22. *The Reaction of Mercuric and Mercurous Nitrates with Formic Acid.*

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The kinetics of the reduction of mercuric and mercurous nitrates by formic acid in aqueous solutions have been studied under a wide range of conditions. The effect on the rates of reaction of temperature, hydrogen-ion concentration, and formic acid concentration have been studied at a constant ionic strength. The results obtained indicate that both hydrolysed and unhydrolysed mercury ions take part in the reaction and that only the formate ion, and not undissociated formic acid, is capable of causing the reduction.

THE reaction of formic acid with the cobaltic ion has recently been studied by Bawn and White (*J.*, 1951, 339), who conclude that the most probable rate-determining steps are electron-transfer reactions between the cobaltic ion and formic acid or formate ion. It therefore seemed of interest to study analogous reactions of the formate ion in the hope of obtaining some information on the factors controlling such electron-transfer processes. The reactions of formic acid with mercury and silver salts seemed to be suitable, and the present paper presents a detailed examination of the kinetics of the reactions of mercuric and mercurous nitrates with formic acid in aqueous solution.

The reaction of formic acid with mercuric chloride has been investigated by Dhar (*J.*, 1917, **111**, 707), but his results are of little value for the present purposes. Control of experimental conditions was not sufficiently rigorous and the use of the largely covalent mercuric chloride introduced complications. Consequently, we have re-examined the reaction. In an attempt to ensure the presence of mercuric and mercurous ions, the nitrates were used in an aqueous medium of nitric acid–potassium nitrate at constant ionic strength. In the course of the work, it soon became clear that the mercurous ion formed by the reaction of mercuric ion was also reduced by formic acid as shown by the precipitation of metallic mercury in the final stages of the reaction; it was this which prompted the extension of the investigation to the mercurous salt. Fortunately, the reaction rates of the mercuric and the mercurous ion proved to differ sufficiently for the two reactions to be studied independently.

The data obtained for the two reactions are presented in the following section and then discussed jointly, as a similar interpretation is possible in both cases.

EXPERIMENTAL

Materials.—"AnalaR" Reagents were used throughout, and no further purification was attempted.

Analytical Method.—Determination of mercuric ion in aqueous nitric acid solution in the presence of mercurous ion was carried out by a method based on that described by Warshowsky and Elving (*Anal. Chem.*, 1947, **19**, 112), *i.e.*, oxidation of mercurous to mercuric ion by reaction with iodine and titration of excess of iodine with thiosulphate. The mercuric-ion concentration could be calculated from the known initial mercuric-ion concentration and the concentration of mercurous ion found by titration. For reactions of the mercurous ion the titration gave the concentration directly. Tests showed that nitric acid in the concentrations which would occur under our experimental conditions had no effect on the titrations provided that these were carried out within 10 min. of addition of the reagents. Formic acid was also without effect on the titration. Mercuric-ion concentrations in stock solutions were determined by titration with potassium thiocyanate.

Kinetic Measurements.—All experiments were carried out at a constant ionic strength of 1·0 and in a pH range of 0—1·7 (calculated from the nitric acid content of the solutions), these conditions being obtained by the use of nitric acid–potassium nitrate solutions. Approx. 0·1M-stock solutions of mercuric and mercurous nitrates in dilute nitric acid of known concentration were made, and the mercury salt content determined accurately by the methods described above. To prepare a reaction mixture the appropriate volume of stock mercury salt solution was diluted with water and nitric acid and potassium nitrate solutions, the mixture brought to the desired temperature in a bath thermostatically controlled to ±0·02°, and the requisite volume of standard formic acid solution (also previously brought to bath-temp.) added to start the reaction. Samples were removed at suitable time intervals, added to acidified potassium iodide and potassium iodate solution, and immediately titrated with standard thiosulphate. In those cases where the reaction was rapid (90% complete in less than 10 min.), samples taken with a fast delivery pipette were run into 2N-sulphuric acid immersed in a freezing mixture, to stop the reaction, and titrated as soon as possible thereafter.

In all experiments a large excess of formic acid was employed, enabling the concentration of this reactant to be regarded approximately as constant.

Results.—(1) *Reaction of mercuric nitrate with formic acid.* Under all the conditions studied the reaction was found to be of first order with respect to the mercuric-ion concentration. The following tables present values of the experimentally determined first-order constant $k_e \times 10^5$ (sec.$^{-1}$). The initial concentration of mercuric ion in all experiments was 0·0096 M. The ionic strength throughout was 1·0. The hydrogen-ion concentrations in all cases were calculated from the known amounts of nitric acid in the reaction mixtures. Data for a typical run are shown in Fig. 1.

