CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
TEXAS TECH UNIVERSITY, LUBBOCK, TEXAS 79409

Mercury(II)-Catalyzed Aquation of Monochloroiron(III)[1a]

BY DWIGHT GIBSON[1b] AND DAVID W. CARLYLE*

Received December 17, 1970

Mercury(II) catalyzes the aquation of chlorometal complexes, presumably by formation of a chloride-bridged dinuclear transition state; the dinuclear configuration is a detectable intermediate in some reactions. Earlier studies of these mercury-catalyzed reactions are described or referred to in ref 2 and 3 No previous study has dealt with the mercury(II)-catalyzed aquation of chloroiron(III), although thallium(III) catalysis is reported,[3,4] and the uncatalyzed reaction is well characterized.[5-8] We have measured the rate of approach to equilibrium by reaction 1, as catalyzed by mercury(II) species.

$$Fe^{3+} + Cl^- = FeCl^{2+} \quad Q_1 \qquad (1)$$

Experimental Section

Iron(III) perchlorate, sodium perchlorate, perchloric acid, and water were prepared and handled as described previously.[9] Reagent grade hydrochloric acid was diluted and used without purification and was analyzed by titration with base.

Mercury(II) perchlorate solutions were prepared by dissolution of mercury(II) oxide in excess perchloric acid, followed by filtration, precipitation by diluting with water, washing with water, and redissolution in perchloric acid. Mercury(II) solutions were analyzed for mercury by an ion-exchange procedure[10] and for acid by direct titration with base in the presence of excess bromide.[10]

All rate measurements involving mercury were done at 25°, 0.45 M H^+, and 0.50 M ionic strength, using a stopped-flow apparatus.[9] The decrease in chloroiron(III) concentration was followed spectrophotometrically, using wavelengths in the range 335–370 nm. Reactions were initiated by diluting an equilibrium chloroiron(III) solution with perchloric acid solution, with mercury(II) being added to one of the solutions. The total chloride concentration was always much larger than the initial chloroiron(III) concentration, and a pseudo-first-order approach to equilibrium was always observed. Under these conditions, as noted before,[11,12] the observed rate of approach to equilibrium is a function of both formation and aquation rate constants and is the same for approach from either side. Three to eight measurements were obtained from each pair of reactant solutions, giving rate constants with average deviation from the mean of typically 4–8%.

Our attempts to duplicate previous rate[5,8,13] measurements on the uncatalyzed reaction 1, at 25°, 1.00 M ionic strength, 0.90 M H^+, and 0.01 M Cl^-, gave $k_{obsd} = 9.7 \pm 0.4$ sec^{-1} in measurements involving four sets of solutions, two sources of all reagents, and two workers working independently. This value is only in fair agreement with the values 7.6,[5] 8.3,[8] and 6.9,[13] calculated for the same conditions, from the data of the previous studies. In a further check of our procedure, we agreed quite well with reported[11] rate of approach to equilibrium in the iron(III)–hydrazoic acid reaction.

Results

Rate measurements were done in three series, with the free chloride concentration held constant in each series. The free chloride concentration was calculated from the stability quotients, $Q_{nCl} = [HgCl_n^{2-n}]/[HgCl_{n-1}^{3-n}][Cl^-]$, determined[14] under the conditions employed in this study.

At a particular free chloride concentration, the measured rate constant is a linear function of total mercury concentration, according to eq 2, where [Hg] represents the total mercury(II) concentration. The

$$k_{obsd} = a + b[Hg] \qquad (2)$$

measured rate constant is defined by eq 3.[11,12] The detailed data are listed in Table I.

TABLE I
MEASURED AND CALCULATED RATE OF APPROACH TO EQUILIBRIUM BY REACTION 1, AT 25°, 0.45 M H^+, AND 0.50 M IONIC STRENGTH

[Free Cl^-], M	10^3[Fe(III)], M	10^3[Hg(II)], M	k_{obsd}, sec^{-1}	k_{calcd},[a] sec^{-1}
0.0010	13.9	None	19.7	20.2
0.0010[b]	13.9	0.844	25.7	26.0
0.0010	13.9	1.41	30.0	29.9
0.0010	13.9	2.26	34.8	35.6
0.010	6.95	None	20.9	19.8
0.010	6.95	None	20.5	19.8
0.010[c]	6.95	0.795	21.1	20.9
0.010	6.95	1.59	22.6	22.1
0.010	6.95	5.63	28.3	27.9
0.010	6.95	11.3	37.9	36.1
0.010	6.95	14.1	39.7	40.2
0.010	6.95	16.0	42.9	42.9
0.10	0.695	None	27.9	27.4
0.10[d]	0.695	5.63	32.1	30.7
0.10	0.695	11.3	35.8	34.1
0.10	0.695	22.5	39.7	40.7

[a] Calculated from eq 2, 4, and 5, using values for the rate constants given in the text. [b] $f_1 = 3.27 \times 10^{-4}$, $f_2 = 0.993$, $f_n = [HgCl_n^{2-n}]/[Hg(II)]$. [c] $f_1 = 3.08 \times 10^{-5}$, $f_2 = 0.929$. [d] $f_1 = 1.38 \times 10^{-6}$, $f_2 = 0.415$.

