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Kinetics of the Disproportionation Reaction of Mercury(I) in Alkaline Solutions

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The kinetics of the disproportionation reaction of mercury(I) in alkaline solutions have been measured by the stopped-flow method. The rate law is given by $-d[Hg_2OH^+]/dt = k_1[Hg_2OH^+] + k_2[Hg_2OH^+][OH^-]$ in alkaline concentrations of 0.004 54–0.049 15 M. The values for k_1 and k_2 at 25 °C and $\mu = 0.1$ are estimated to be 9.0 ± 0.2 s^{-1} and $(2.8 \pm 0.1) \times 10^2$ M^{-1} s^{-1}, respectively. The activation parameters associated with k_1 and k_2 are $\Delta H_1^* = \Delta H_2^* = 12 \pm 1$ kcal mol^{-1}, $\Delta S_1^* = -14 \pm 4$ cal mol^{-1} deg^{-1}, and $\Delta S_2^* = -7.2 \pm 1.8$ cal mol^{-1} deg^{-1}. The proposed mechanism is as follows: $Hg_2^{2+} + OH^- \rightleftharpoons Hg_2OH^+$, rapid equilibrium; $Hg_2OH^+ \rightarrow Hg^0 + HgOH^+$, k_1; $Hg_2OH^+ + OH^- \rightarrow Hg^0 + Hg(OH)_2$, k_2. General discussions on the disproportionation mechanism of mercury(I) ions were made.

Introduction

In the presence of complexing ligands such as ammonia, cyanide ion, and hydroxide ion, disproportionation of mercury(I) ions occurs to give elemental mercury and the corresponding mercury(II) complexes, because of the relatively greater stability of the mercury(II) complexes.[1] One of the major problems in mercury(I) chemistry is the disproportionation of this ion which greatly depends on ligands attached to it.[2] However, there have been few data concerning the kinetics of the disproportionation reaction. The author has recently studied the kinetics with HCN and reported that $(Hg-Hg-CN)^+$ species, formed as an intermediate, weakens the Hg–Hg bond and leads to disproportionation.[3]

The compound claimed to be "mercurous oxide" by earlier investigators has been shown to be a mixture of metallic mercury and mercuric oxide.[4] It is worthwhile to study the kinetics in alkaline solutions. Moreover, it has been of interest to many investigators to determine the rate of disproportionation equilibrium of mercury(I), $Hg_2^{2+} \rightleftharpoons Hg^0 + Hg^{2+}$, which has been recognized to be rapidly established. For this purpose, the kinetic studies must be designed under simplified conditions, in which only OH^- ion is present and leads to disproportionation. The data obtained from this study will be available for consideration of the mechanism of mercury(I) disproportionation.

Experimental Section

Materials. Doubly distilled water free of carbon dioxide was used throughout this work. Mercurous perchlorate solutions in 0.05 M perchloric acid were prepared and the concentrations of Hg_2^{2+} and $HClO_4$ were standardized as described previously.[3] All kinetic data were obtained with $[Hg_2^{2+}]_0 = 2.5 \times 10^{-5}$ M. At higher or lower concentrations it proved to be difficult to follow absorbance changes, owing to occurrence of a grayish dark turbidity, probably mercuric oxide, or to lower absorbance change. Sodium hydroxide sample solutions, 0.06–0.15 M, were prepared by dilution with water from a NaOH stock solution (1 M), and their alkaline concentrations were determined titrimetrically with standard $HClO_4$ solution. Sodium perchlorate solutions (2 M) were added to maintain the ionic strength at $\mu = 0.1$.

Table I. Amount of Metallic Mercury Found with and without Reductant (25 °C, $\mu = 0.1$)

[NaOH], M	Amt of Hg_2^{2+} taken, 10^{-8} mol	Amt found, 10^{-8} mol	
		Hg^0	Hg^0_{Red}
0.03	0.50		0.85
0.03	1.0		2.0
0.03	1.5		2.6
0.03	2.0		4.2
0.005	2.0	1.8	
0.01	2.0	1.7	
0.03	2.0	2.2	
0.05	2.0	2.1	

Stoichiometric Measurements. Stoichiometry with regard to elemental mercury was measured by the cold-vapor atomic absorption method. The method was essentially similar to that of the previous paper.[3] Aliquots, 0.5–2 mL, of the mercurous solution (10^{-5} M) were added to reaction vessels containing 200 mL of various NaOH concentrations (0.005–0.05 M), and then the mixed solutions were aerated with and without reductant for 30 min into the permanganate–sulfuric acid absorbing solutions.