(2) *Reaction of mercurous nitrate with formic acid.* As in the previous case, the reaction was of first order with respect to mercurous-ion concentration. The tables present the experimental first-order constant $k_e \times 10^5$ (sec.$^{-1}$): initial concentration of mercurous ion 0·0101M throughout, ionic strength 1·0, hydrogen-ion concentration calculated from the amount of nitric acid. Data for a typical run are shown in Fig. 1.

Reduction of mercuric nitrate.

Formic acid concentration = 0·198 g.-mol./l.

$1/[H^+]$, (g.-ion/l.)$^{-1}$	Temperature (K)			
	298·1°	308·2°	318·1°	328·1°
0·66	—	4·2	—	—
1·03	—	9·1	—	—
1·29	3·8	12·6	35·9	104
2·70	—	28·3	—	—
5·88	15·6	57·4	159	432

$1/[H^+]$ (g.-ion/l.)$^{-1}$	Temperature (K)			
	298·1°	308·2°	318·1°	328·1°
11·0	—	92·2	—	—
17·0	29·2	115	307	780
24·0	—	125	—	—
30·0	34·0	141	384	937

Temperature 328·1° (K)

$[H{\cdot}CO_2H]$, g.-mol./l.	$1/[H^+]$ (g.-ion/l.)$^{-1}$			
	1·00	1·30	1·60	2·70
0·108	—	56·8	70·1	119
0·119	49·9	—	—	—
0·199	—	123	143	215
0·319	128	—	—	—

$[H{\cdot}CO_2H]$, g.-mol./l.	$1/[H^+]$ (g.-ion/l.)$^{-1}$			
	1·00	1·30	1·60	2·70
0·401	—	213	260	408
0·602	228	289	358	543
1·002	319	—	—	—

$1/[H^+]$ = 2·7 (g.-ion/l.)$^{-1}$

$[H{\cdot}CO_2H]$, g.-mol./l.	Temperature (K)			
	298·1°	308·2°	318·1°	328·1°
0·048	—	6·5	—	—
0·099	—	13·4	—	—
0·108	—	—	—	119
0·119	4·7	15·8	50·2	—
0·199	—	28·3	—	215
0·319	11·3	39·1	120	—
0·401	—	—	—	408

$[H{\cdot}CO_2H]$, g.-mol./l.	Temperature (K)			
	298·1°	308·2°	318·1°	328·1°
0·492	—	57·0	—	—
0·595	—	—	198	—
0·602	19·3	—	—	543
0·695	—	71·5	—	—
0·982	—	89·9	—	—
0·991	—	—	262	—
1·000	25·9	—	—	—

Reduction of mercurous nitrate.

Formic acid concentration = 0·198 g.-mol./l.

$1/[H^+]$, (g.-ion/l.)$^{-1}$	Temperature (K)			
	308·2°	318·1°	328·1°	338·1°
0·64	0·13	—	—	—
2·81	0·25	—	—	—
6·35	0·60	2·31	8·17	26·9
12·0	1·15	—	—	—
20·0	—	7·16	21·1	61·6

$1/[H^+]$, (g.-ion/l.)$^{-1}$	Temperature (K)			
	308·2°	318·1°	328·1°	338·1°
22·9	2·45	—	—	—
32·1	2·98	10·2	30·0	82·2
42·1	3·76	—	—	—
51·3	4·25	12·5	39·3	105

$1/[H^+]$ = 42·1 (g.-ion./l.)$^{-1}$

$[H{\cdot}CO_2H]$, g.-mol./l.	Temperature (K)			
	308·2°	318·1°	328·1°	338·1°
0·048	1·25	4·14	11·5	30·8
0·103	2·24	—	—	—
0·159	3·28	10·9	32·3	86·4
0·199	3·76	—	—	—
0·300	—	16·2	50·7	137

$[H{\cdot}CO_2H]$, g.-mol./l.	Temperature (K)			
	308·2°	318·1°	328·1°	338·1°
0·337	5·37	—	—	—
0·496	6·71	—	—	—
0·501	—	20·5	67·5	178
0·695	7·86	—	—	—
0·991	8·91	—	—	—

DISCUSSION.

As the reactions of both mercuric and mercurous nitrate with formic acid are of first order with respect to the mercury salt it would seem reasonable to suggest that the rate-determining processes are

$$(1)\ Hg^{++} + H{\cdot}CO_2H \xrightarrow{k_1} Hg^{+} + H{\cdot}CO{\cdot}O + H^{+}$$

$$(2)\ Hg^{+} + H{\cdot}CO_2H \xrightarrow{k_2} Hg + H{\cdot}CO{\cdot}O + H^{+}$$

respectively. The well-known existence of the mercurous ion in the double form Hg_2^{++} would not alter the observed kinetics and would merely necessitate the writing of process (2) as

$$Hg_2^{++} + H{\cdot}CO_2H \longrightarrow Hg_2^{+} + H{\cdot}CO{\cdot}O + H^{+}$$

For convenience the mercurous ion will be written as Hg^+, but this must not be taken to indicate that the authors consider it to exist as such.