$$\frac{-d([FeCl^{2+}] - [FeCl^{2+}]_\infty)}{dt} = k_{obsd}([FeCl^{2+}] - [FeCl^{2+}]_\infty) \qquad (3)$$

Previous work has shown[5,8,13,15] that the mercury-independent term in eq 2 is of the form

$$a = k + k'[R] \qquad (4)$$

where k and k' are the acid-dependent reverse and forward rate constants, respectively, for reaction 1. The quantity [R] is the sum of [Cl^-] and [Fe^{3+}]. The quotient $Q_1 = k'/k = 4.4\ M^{-1}$ has been measured in an equilibrium study,[7] under the conditions used in this work. Approximate evaluation of k and k' is possible, using the data in Table I involving zero [Hg(II)]. The value of Q_1 obtained is 4.6 M^{-1}, in good agreement with the earlier work.[7] Our k' value is uncertain, however, and we prefer to calculate it as 84 M^{-1} sec^{-1} from the more carefully determined[7] equilibrium quotient and from the experimental $k = 19$ sec^{-1}.

The values of b for experiments at each free chloride

---

[1] (a) Supported by the Project Catalyst Task Force, American Chemical Society. (b) Project Catalyst student, summer 1970.

[2] J. P. Birk, *Inorg. Chem.*, **9**, 735 (1970).

[3] N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

[4] J. J. Conocchioli, G. H. Nancollas, and N. Sutin, *Proc. Chem. Soc., London*, 113 (1964).

[5] R. E. Connick and C. P. Coppel, *J. Amer. Chem. Soc.*, **81**, 6389 (1959).

[6] M. J. M. Woods, P. K. Gallagher, and E. L. King, *Inorg. Chem.*, **1**, 55 (1962).

[7] N. Sutin, J. K. Rowley, and R. W. Dodson, *J. Phys. Chem.*, **65**, 1248 (1961).

[8] J. K. Rowley and N. Sutin, *ibid.*, **74**, 2043 (1970).

[9] D. W. Carlyle, *Inorg. Chem.*, **10**, 761 (1971).

[10] J. H. Espenson and J. P. Birk, *ibid.*, **4**, 527 (1965).

[11] D. Seewald and N. Sutin, *ibid.*, **2**, 643 (1963).

[12] D. W. Carlyle and J. H. Espenson, *ibid.*, **6**, 1370 (1967).

[13] G. Dulz and N. Sutin, *J. Amer. Chem. Soc.*, **86**, 829 (1964).

[14] B. Lindgren, A. Jonsson, and L. G. Sillén, *Acta Chem. Scand.*, **1**, 479 (1947).

[15] T. W. Newton, G. E. McCrary, and W. G. Clark, *J. Phys. Chem.*, **72**, 4333 (1968).

concentration were obtained by least-squares fits[16] to eq 2. The values are $b = 6900 \pm 200$, 1420 ± 40, and 540 ± 70 M^{-1} sec^{-1}, at 0.0010, 0.010, and 0.10 M free chloride, respectively. These b values were fitted to eq 5, where f_n represents the fraction of total

$$b = (k_1 + k_{-1}[\mathrm{R}])f_1 + (k_2 + k_{-2}[\mathrm{R}])f_2 \qquad (5)$$

mercury that is $HgCl_n^{2-n}$. These calculated[14] fractions are listed with Table I. Using the above b values and $Q_1 = 4.4$ M^{-1}, the values $k_1 = 1.7 \times 10^7$ M^{-1} sec^{-1}, $k_{-1} = 7.4 \times 10^7$ M^{-2} sec^{-1}, $k_2 = 8.5 \times 10^2$ M^{-1} sec^{-1}, and $k_{-2} = 3.7 \times 10^3$ M^{-2} sec^{-1} were obtained. These values for the rate constants were used in the calculated constants given in Table I.

Terms involving Hg^{2+} and $HgCl_3^-$ were omitted from eq 5 because this two-term expression provides an adequate fit. Further, even at 0.001 M chloride, the value of f_0 is so small (6×10^{-8})[14] that postulation of a diffusion-controlled process would not permit k_0 to make more than a few per cent contribution to the observed b value. A two-term expression involving $HgCl_2$ and $HgCl_3^-$ gives an extremely poor fit. Preliminary experiments indicated that Hg^{2+} does provide catalysis when it is present at significant concentrations; it is likely that $HgCl_3^-$ also provides catalysis at very high chloride concentration, but eq 5 describes the catalysis in the region 0.0010–0.10 M chloride.

Though it was not the purpose of this study to search for stable binuclear $FeClHgCl_{n-1}^{5-n}$ complexes, a few absorbance measurements were done on equilibrium iron(III)–mercury(II)–chloride mixtures. These measurements provided no evidence for binuclear complex formation, even in solutions containing up to 0.02 M $HgCl_4^{2-}$.

