of acidity.[10] It is reasonable to expect that the true H_0 values lie somewhere in between these limits, which would bring the experimental points into fair agreement with curve A. It would appear, then, that in the presence of a constant excess of H_2O_2 and H_2SO_4, the position of equilibrium is governed solely by acidity.

The behavior of the peroxy–niobium system is best exemplified by comparison to the chromate–dichromate system. The similarity of (9) to (1) is readily apparent. An additional point of interest may be noted in that a bathochromic shift

$$Cr_2O_7^{-} + H_2O \rightleftarrows 2HCrO_4^{-} \qquad (9)$$

of the spectra occurs for both systems on condensation.

Acknowledgment.—The authors wish to thank Professor J. Steigman for many fruitful discussions and for his encouragement during the course of this work and Dean R. E. Kirk for his support in the final stages of manuscript preparation.

BROOKLYN, N. Y.

[10] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[CONTRIBUTION NO. 497 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

Dismutation of the Mercurous Dimer in Dilute Solutions

BY HERBERT C. MOSER AND ADOLF F. VOIGT

RECEIVED DECEMBER 10, 1956

The dismutation of the mercurous dimer into mercuric ions and dissolved free mercury has been studied in highly dilute mercurous nitrate solutions. Radioactive tracer techniques have been used to permit measurements in the 10^{-7} *M* range. Use is made of the extraction of free mercury into non-polar organic solvents to measure the extent of dismutation. The equilibrium constant for the dismutation reaction was found to be 5.5×10^{-9}. The solubility of mercury metal in aqueous solutions was found to be $(3.0 \pm 0.1) \times 10^{-7}$ *M* at 25°.

Introduction

It has been shown in a number of ways that mercurous ions exist in solution in the form of dimers.[1-3] The instability of these dimeric ions with respect to the formation of liquid mercury and mercuric ions is also well established. Values of 0.0060 to 0.0120 have been reported for the equilibrium constant at 25° of the reaction[2,4-7]

$$Hg_2^{++} = Hg(l) + Hg^{++}$$

Higginson[8] added a new consideration about the instability of the mercurous ion by suggesting that, at concentrations below 10^{-6} *M* in mercurous perchlorate, there is a significant degree of dissociation of the dimer into individual mercurous ions. He estimated a dissociation constant within the limits 10^{-8} to 10^{-6}. No other experimental value appears to have been reported although values of 10^{-30} and 10^{-18} have been inferred from other observations and calculations.[8-10]

This paper presents results of a study of the dismutation reaction

$$Hg_2^{++} = Hg^{++} + Hg(aq)$$

using radioactive tracer techniques to permit the measurement of concentrations in the 10^{-7} *M* range. Use is made of the fact that while metallic mercury is soluble to a very limited extent in water, it is considerably more soluble in non-polar organic solvents.[11-13] Thus free mercury can be extracted into solvents such as *n*-hexane and cyclohexane from highly dilute solutions of mercurous nitrate in dilute nitric acid. This extraction is related to the dismutation equation in such a way that the equilibrium constant for this reaction can be calculated.

The Distribution Ratio.—Providing that the oxidized forms of mercury do not extract into the organic phase, a distribution ratio, *E*, and a distribution constant, E^0, can be defined as

$$E = [Hg]_{tot,aq}/[Hg]_o$$

and

$$E^0 = [Hg]_{aq}/[Hg]_o$$

In these expressions $[Hg]_{tot,aq}$ is the total molar concentration of mercury in the aqueous phase, and $[Hg]_{aq}$ and $[Hg]_o$ are the concentrations of dissolved free mercury in the aqueous and organic phases. In the condition of both dismutation and dissociation occurring in a dilute solution of mercurous ions

$$[Hg]_{tot,aq} = [Hg]_{aq} + [Hg^{++}] + [Hg^{+}] + 2[Hg_2^{++}]$$

If a sample of pure mercurous nitrate in the absence of any mercuric nitrate or free mercury were diluted to a certain volume and extracted with an equal volume of an organic solvent, then

$$[Hg^{++}] = [Hg]_{aq} + [Hg]_o$$
$$= (1 + E^o)[Hg]_o$$

The distribution ratio, *E*, can now be expressed in

---

[1] A. Ogg, *Z. physik. Chem.*, **27**, 285 (1898).

[2] E. Abel, *Z. anorg. Chem.*, **26**, 373 (1901).

[3] L. A. Woodward, *Phil. Mag.*, [7] **18**, 823 (1934).

[4] W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall Inc., New York, N. Y., 1952, p. 179.

[5] W. Forsling, S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **6**, 901 (1952).

[6] S. Hietanen and L. G. Sillén, *Suomen Kemistilehti*, **29B**, No. 2 31 (1956).

[7] G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta*, **37**, 1289 (1954).

