concn. of the addition compd., mole/l.	$k_2 \times 10^5$, l./mole sec.
75.0	1.60	1.007	0.0425	2.49
		0.9976	.0996	2.49
		0.9976	.2000	2.37
		1.007	.2178	2.42
		1.007	.2659	2.31
		0.9976	.3493	1.92
		0.9976	.4995	1.66
		1.007	.5318	1.48
		0.4989	.2001	2.37
		.7995	.2001	2.30
		.9976	.2001	2.37
	1.00	.9972	.2000	0.373
	1.32	.9972	.2000	0.992
	1.60	.9972	.2000	2.37
	1.99	.9972	.2000	8.43
	2.40	.9972	.2000	32.1
80.0	0.995	.9972	.2000	0.766
	1.60	.9972	.2000	4.58
	2.03	.9972	.2000	19.0
40.0	1.60	.1009	.0500	0.20
50.0		.1009	.0500	0.40
61.4		.1009	.0500	0.765
67.4		.0514	.0500	1.14
75.0		.9972	.2000	2.37
80.0		.9972	.2000	4.58
86.5		.9976	.0997	15.5
86.5		.9976	.2000	15.2

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

[2] W. Manchot and Klug, *Ann.*, **420**, 170 (1920).

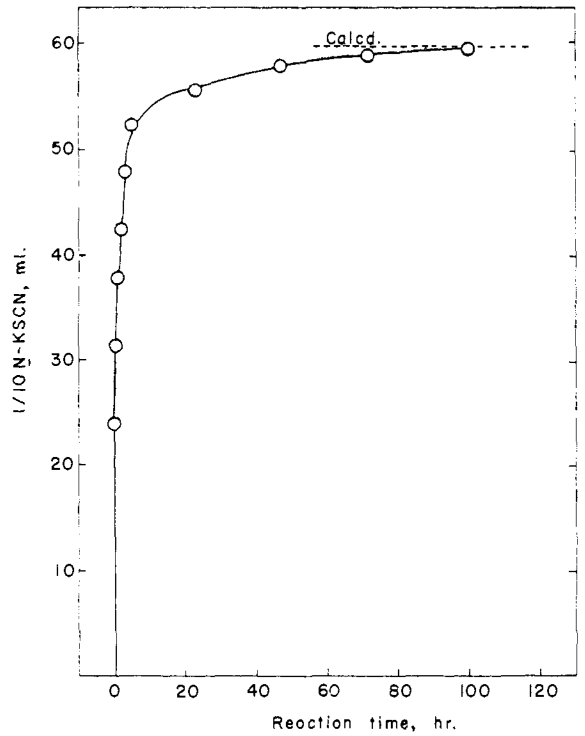

Fig. 1.—Titration curve of ethylene–mercuric acetate addition compound with potassium thiocyanate.

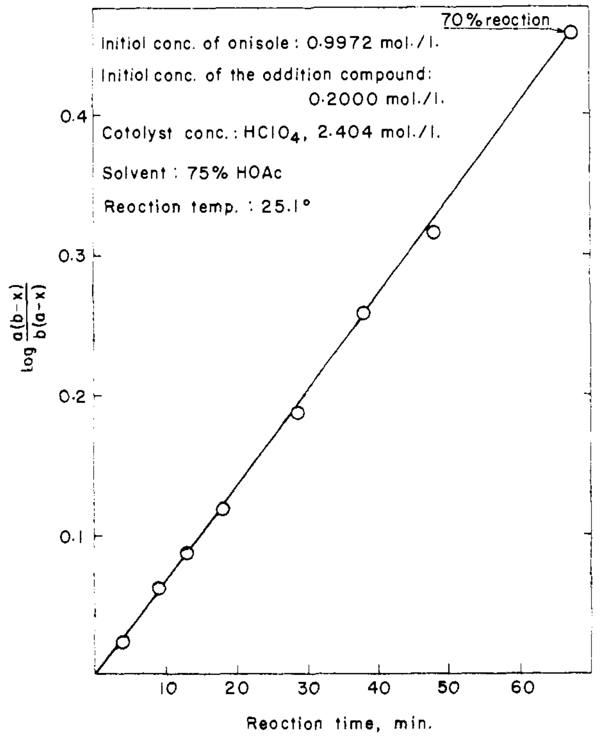

Fig. 2.—Typical example of the second-order plot for the reaction of ethylene–mercuric acetate addition compound with anisole.