It was obviously necessary to determine whether only undissociated formic acid molecules could undergo reaction or whether the formate ion also took part (cf. the reaction with the cobaltic ion; Bawn and White, *loc. cit:*). If the latter were the case then the reactions

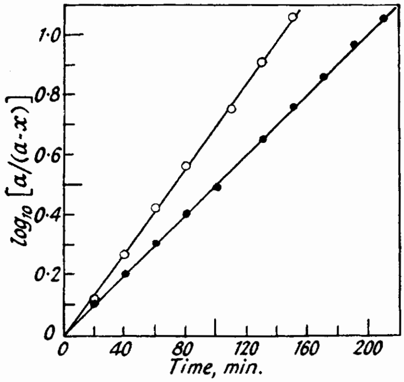
$$(3)\ Hg^{++} + H{\cdot}CO{\cdot}O^- \xrightarrow{k_3} Hg^+ + H{\cdot}CO{\cdot}O$$

$$(4)\ Hg^{+} + H{\cdot}CO{\cdot}O^- \xrightarrow{k_4} Hg + H{\cdot}CO{\cdot}O$$

would also need to be considered. The relative importance of the reactions (1) or (2) and (3) or (4) may readily be decided from the effect of hydrogen-ion concentration on the rate of reaction. The case of the mercuric ion, *i.e.*, reactions (1) and (3) being considered, the rate of reaction will be given by

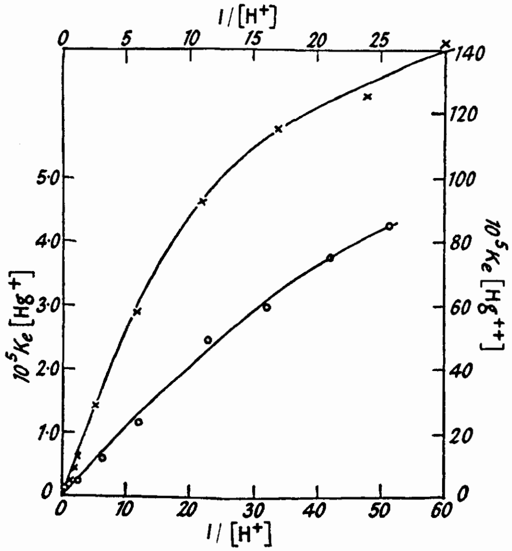
$$- d[Hg^{++}]/dt = k_1[Hg^{++}][H{\cdot}CO_2H] + [k_3[Hg^{++}][H{\cdot}CO{\cdot}O^-]$$

FIG. 1. *Typical first-order plots.*



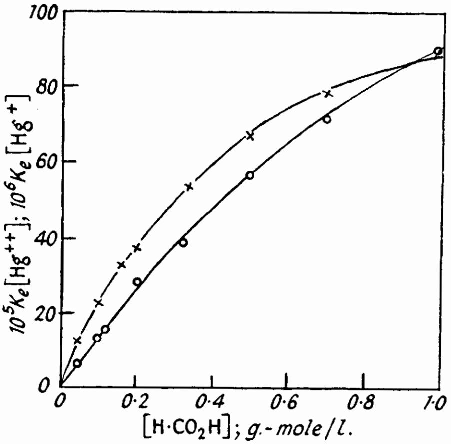
● Hg^{++}; $[H{\cdot}CO_2H] = 0{\cdot}602$ *g.-mol./l.*; $1/[H^+] = 2{\cdot}7$ *(g.-ion/l.)*$^{-1}$; $T = 25°$.
○ Hg^{+}; $[H{\cdot}CO_2H] = 0{\cdot}198$ *g.-mol./l.*; $1/[H^+] = 6{\cdot}5$ *(g.-ion/l.)*$^{-1}$; $T = 65°$.

FIG. 2.



○ Hg^+;
× Hg^{++}; $T = 308{\cdot}2°$ (K);
$[H{\cdot}CO_2H] = 0{\cdot}198$ *g.-mol./l.*

FIG. 3.