[8] W. C. E. Higginson, *J. Chem. Soc.*, 1438 (1951).

[9] I. M. Kolthoff and C. Barnum, THIS JOURNAL, **62**, 3061 (1940).

[10] G. H. Cartledge, *ibid.*, **63**, 906 (1941).

[11] H. Reichardt and K. F. Bonhoeffer, *Z. Physik.*, **67**, 780 (1931).

[12] A. Stock, F. Cucuel, F. Gerstner, H. Köhle and H. Lux, *Z. anorg. allgem. Chem.*, **217**, 241 (1934).

[13] J. C. Pariaud and P. Archinard, *Bull. soc. chim., France*, 454 (1952).

terms of a dismutation constant K, a dissociation constant k, E^0 and $[\mathrm{Hg}]_o$ by the relation

$$E = 1 + 2E^0 + [kE^0(1 + E^0)/K]^{1/2} + 2E^0(1 + E^0)[\mathrm{Hg}]_o/K$$

in which

$$K = [\mathrm{Hg}^{++}][\mathrm{Hg}]_{\mathrm{aq}}/[\mathrm{Hg_2}^{++}]$$

and

$$k = [\mathrm{Hg}^{+}]^2/[\mathrm{Hg_2}^{++}]$$

The expression is more properly written using the individual activity coefficients of the ions

$$E = 1 + 2E^0 + \gamma_{\mathrm{Hg}^{++}}{}^{1/2}\,[kE^0(1 + E^0)/K]^{1/2}/\gamma_{\mathrm{Hg}^+} + \gamma_{\mathrm{Hg}^{++}}\,2E^0(1 + E^0)[\mathrm{Hg}]_o/\gamma_{\mathrm{Hg_2}^{++}}\,K$$

with the activity coefficient of dissolved free mercury taken as unity.

From either form of the equation it can be seen that an independent determination of E^0 and a linear plot of E as a function of $[\mathrm{Hg}]_o$ will permit the determination of K from the slope and the estimation of k from the intercept at zero mercury concentration.

Experimental

Aqueous Solutions.—A solution of high specific activity mercuric nitrate containing radioactive mercury 203 was obtained from the Oak Ridge National Laboratory. A stock solution of mercurous nitrate was prepared from this by dilution with 0.01 M nitric acid and shaking with a drop of metallic mercury. The latter was prepared by reducing some of the radioactive mercuric nitrate with hypophosphorous acid. The final mercurous ion concentration in the stock solution was approx. 1.8×10^{-3} M.

Aliquots of this solution were diluted with 0.01 M nitric acid to final concentrations in the range of 10^{-8} to 10^{-5} M, and the diluted solutions were used in the distribution experiments.

The nitric acid solutions were prepared from Baker and Adamson C.P. nitric acid and doubly distilled water.

Distribution and Analysis.—It was considered best to run the experiments in 0.01 M nitric acid since at lower acid concentrations, mercury ions hydrolyze to an appreciable extent and at a higher nitrate concentration nitrato complexes would be formed. In 0.01 M nitric acid 96% of the mercuric mercury should be in the form of mercuric ions and 99% of the mercurous in simple ionic form according to calculations using reported values[5,14,15] of the hydrolysis and complexing constants.

The dilute solutions of mercurous nitrate were shaken with an equal volume of an organic solvent for a period of about 12 hours at 25.0°. The mercury concentrations in both phases were determined radiochemically after a measurement of the specific activity of the mercury was made. Aliquots for analysis were added to aqueous mercuric nitrate carrier; the sulfide was precipitated and mounted on stainless steel planchets for counting with a thin window Geiger counter. In analyzing the organic phase, enough acetone was added to the mixture of solvent and the aqueous mercuric nitrate carrier to make it one phase. This was done to ensure exchange between the two forms of mercury. After evaporation of the acetone and solvent, the sulfide was precipitated and mounted for counting as mentioned above.

Measurements of the distribution constant, E^0, were made by dissolving radioactive mercury metal in the organic solvents, shaking these solutions with 0.01 M nitric acid, and analyzing both phases for mercury concentration.

The solubility of mercury metal in aqueous dilute acid solutions was determined at 25.0° by shaking them with a drop of mercury of known specific activity. It was found necessary to add a small amount of hypophosphorous acid to the solutions to eliminate oxidation of the mercury metal by radiolysis.

Organic Solvents.—Phillips Pure Grade *n*-hexane and Eastman Spectro Grade cyclohexane were used in the experiments.

When the solvents were used without any purification the oxidized forms of mercury were found to extract into them. The following treatment appeared adequate to remove the interfering impurities. The solvents were shaken with concentrated sulfuric acid and with alkaline potassium permanganate were passed through a column packed with dry activated alumina, and were redistilled. In purifying the cyclohexane, a silica gel column also was used. When samples of the purified solvents were shaken with a 3.4×10^{-4} M aqueous solution of mercuric nitrate, the concentration of mercury in the organic phase was below the limit of detection of about 2×10^{-9} M.