curic chloride quantitatively with dilute hydrochloric acid at room temperature.[3]

The rates of reaction 1 were measured in acetic acid–water mixtures containing various amounts of perchloric acid. It was shown in each kinetic run that the rates could be expressed by the equation $dx/dt = k_2(a - x)(b - x)$, where a is the initial molar concentration of anisole, b is the initial concentration of the ethylene–mercuric acetate addition compound and x is the amount of the both reactants which have reacted at time t. Plots of the quantity $\log b(a - x)/a(b - x)$ against time t gave straight lines which passed through the origin (Fig. 2), showing that the reaction is second order. In the concentration range of the addition compound below 0.2 mole/l., the second-order constants were not affected by the initial concentrations, but at higher concentrations these constants decreased with an increase of initial concentration. This is due probably to the ionic character of this reaction as is mentioned later. Change in the initial concentration of anisole, however, did not affect the rate constants. The results obtained are summarized in Table I.

An Arrhenius plot of the second-order constants in 75% acetic acid containing 1.32 moles/l. perchloric acid gave a good straight line (see Fig. 3 and Table II).

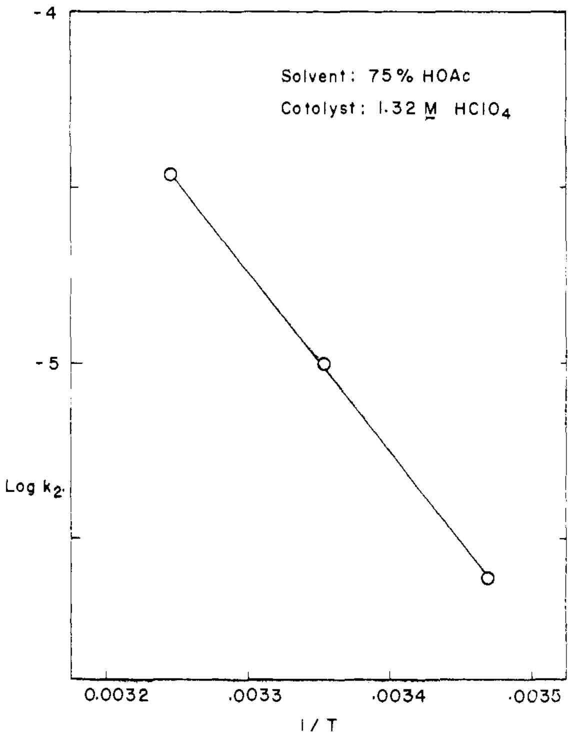

Fig. 3.—Arrhenius plot of log k_2 against $1/T$.

The concentrations of both perchloric (catalyst) and acetic (solvent) acids affected the rates remarkably. Figures 4 and 5 show the plots of log k_2 at 25.15° in 75% acetic acid against perchloric acid concentration and the plots of log k_2 in the presence of 1.6 molar perchloric acid at the same temperature against acetic acid concentration, respectively. Since the rates increase much more rapidly than perchloric acid concentration, it was of interest to examine these relationships in terms of the acidity function H_0 of the reaction medium. Un-