○ Hg^{++}; $T = 308{\cdot}2°$ (K); $1/[H^+] = 2{\cdot}7$ *(g.-ion/l.)*$^{-1}$.
× Hg^{+}; $T = 308{\cdot}2°$ (K); $1/H^+] = 42{\cdot}1$ *(g.-ion/l.)*$^{-1}$.

which, with the expression for the dissociation constant, K, of formic acid, becomes

$$-\,\mathrm{d}[\mathrm{Hg}^{++}]/\mathrm{d}t = \{k_1 + k_3K/[\mathrm{H}^+]\}[\mathrm{H{\cdot}CO_2H}][\mathrm{Hg}^{++}]$$

Hence, in the presence of a large excess of formic acid the experimentally determined first-order constant k_e is given by

$$k_e = \{k_1 + k_3K/[\mathrm{H}^+]\}[\mathrm{H{\cdot}CO_2H}]$$

and it should thus show a linear dependence on $1/[\mathrm{H}^+]$ with a non-zero intercept at $1/[\mathrm{H}^+]$ — 0. An identical equation is obtained for the mercurous ion. Typical plots of k_e against $1/[\mathrm{H}^+]$ are shown in Fig. 2 for both reactions. Two important facts are immediately apparent: (1) the plots are non-linear, and (2) the intercepts appear to be at the origin in both cases. The latter fact indicates at once that processes (1) and (2) can play no significant part in the reactions studied, and hence that only the formate ion is capable of reducing mercuric and mercurous ions under these conditions.

The non-linearity of the curves in Fig. 2 may be readily interpreted in terms of the hydrolysis of the mercuric and mercurous ions. It is to be expected that the two equilibria

$$\mathrm{Hg}^{++} + \mathrm{H_2O} \overset{K_1}{\rightleftharpoons} \mathrm{Hg{\cdot}OH}^+ + \mathrm{H}^+$$

$$\mathrm{Hg}^{+} + \mathrm{H_2O} \overset{K_2}{\rightleftharpoons} \mathrm{Hg{\cdot}OH} + \mathrm{H}^+$$

will be set up in the solutions. If it be conceded that the hydrolysed species are also able to react with the formate ion, then the processes

$$(5)\quad \mathrm{Hg{\cdot}OH}^+ + \mathrm{H{\cdot}CO{\cdot}O}^- \xrightarrow{k_5} \mathrm{Hg{\cdot}OH} + \mathrm{H{\cdot}CO{\cdot}O}$$

$$(6)\quad \mathrm{Hg{\cdot}OH} + \mathrm{H{\cdot}CO{\cdot}O}^- \xrightarrow{k_6} \mathrm{Hg{\cdot}OH'} + \mathrm{H{\cdot}CO{\cdot}O}$$

must also be considered. Again, for the mercuric ion, the rate equation becomes

$$-\,\mathrm{d}[\mathrm{Hg}^{++}]/\mathrm{d}t = \{k_3K/[\mathrm{H}^+] + k_5K_1K[\mathrm{H_2O}][\mathrm{H}^+]^2\}[\mathrm{H{\cdot}CO_2H}][\mathrm{Hg}^{++}]$$

Experimentally it is only possible to determine (by our method) the total mercuric mercury concentration $[\mathrm{Hg}^{++}]_{\mathrm{T}}$ and

$$[\mathrm{Hg}^{++}]_{\mathrm{T}} = [\mathrm{Hg}^{++}] + [\mathrm{Hg{\cdot}OH}^+]$$

giving for the experimentally measured rate

$$-\,\mathrm{d}[\mathrm{Hg}^{++}]/\mathrm{d}t = \left\{\frac{k_3K/[\mathrm{H}^+] + k_5K_1K[\mathrm{H_2O}]/[\mathrm{H}^+]^2}{(1 + K_1[\mathrm{H_2O}]/[\mathrm{H}^+])}\right\}[\mathrm{H{\cdot}CO_2H}][\mathrm{Hg}^{++}]_{\mathrm{T}}$$

Thus the measured velocity constant k_e would be expected, on this basis, to show a complex, non-linear dependence on $1/[\mathrm{H}^+]$ but to have the value zero when $1/[\mathrm{H}^+] = 0$. An identical expression can be derived for the mercurous case. Suitable data on the hydrolysis of mercuric and mercurous salts are not yet available and hence the validity of the expression just derived cannot be further tested.

An examination of the dependence of the rate on formic acid concentration is shown in Fig. 3, where values of k_e determined at a constant hydrogen-ion concentration are plotted against formic acid concentration. It will be seen that with both the mercuric and the mercurous ion reaction the dependence is non-linear, although in the case of the mercuric ion it is approximately so up to a value of *ca.* 0·2M. However, if k_e is plotted against the square-root of the formic acid concentration then a linear relationship is found at concentrations above 0·2M. This relationship is both surprising and interesting. Such behaviour could readily be accounted for if extensive dimerisation of the formic acid occurred in aqueous solution, but all available evidence militates against this view.

Although we are unable, at present, to give a complete interpretation of our results, it does at least appear that they are not inconsistent with the occurrence of the various rate-determining steps which we have postulated. It is hoped to give a more satisfactory interpretation when further data on the hydrolysis of the mercury salts and on the state of formic acid in aqueous electrolyte solutions have been obtained.

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