Results and Discussion

Figures 1 and 2 demonstrate the linear dependence of the distribution ratio on the concentration of mercury in the organic phase, Fig. 1 being for *n*-hexane and Fig. 2 for cyclohexane. The increasing slope of the curves at higher value of $[\mathrm{Hg}]_o$ can be explained by realizing that the stock solution of mercurous nitrate contained a small amount of mercuric nitrate and a trace of free mercury. As long as the amount of mercuric mercury produced in the dismutation is large compared to the amount already present, the linear dependence is held. When this is not the case, an increasing slope is expected.

Measurements of the distribution constant, E^0, and calculated values of the dismutation constant, K, taking the activity coefficient ratio $\gamma_{\mathrm{Hg}^{++}}/\gamma_{\mathrm{Hg_2}^{++}}$ as unity, are given in Table I.

TABLE I

Solvent	E^0	K
n-Hexane	0.048	5.6×10^{-9}
Cyclohexane	.031	5.3×10^{-9}

The *n*-hexane distribution experiments were performed first while the mercury had a higher specific activity than in the later studies. Hence lower concentrations could be measured in the *n*-hexane experiments, and it was possible to obtain experimental values very close to the ordinate axis. The intercept was found to be approximately 0.8.

If a measurable dissociation of the dimer is taking place in the diluted solutions, the effect would be to increase the ordinate intercept by an amount

$$\gamma_{\mathrm{Hg}^{++}}{}^{1/2}\,[kE^0(1 + E^0)/K]^{1/2}/\gamma_{\mathrm{Hg}^+}$$

Approximating a value of 0.9 for $\gamma_{\mathrm{Hg}^{++}}{}^{1/2}/\gamma_{\mathrm{Hg}^+}$[16] this expression has values, from the hexane study, of 2.7 for $k = 10^{-6}$, 0.85 for $k = 10^{-7}$, and 0.27 for $k = 10^{-8}$.

If no dissociation is taking place, an ordinate intercept of approximately 1.1 should be found, and if dissociation is occurring with $k = 10^{-7}$ the intercept should be about 2. The results of this study indicate that a value of k as large as 10^{-7} is highly unlikely.

Higginson[8] interpreted his results on the absorption spectra of very dilute solutions of mercurous perchlorate as indicating the dissociation of the dimer rather than its dismutation. Since his article appeared the absorption spectrum of mercuric per-

---

(14) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **6**, 747 (1952).

(15) G. Infeldt and L. G. Sillén, *Svensk. Kem. Tid.*, **58**, 104 (1946).

(16) The value of γ_{Hg^+} is assumed nearly equal to γ_{Ag^+} or γ_{Tl^+}. Values of $\gamma_{\mathrm{Hg}^{++}}$ and γ_{Ag^+} have been calculated at various ionic strengths by J. Kielland, THIS JOURNAL, **59**, 1675 (1937).

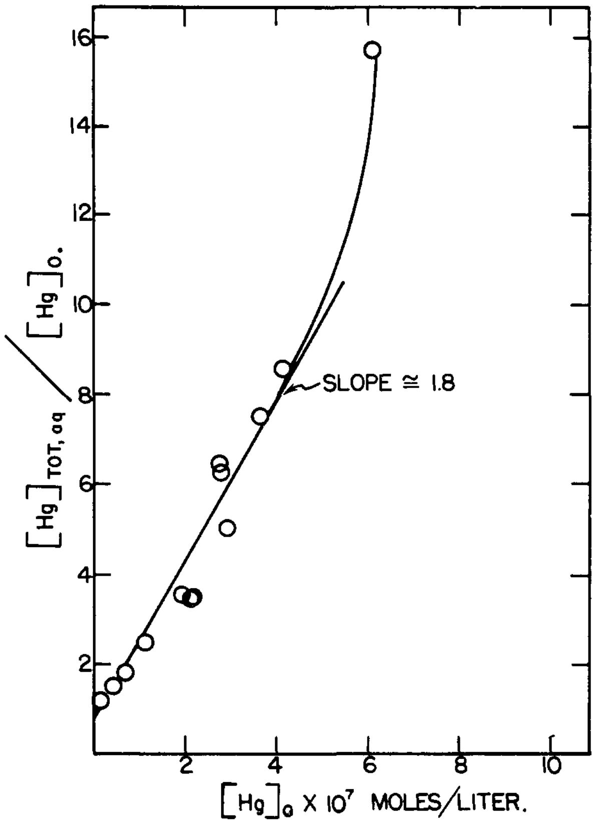

Fig. 1.—Distribution of mercury between *n*-hexane and dilute nitric acid.