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

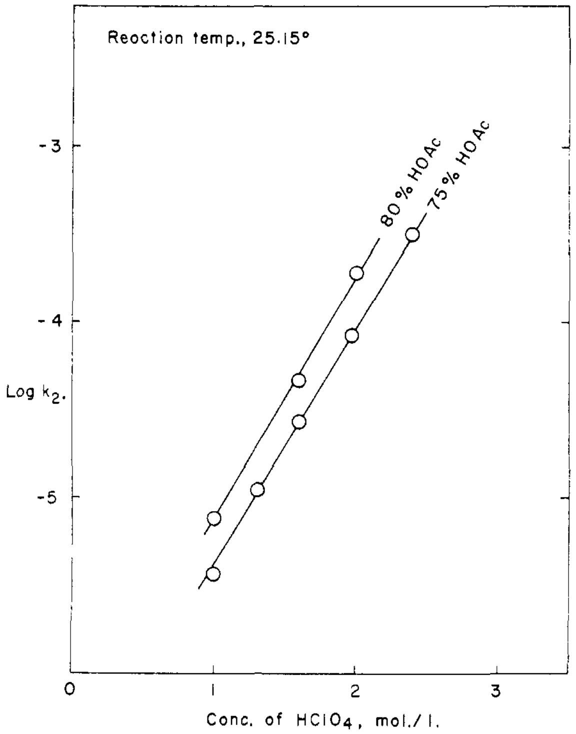

Fig. 4.—Effects of perchloric acid concentration on the rates.

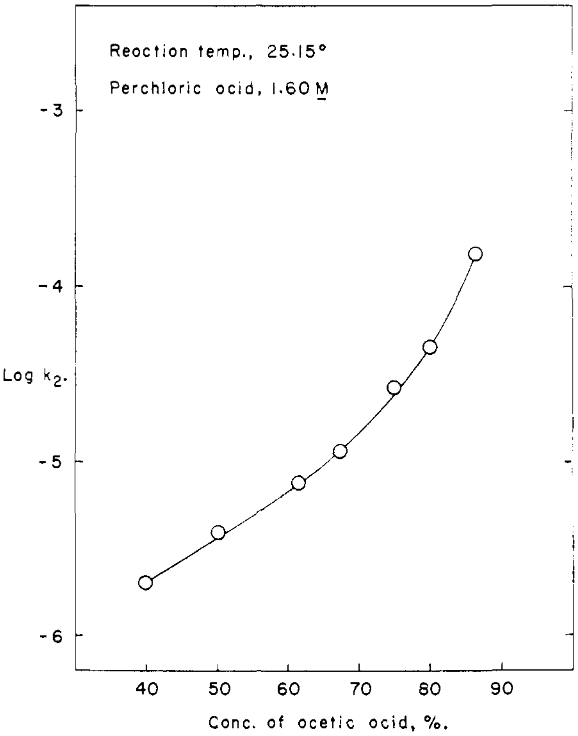

Fig. 5.—Effects of acetic acid concentration on the rates.

fortunately no H_0 data on acetic acid–water mixtures containing moderately concentrated perchloric acid are available, although data for the same system containing acid up to 0.3 mole/l. were reported by Wiberg and Evans[4] and aqueous solutions were studied by Hammett and his co-workers.[5] The necessary data, therefore, were determined by examining spectrophotometrically the ratio of conjugate acid to base using *o*-nitroaniline. The results are given in Table III.

TABLE II

TEMPERATURE DEPENDENCE OF THE SECOND-ORDER CONSTANT[a]

Temp., °C.	$k_2 \times 10^5$, l./mole sec.	
15.15	0.245	E = 23.3 kcal./mole
25.15	0.992	log PZ = 12.1
35.15	3.42	

[a] Solvent, 75% acetic acid, perchloric acid, 1.32 moles/l., initial concn. of anisole, 0.9978 mole/l., initial concn. of the addition compound, 0.2000 mole/l.

TABLE III

ACIDITY FUNCTION OF THE ACETIC ACID–WATER MIXTURES CONTAINING PERCHLORIC ACID AT ROOM TEMPERATURE

Acetic acid, wt. %	Perchloric acid, moles/l. 0.96	1.28	1.60	2.24	2.90	3.20
40	−0.32	−0.57	−0.80	−1.23	−1.70	−1.90
50	− .44	− .69	−0.95	−1.46	−2.00	
65	− .61	− .98	−1.28	−1.91	−2.51	
75	− .95	−1.33	−1.70	−2.36	−3.12	
80	−1.24	−1.58	−1.99	−2.79		

Figure 6 shows that a linear relationship exists between log k_2 and H_0 values in the whole range of both acid concentrations, the slope being 1.2.