Kinetics. Rates of reaction were followed spectrophotometrically using an Aminco-Morrow stopped-flow apparatus attached to an Aminco DW-2 UV–visible spectrophotometer. The change in the transmittance was monitored at 235 nm (Figure 1, top). Triplicated experiments were conducted using freshly prepared Hg_2^{2+} and NaOH solutions. The rapid-scanning spectrum[5] for the reaction of Hg_2^{2+} with excess NaOH reveals that a new band appears at the lower wavelength region immediately after mixing (Figure 2). Then, the stopped-flow measurements were also made at 228 nm. The results obtained at this wavelength were, however, less reliable than those at 235 nm because of the higher noises of our instrument in the lower wavelength region. All other kinetic measurements were made in the same manner as described previously.[3]

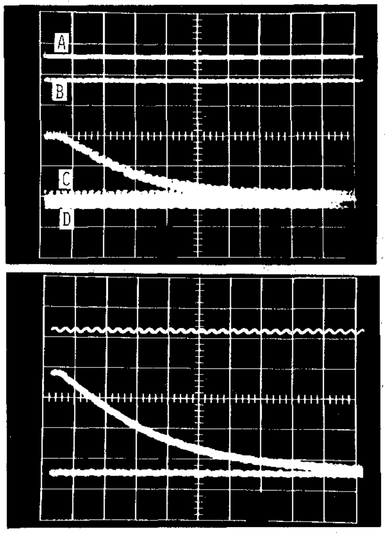


Figure 1. Stopped-flow oscilloscope tracings. Top photo: reaction conditions are 25 °C, $[Hg_2^{2+}]_0 = 2.5 \times 10^{-5}$ M, $[NaOH]_0 = 0.049\,15$ M, 20 ms/dev, and λ 235 nm; A and D indicate 0–100% T (4.8 dev), B represents transmittance of Hg_2^{2+} before mixing, i.e., $[Hg_2^{2+}] = 5.0 \times 10^{-5}$ M, and C represents transmittance at t_∞ of the decay curve (C and D are partly superposed upon each other). Bottom photo: reaction conditions are 20 °C, $[Hg_2^{2+}]_0 = 2.54 \times 10^{-5}$ M, $[HCN]_0 = 0.995 \times 10^{-3}$ M, $[H^+]_0 = 0.204$ M, 50 ms/dev, and λ 236.5 nm; top and bottom lines in this photo indicate 0–100% T (4.8 dev); this photo was used in ref 3 to determine the rate constant, $k_{obsd} = 8.7 \times 10^3$ M^{-1} s^{-1}.

Results

Stoichiometry. The results of the stoichiometric study with respect to elemental mercury are given in Table I. In the presence of the reductant, the total amount of mercury species were obtained, whereas only elemental mercury formed by the disproportionation of Hg_2^{2+} in alkaline solutions was determined in the absence of the reductant. That is, equimolecular quantities of elemental mercury atoms and mercuric ions were formed from the mercurous dimeric ions in NaOH concentration range employed for the kinetic measurements.

Rapid-Scan Measurements. A typical stopped-flow tracing for Hg_2^{2+}–NaOH is illustrated in Figure 1 (top), together with that for Hg_2^{2+}–HCN (bottom) as a reference; in both cases $[Hg_2^{2+}]_0 = 2.5 \times 10^{-5}$ M. A marked difference between two photos is noticeable; that is, Hg_2^{2+}–NaOH exhibits small transmittance change during the course of the reaction. This may be ascribed to the occurrence of unmeasurably rapid decrease in initial transmittance at mixing, which is caused by hydrolytic equilibrium of Hg_2^{2+}. Then, rapid-scan measurements were made. The spectra for the reaction of Hg_2^{2+} (2.5×10^{-5} M) with NaOH (0.029 M) at room temperature are illustrated in Figure 2, which reveals that a new band appears at the lower wavelength region immediately after mixing and disappears with time. This absorbance band, which has not been reported in the literature to date, can be attributed to Hg_2OH^+ species if the assumption is made that the hydrolytic step of Hg_2^{2+} is a rapid equilibrium. The absorbance at t_∞ in the lower wavelength region is due to that for Hg^{2+}[1,6] and probably due to NaOH. Judged from Figures 1 and 2, it is concluded that the traced species is Hg_2^{2+} for Hg_2^{2+}–HCN while it is Hg_2OH^+ for Hg_2^{2+}–NaOH.