The mercury(II)-catalyzed pathways for aquation and formation probably involve chloride bridging,[2,3] leading to elementary reactions 6 and 7, consistent with the transition-state compositions specified by eq 5. The primed rate constants in eq 6 and 7 are related to

$$Fe^{3+} + HgCl_2 \underset{k_1}{\overset{k_1'}{\rightleftharpoons}} FeCl^{2+} + HgCl^+ \quad Q(2,1) \qquad (6)$$

$$Fe^{3+} + HgCl_3^- \underset{k_2}{\overset{k_2'}{\rightleftharpoons}} FeCl^{2+} + HgCl_2 \quad Q(3,2) \qquad (7)$$

parameters in eq 5 as follows: $k_1' = k_{-1}/Q_{2\mathrm{Cl}} = 7.4 \times 10^7/3.02 \times 10^6 = 25$ M^{-1} sec^{-1} and $k_2' = k_2/Q_{3\mathrm{Cl}} = 3.7 \times 10^3/7.08 = 520$ M^{-1} sec^{-1}.

It has been pointed out[11] that second-order rate constants for substitution of $Fe(H_2O)_6^{3+}$ fall in a rather narrow range, 2–127 sec^{-1},[9] and, similarly,[11] rate constants for substitution of $Fe(H_2O)_5OH^{2+}$ fall in another rather narrow range, 2×10^3 to 3×10^5 M^{-1} sec^{-1}.[9] It is proposed[11] that the rate-determining step is elimination of water from the inner coordination shell of Fe(III), accounting for the lack of rate dependence on identity of the entering ligand. Since the rate constants k_1' and k_2' are presumably composites, containing contributions from both acid-independent and -dependent pathways, their magnitudes should not necessarily fit into either of the ranges listed above.[17] However, if it is assumed that 20% of k_1' and k_2' arise from reaction with $Fe(H_2O)_6^{3+}$ and 80% from reaction with $Fe(H_2O)_5OH^{2+}$, as is true when chloride ion is the ligand,[5] at 0.45 M H^+, then all the formation rate constants fall in the previously observed ranges. Thus, our data appear consistent with the tentative conclusion that the metal complexes $HgCl_2$ and $HgCl_3^-$ coordinate to iron(III) by mechanisms similar to those for simpler ligands.

The ratio k_2/k_1 is 5.0×10^{-5}. The analogous ratio for the mercury(II)-catalyzed aquation of $Cr(H_2O)_5Cl^{2+}$ is about 2×10^{-5} at 25°, 0.3 M H^+, and 1.00 M ionic strength.[10] The similarity of these ratios, together with the fact that the equilibrium quotient ratios, $Q(3,2)/Q(2,1)$, are identical (except for ionic strength effects) for the two systems is consistent with other evidence that chromium(III) complex formation rates are also approximately independent of the nature of the entering ligand.[18]

---

[16] The calculations were done using a computer program based on reports from Los Alamos Scientific Laboratory, LASL-2367 + Addenda.

[17] At hydrogen ion concentrations as low as 0.2 M, the rate of the uncatalyzed reaction alone is near the upper limit of our ability to measure.

[18] (a) J. H. Espenson, *Inorg. Chem.*, **8**, 1554 (1969); (b) T. W. Swaddle and G. Guastalla, *ibid.*, **7**, 1915 (1968).

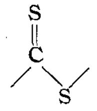
CONTRIBUTION FROM BELL LABORATORIES,
MURRAY HILL, NEW JERSEY 07974

Pressure-Induced Polymerization and Decomposition of Carbon Subsulfide

BY A. P. GINSBERG,* J. L. LUNDBERG, AND W. E. SILVERTHORN

Received January 15, 1971

At pressures of about 45 kbars and temperatures in the range 165–235° or at 27 kbars and 220–280°, carbon disulfide slowly transforms into a black polymer $(CS_2)_x$ which gives a broad, diffuse X-ray diffraction pattern.[1,2] The infrared spectrum of the black solid is consistent with the presence of the repeating unit



A black polymeric solid is also slowly formed by carbon subsulfide at atmospheric pressure and room temperature.[3] This has the stoichiometry $(C_3S_2)_x$, and an infrared investigation[4] has shown the presence of ν(C=C) bands at almost the same frequencies as in the carbon suboxide polymer $(C_3O_2)_x$. Bands due to ν(C=S) and ν(C—S) are also reported to be present. Since we had available considerable quantities of liquid carbon subsulfide from our study of its use as a ligand for transition metals,[5] it appeared to be of interest to examine the effect of pressure on its polymerization and decomposition.

Experimental Section

Infrared spectra were measured with a Perkin-Elmer Model

---

[1] P. W. Bridgman, *Proc. Amer. Acad. Arts. Sci.*, **74**, 399 (1941).

[2] E. G. Butcher, M. Alsop, J. A. Weston, and H. A. Gebbie, *Nature (London)*, **199**, 756 (1963).

[3] B. V. Lengyel, *Ber.*, **26**, 2960 (1893).

[4] A. O. Diallo and J. H. Dixmier, *C. R. Acad. Sci., Ser. C*, **263**, 375 (1966).

[5] A. P. Ginsberg and W. E. Silverthorn, *Chem. Commun.*, 823 (1969).