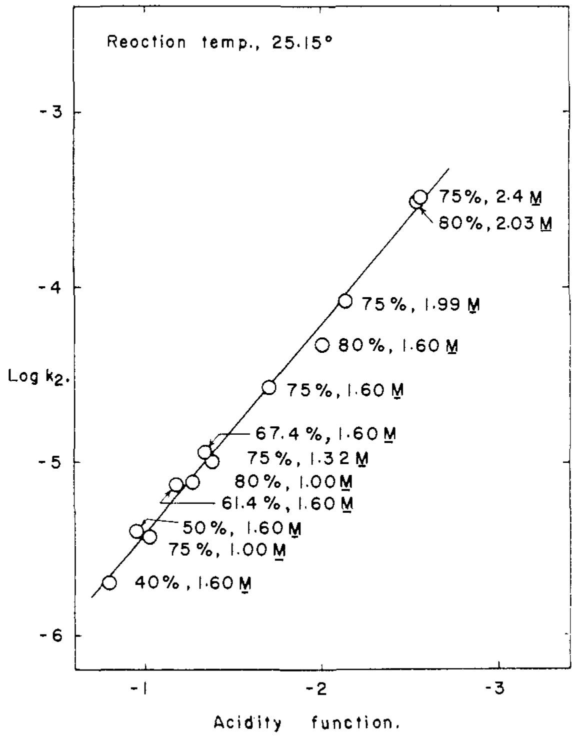

Fig. 6.—Relationship between log k_2 and acidity function H_0.

The structures of the olefin–mercuric acetate addition compounds have been discussed by many authors.[3] Recent studies by proton resonance

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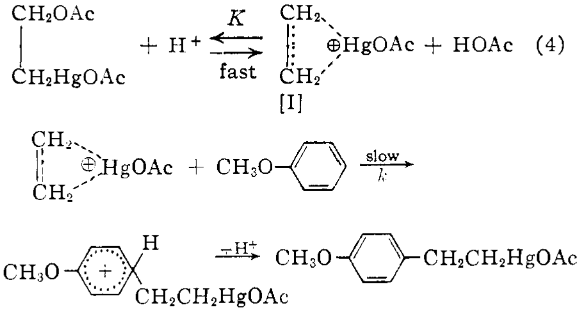
[4] K. B. Wiberg and R. J. Evans, THIS JOURNAL, **80**, 3019 (1958).

[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 269.

spectra, however, show that the addition compound of ethylene with mercuric acetate (prepared in methanol solution) has the σ-bonded structure, *i.e.*, $CH_3OCH_2CH_2HgOAc$ (in carbon tetrachloride)[6] and not the π-bonded complex form proposed by Lucas, Hepner and Winstein.[7] Although no results on the structure of the addition compound which is prepared in acetic acid and is thought to be β-acetoxyethyl mercuric acetate have been reported, the same conclusion as in the case above can be expected in alkaline or neutral medium. From these considerations and the present results, the qualitative mechanism which was proposed previously on the basis of synthetic results[1b] can be written in more quantitative form as



(4)

The essential role of the catalyst in this reaction is not specific attack on the addition compound but its acidity. For example, perchloric acid which is a weak catalyst in the Friedel–Crafts reaction is as effective as sulfuric acid or boron trifluoride in this reaction. Phosphoric acid which is used usually at about 100° or higher is effective also even at room temperature.[1] Any acids which will give the solvent enough acidity to produce the intermediate I without decomposing the addition compound to the original ethylene and mercuric salt are expected to be effective.

It is interesting that a linear relationship between log k_2 and H_0 is observed, since this reaction belongs to the A-2 type and therefore log k_2 should be proportional to log C_{H^+} rather than H_0 according to Long and Paul.[8] Recently, however, Taft, Deno and Skell showed that the rate constants of reactions of the A-2 type are not necessarily proportional to C_{H^+} but can be proportional to H_0 in some cases.[9] The results obtained here support their interpretation of the meaning of such relationships.

Experimental

Materials.—Acetic acid was purified by distillation with 1% potassium permanganate through a packed column, b.p. 117.5–118° at 760 mm. The acetic acid–water mixtures were made up by weight. Anisole was dried over sodium sulfate and distilled twice through a packed column, b.p. 154–155° at 760 mm., n^{20}_D 1.5180. Mercuric acetate and perchloric acid were C.P. grade and used without further purification.