Kinetics. All the kinetic runs were carried out in the presence of excess NaOH. Plots of ln $(A_t - A_\infty)$, where A_t and A_∞ represent the absorbance at time t and infinity time, respectively, were linear for over 3 half-lives. This linearity was taken as evidence that the reaction is first order with respect to Hg_2OH^+:

$$-d[Hg_2OH^+]/dt = k_{obsd}[Hg_2OH^+]$$

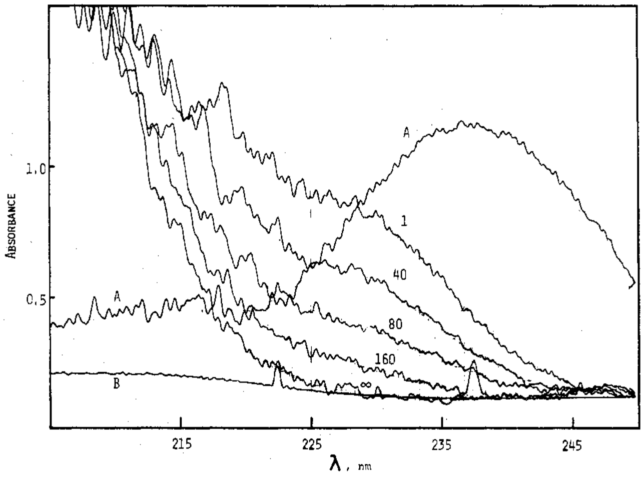


Figure 2. Change of absorption spectra observed by a rapid-scan spectrophotometer after mixing Hg_2^{2+} (2.5×10^{-5} M) with NaOH (0.029 M) at room temperature and $\mu = 0.1$; the numbers beside the curves refer to time delay after mixing, in ms; the lowest curve is essentially an infinity-time spectrum. B indicates baseline for these decay curves. Curve A is the absorption spectrum of Hg_2^{2+} (2.5×10^{-5} M) and is recorded on a single chart together with decay curves (unfortunately, the baseline for curve A is not adjusted to B).

Table II. Dependence of the Observed Rate Constant on NaOH Concentration and Temperature ($\mu = 0.1$)

	k_{obsd}, s^{-1}				
$[NaOH]_0$, M	10 °C	15 °C	20 °C	25 °C	30 °C
0.004 54	4.0	5.8	7.8	11	17
0.006 90	3.7	5.9	8.3	11	16
0.009 51	3.9	5.9	8.0	11	17
0.011 97	4.0	6.0	8.8	12	18
0.014 48	4.3	6.6	9.0	13	19
0.019 43	4.7	7.0	10	15	20
0.024 33	5.5	7.8	11	16	21
0.029 23	6.0	8.5	12	17	23
0.034 53	6.2	9.0	13	18	27
0.038 00	6.3	9.5	14	20	28
0.044 30	7.1	10	15	22	29
0.049 15	8.0	11	16	23	32

Table III. Values of Rate Constants k_1 and k_2 ($\mu = 0.1$)