chlorate has been published.[17] Maxima are shown at almost exactly the same wave lengths as those given by Higginson for mercurous perchlorate, and the molar extinction coefficient at the wave length of maximum absorption is one-half the value for mercurous perchlorate. Under these circumstances it would be extremely difficult to use absorption spectra to distinguish between the two processes of dissociation and dismutation.[18]

An alternate calculation of the dismutation constant, K, has been made, using the equilibrium constant of the reaction

$$Hg_2^{++} = Hg(l) + Hg^{++}$$

and the solubility of mercury metal in water.[19] The solubility of mercury in aqueous solutions was determined in this study, and the results along with those reported in the literature are given in Table II.

It is felt that measurements found in this study are more accurate because of the superior sensitivity of the radiochemical method. Using the reported values of 0.0060 and 0.0120 for the concentration ratio $[Hg^{++}]/[Hg_2^{++}]$ and 3.0×10^{-7} M for the concentration of free mercury, values of 1.8×10^{-9} to 3.6×10^{-9} are calculated for the dismutation constant K.

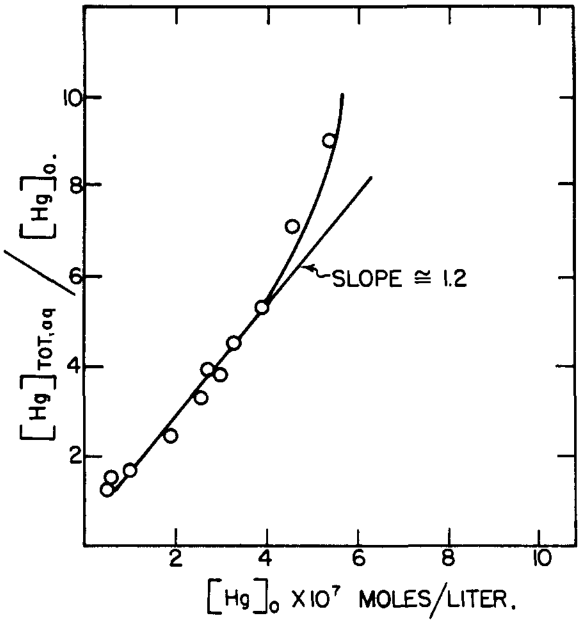

Fig. 2.—Distribution of mercury between cyclohexane and dilute nitric acid.

While these values are lower than the 5.3 to 5.6×10^{-9} determined in this study, the agreement is reasonable considering the assumptions that have been made and the low concentrations that were used.

TABLE II

SOLUBILITY OF MERCURY METAL

Soln. and temp. (°C.)	Concn. of Hg in g. moles/l.
0.1 M H_3PO_2; 25° (this study)	$(3.0 \pm 0.3) \times 10^{-7}$
0.01 M H_3PO_2, 0.01 M HNO_3; 25° (this study)	$(2.9 \pm 0.1) \times 10^{-7}$
0.001 M H_3PO_2, 0.01 M HNO_3; 25° (this study)	$(3.0 \pm 0.1) \times 10^{-7}$
Triple distilled water (25–28°) (Pariaud and Archinard)	$(1.5 \pm 0.5) \times 10^{-7}$
Air-free water; 30° (Stock)	$(1\text{-}1.5) \times 10^{-7}$

Summary.—Dismutation of mercurous dimer into mercuric ions and dissolved mercury has been studied in highly dilute aqueous solutions by making use of the extraction of the free mercury into organic solvents. The dismutation constant was found to be 5.5×10^{-9} at 25°. The distribution constant, defined as the quotient of the concentration of free mercury in the aqueous phase divided by the concentration in the organic phase, was found to be 0.031 for cyclohexane and 0.048 for n-hexane. The solubility of mercury in water was determined to be 3.0×10^{-7} g. mole/l. Values of the dismutation constant of 1.8×10^{-9} to 3.6×10^{-9} were calculated, using the solubility measurement and the reported values for the concentration ratio $[Hg^{++}]/[Hg_2^{++}]$ for systems containing mercurous ions, mercuric ions and liquid mercury metal. No indication was found for the dissociation of the mercurous dimer into monomeric ions, and it can be inferred that the dissociation constant is less than 10^{-7}.

AMES, IOWA

---

(17) R. Buck, Samang Singhadeja and L. B. Rogers, *Anal. Chem.*, **26**, 1240 (1954).

(18) In work published after submission of this paper, Higginson indicates that he has come to the same conclusion [A. M. Armstrong, J. Halpern and W. C. E. Higginson, *J. Phys. Chem.*, **60**, 1661 (1956)].

(19) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. I, Oxford University Press, London, 1950, p. 291.