Ethylene–Mercuric Acetate Addition Compound (β-Acetoxyethyl Mercuric Acetate).—At a rate of about 5 l./hr., ethylene was introduced into the mixture of 100 g. of mercuric acetate and 100 g. of glacial acetic acid with stirring at room temperature. After about 2 hr. when the crystals of mercuric acetate dissolved and the sodium hydroxide test for mercuric ion became negative, the reaction mixture was filtered to remove a small amount of insoluble material. From this filtrate, about 40 ml. of acetic acid was distilled off under vacuum to give 93 g. of raw crystals, m.p. 95–98°. Recrystallization from ligroin gave 89 g. of β-acetoxyethyl mercuric acetate, m.p. 96–98°. This material was decomposed with zinc and aqueous sodium hydroxide. The resultant mercury in the form of an amalgam was separated from the aqueous layer, dissolved in nitric acid and then analyzed.[10] Calcd. for $C_6H_{10}O_4Hg$: Hg, 57.86. Found: Hg, 57.71.

Titration of β-Acetoxyethyl Mercuric Acetate with Thiocyanate.—The following examples show the experimental procedure. (a) Into 50 ml. of water containing 2 ml. of 5 *N* nitric acid and 1 ml. of saturated solution of ferric alum, 5.00 ml. of 0.600 molar solution of the sample in glacial acetic acid was added and titrated with potassium thiocyanate solution (0.1 *N*, *f* 1.018) (Fig. 1).

(b) Into the mixture of 50 ml. of water, 1.5 ml. of 60% perchloric acid and 1 ml. of ferric alum solution, 5.00 ml. of the same sample as in (a) was added. To this solution, 61.93 ml. of 0.1 *N* potassium thiocyanate was added and allowed to stand at room temperature for 24 hr. Then 5.00 ml. of silver nitrate (0.1 *N*, *f* 1.058) was added and the excess silver ion was titrated with 0.1 *N* thiocyanate. Since 2.99 ml. of thiocyanate was required, the amount of thiocyanate reacted with the sample is 59.63 ml. (calcd. 60.00 ml.).

Stability Test of the Ethylene–Mercuric Acetate Addition Compound in the Presence of Perchloric Acid.—No ethylene evolution was observed when 10 ml. of 1 molar addition compound solution in 75% acetic acid was mixed with 10 ml. of 3 molar perchloric acid solution in 75% acetic acid at 25°. Aliquots (5 ml. each) were taken out of this mixture and decomposed with 30 ml. of 5 *N* hydrochloric acid. The volumes of ethylene evolved show that the addition compound is stable to perchloric acid at room temperature for at least 10 hr.

Reaction time, hr.	0	3	10	Blank (no perchloric acid)
Vol. of ethylene, ml.	52	51	52	51

Rate Measurement.—Standardized solutions of β-acetoxyethyl mercuric acetate and of perchloric acid in acetic acid were prepared. A known volume of the former was placed in a reaction flask immersed in the constant temperature bath. A known volume of the latter was added with vigorous stirring. At proper intervals, 5-ml. portions of the reaction mixture were withdrawn and added to 100 ml. of water. Known excess amounts (*ca.* 5 ml.) of 0.1 *N* thiocyanate were added therein and the mixtures were allowed to stand overnight at room temperature. After adding excess amounts of 0.1 *N* silver nitrate (*ca.* 5–10 ml.), the unreacted silver ion was titrated with thiocyanate.

H_0 Measurement.—The spectrophotometric measurements were carried out with a Beckman DU type spectrophotometer. The value of −0.57 was taken as the pK_a of *o*-nitroaniline.[4]

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YOSHIDA, KYOTO, JAPAN

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[6] F. A. Cotton and J. R. Leto, THIS JOURNAL, **80**, 4823 (1958).

[7] H. J. Lucas, F. R. Hepner and S. Winstein, *ibid.*, **61**, 3102 (1939).

[8] F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957).

[9] R. W. Taft, Jr., N. C. Deno and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 287 (1958).

[10] The American Pharmaceutical Association, "The National Formulary," 10th Ed., J. B. Lippincott Co., Philadelphia, Pa., 1955, p. 606.