	10 °C	15 °C	20 °C	25 °C	30 °C
k_1, s^{-1}	3.1 ± 0.1	4.9 ± 0.1	6.6 ± 0.2	9.0 ± 0.2	13.8 ± 0.5
$10^{-2}k_2$, M^{-1} s^{-1}	0.92 ± 0.04	1.2 ± 0.1	1.9 ± 0.1	2.8 ± 0.1	3.6 ± 0.2

where k_{obsd} is the observed first-order rate constant. The dependence of k_{obsd} on [NaOH] and temperature was measured. The results are listed in Table II. The plots of k_{obsd} vs. [NaOH] at each temperature fall on a straight line. The observed rate constant can be expressed as

$$k_{obsd} = k_1 + k_2[OH^-]$$

The estimated values of k_1 and k_2 at each temperature are shown in Table III. Activation parameters associated with k_1 and k_2 are calculated by the least-squares method: $\Delta H_1^* = \Delta H_2^* = 12 \pm 1$ kcal mol^{-1}, $\Delta S_1^* = -14 \pm 4$ cal mol^{-1} deg^{-1}, and $\Delta S_2^* = -7.2 \pm 1.8$ cal mol^{-1} deg^{-1}. The observed rate constants exhibit negligible effect over the ionic strength range $\mu = 0.045$–0.8 ($NaClO_4$) at 25 °C and [NaOH] = 0.02 M (the data are not cited).

Discussion

Assuming that hydrolytic equilibrium with respect to Hg_2^{2+} is rapidly established, the disproportionation reaction with NaOH will proceed via Hg_2OH^+. This seems quite reasonable judged from the rapid-scanning spectra. The mechanism of the reaction is suggested from the form of the observed rate law to be as follows

$$Hg_2{}^{2+} + OH^- \rightleftharpoons Hg_2OH^+, \quad \text{rapid equilibrium}$$

$$Hg_2OH^+ \xrightarrow{k_1} Hg^0 + HgOH^+ \tag{1}$$

$$Hg_2OH^+ + OH^- \xrightarrow{k_2} Hg^0 + Hg(OH)_2 \tag{2}$$

The k_1 value thus obtained can be used to estimate the reverse rate constant, k_{-1}, for the reaction

$$Hg_2OH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Hg^0 + HgOH^+ \tag{3}$$

The equilibrium constant for reaction 3, $K_{d'}$, can be calculated from the equilibria

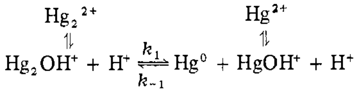
$$Hg_2{}^{2+} \rightleftharpoons Hg^0 + Hg^{2+} \quad K_d \tag{4}$$

$$Hg_2{}^{2+} \rightleftharpoons Hg_2OH^+ + H^+ \quad K_h \tag{5}$$

$$Hg^{2+} \rightleftharpoons HgOH^+ + H^+ \quad K_h{}' \tag{6}$$

where $K_d = 5.5 \times 10^{-9}$ M,[7] $K_h = 10^{-5}$ M,[8] and $K_{h'} = 2 \times 10^{-4}$ M,[9] at 25 °C; hence $K_{d'} = 10^{-7}$ M. Since $k_1/k_{-1} = K_{d'}$, we find $k_{-1} = 9.0 \times 10^7$ M^{-1} s^{-1} at 25 °C for the reproportionation reaction between Hg^0 and $HgOH^+$.

It is worthwhile to discuss the main process of the disproportionation of mercury(I) ions in aqueous solutions. In the absence of any ligands besides OH^- which derived from the dissociation of water, all the species exist according to eq 4–6. If the mercurous disproportionation process occurs via reaction 4, that is, $k_d > k_1$, then $k_{-d} > k_1/K_d = 2 \times 10^9$ M^{-1} s^{-1} at 25 °C, where k_d and k_{-d} represent forward and reverse rate constants for reaction 4, respectively. This value is large enough to be comparable to the upper limit of the second-order rate constant for an elementary reaction involving neutral species in aqueous solution. On the other hand, although there is no kinetic evidence on the redox reaction of the Hg^0–Hg^{2+} system, $HgOH^+$ will be more favorable than Hg^{2+} for oxidizing Hg^0 as judged from the redox reaction[10] with Tl(III). The disproportionation of mercury(I) ions necessarily involves breaking of the Hg–Hg bond. From this standpoint, Hg_2OH^+ will be also more advantageous than $Hg_2{}^{2+}$. Consequently, it seems more reasonable to consider that the disproportionation of mercury(I) ions in aqueous solutions proceeds via its hydroxide as seen in the scheme



$$\begin{array}{ccc} Hg_2{}^{2+} & & Hg^{2+} \\ \updownarrow & & \updownarrow \\ Hg_2OH^+ + H^+ & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & Hg^0 + HgOH^+ + H^+ \end{array}$$

Isotopic exchange studies between mercury(I) and mercury(II) ions have failed in measuring the rate in the past in spite of their efforts.[11-13] Wolfgang and Dodson[13] have suggested this rapid isotopic exchange, $Hg_2{}^{2+} + (Hg^*)^{2+} \rightarrow Hg^*{}_2{}^{2+} + Hg^{2+}$, proceeds through two simultaneous processes: $Hg_2{}^{2+} \rightarrow Hg^0 + Hg^{2+}$ and $Hg^0 + (Hg^*)^{2+} \rightarrow Hg^*{}_2{}^{2+}$. The present kinetic results seem to support the proposed isotopic exchange mechanism, k_1 and k_{-1} being sufficiently large to completion within the time of isotopic separation handling.

Synthetic investigations of stable mercurous compounds have given many instructive suggestions. Potts and Allred have pointed out that no compounds of mercury(I) are known with ligands above water in the spectrochemical series.[2] Yamane and Davidson have suggested that the formation of a covalent bond diminishes the amount of s charactor in the Hg–Hg bond and thus weakens it and that mercury(I) is stable only with strong "ionic" ligands.[1,14] These suggestions are quite possible. Some hypothetical opinions regarding mercury(I) in alkaline solutions will be hereinafter discussed.

At the beginning of this study, the author expected that the rate of disproportionation would be independent on alkaline concentration if the species traced by stopped-flow technique was considered to be Hg_2OH^+ on mixing $Hg_2{}^{2+}$ with OH^- of enough concentration to form the hydrolyzed form and if it was not necessary to take into account the second hydrolysis equilibrium of $Hg_2{}^{2+}$ as there have been no data reported in the literature. Since the rate of reaction linearly depends on $[OH^-]$, the activated complex for reaction 2 involves one Hg_2OH^+ and one OH^-. Possible structures for the activated complex are [HO–Hg–Hg–OH] and [Hg–Hg–$(OH)_2$]. Since Hg_2OH^+ leads to disproportionation, the OH ligand indeed influences the stability of the Hg–Hg bond. That is, the OH ligand, when attached to $Hg_2{}^{2+}$, will tend to cause one of the two mercury atoms to be more "metallic" in charactor and the other to be more "mercuric", while the bond is not broken. The greater desolvation possible with "metallic" mercury allows the second hydroxide ion to attach to the "mercuric" atom. If this argument is correct [Hg–Hg–$(OH)_2$] is a more reasonable model for the activated complex.[15] The equilibrium constant for reaction 7, K^*, can be estimated on the additional

$$Hg_2OH^+ + OH^- \rightleftharpoons Hg_2(OH)_2 \quad K^* \tag{7}$$

assumption that the first-order rate constant for disproportionation of $Hg_2(OH)_2$, k_3, is taken as twice k_1 as a rough approximation. It follows that $k_2 = k_3K^* = 2k_1K^*$; then $K^* = 16$ M^{-1} at 25 °C. The K^* value thus estimated on the assumption appears extremely small compared with the hydrolysis constant for $Hg_2{}^{2+}$, 10^9 M^{-1}. However, this is not surprising because the K^* does not mean the second hydrolysis constant for mercury(I) but means the equilibrium constant for the additional OH ligand bonded to "mercuric" ion which is already bonded by both "metallic" mercury and OH ligand (6sσ bond in Hg–Hg is weakened by one OH ligand but is not yet broken). Mercury(II), as generally accepted, tends to bind two monodentate ligands strongly in a linear configuration and additional ligands are bound with much weaker affinity.

The rate constant for the reaction reported in the previous paper,[3] $Hg_2OH^+ + HCN \rightarrow Hg^0 + HgCN^+ + H_2O$, 2.2×10^8 M^{-1} s^{-1} at 25 °C, is very much larger than the k_2 obtained in this study. This is probably due to more a strongly covalent bond with the CN ligand than the OH ligand. Yamane and Davidson have suggested a hypothesis that a strongly covalent Hg–X complex weakens the Hg–Hg bond.[1]

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Registry No. $Hg_2{}^{2+}$, 34767-64-1; OH^-, 3352-57-6.

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