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The Kinetics of the Iron(II)-Catalyzed Aquation of the Monochloro Complex of Iron(III)[1]

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Previous studies of the aquation of chloro- and thiocyanatopentaaquoiron(III) have shown that these reactions are catalyzed by iron(II) ions.[2,3]

$$FeX^{2+} + Fe^{2+} \longrightarrow Fe^{2+} + X^- + Fe^{3+} \qquad (1)$$

The acid dependence of these reactions was not investigated in detail. However, it has recently been found that the rates of the chromium(II)-catalyzed aquation of halogenopentaaquochromium(III) ions are inversely proportional to the hydrogen ion concentrations of the solutions.[4] In view of the marked hydrogen ion dependence of the latter reactions, we have made a detailed study of the effect of acid on the rate of the iron(II)-catalyzed aquation of the chloropentaaquoiron(III) ion.

Experimental Section

The preparation of the various materials and the apparatus and techniques employed have been previously described.[2,3,5] The kinetic measurements were made at 25.0° and an ionic strength of 3.0 *M*. The concentration ranges used were $[Fe(III)] = 2.08 \times 10^{-3}$ *M*, $(Cl^-) = 2.30 \times 10^{-3}$ *M*, $(HClO_4) = 0.25$–2.85 *M*, and $[Fe(II)] = 0.10$–0.32 *M*. The ionic strength of the solutions was maintained with magnesium perchlorate.

Results

The approach to equilibrium in the system is described by the rate law

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

where

$$k_{obsd} = \left[k_1 + \frac{k_2}{(H^+)} + k_3(Fe^{2+}) + \frac{k_4(Fe^{2+})}{(H^+)}\right](1 + \alpha) \qquad (3)$$

$$\alpha = K_1\{[Fe(III)] + (Cl^-)\} \qquad (4)$$

and K_1 is the equilibrium constant for the reaction

$$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+} \qquad (5)$$

In the absence of iron(II) the values of k_{obsd} are 15.7, 7.32, 5.26, and 3.19 sec^{-1} at $(HClO_4) = 0.250$, 0.500, 0.750, and 1.50 *M*, respectively.[6] These rate constants, together with those determined in the earlier study,[2] were plotted against $1/(H^+)$. The values of k_1 and k_2 determined from this plot are 1.1 ± 0.1 sec^{-1} and 3.4 ± 0.1 M^{-1} sec^{-1}, respectively, in excellent agreement with the values previously determined over a more limited range of acidity.[2]

The rate constants for the approach to equilibrium in the presence of iron(II) are presented in Table I. Values of $k_3 + k_4/(H^+)$ were obtained from the slopes of plots of $[k_{obsd}/(1 + \alpha) - k_1 - k_2/(H^+)]$ *vs.* (Fe^{2+}) at constant hydrogen ion concentrations. These values were then plotted *vs.* $1/(H^+)$. The values of k_3 and k_4 determined from this plot are 6.2 ± 0.6 M^{-1} sec^{-1} and 14.8 ± 0.7 sec^{-1}, respectively, at 25.0° and ionic strength 3.0 *M*.

TABLE I

RATE CONSTANTS FOR THE APPROACH TO EQUILIBRIUM IN THE IRON(III)–IRON(II)–CHLORIDE SYSTEM AT 25.0° AND IONIC STRENGTH 3.0 M^a

$(HClO_4)$, *M*	(Fe^{2+}), *M*	k_{obsd}, sec^{-1}	$(HClO_4)$, *M*	(Fe^{2+}), *M*	k_{obsd}, sec^{-1}
2.00	0.101	4.53	0.500	0.303	20.5
2.00	0.202	5.78	0.333	0.106	16.5
2.00	0.304	7.46	0.333	0.212	23.2
0.800	0.106	8.52	0.333	0.317	28.5
0.800	0.212	11.5	0.250	0.102	21.6
0.800	0.317	14.1	0.250	0.204	28.2
0.500	0.101	11.8	0.250	0.308	34.2
0.500	0.202	17.1			

[a] $[Fe(III)] = 2.08 \times 10^{-3}$ *M* and $(Cl^-) = 2.30 \times 10^{-3}$ *M*.

Discussion

The k_1 and k_2 terms in the rate law have previously been interpreted in terms of the reaction of $(H_2O)_5FeCl^{2+}$ and of $(H_2O)_4Fe(OH)Cl^+$ with water.[2,7] The two remaining terms can be interpreted in terms of the reactions of these iron(III) species with iron(II)[8]

$$FeCl^{2+} + Fe^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} FeCl^+ + Fe^{3+} \qquad K_3 \quad (6)$$

$$Fe(OH)Cl^+ + Fe^{2+} \underset{k_{-4}'}{\overset{k_4'}{\rightleftharpoons}} FeCl^+ + FeOH^{2+} \qquad K_4 \quad (7)$$

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad K_{1h} \quad (8)$$

$$FeCl^{2+} + H_2O \rightleftharpoons Fe(OH)Cl^+ + H^+ \qquad K_{2h} \quad (9)$$

where $k_4 = K_{2h}k_4'$. Reaction 6, which yields $FeCl^+$ and Fe^{3+} ions, may proceed *via* an outer-sphere or an inner-sphere, water-bridged path. These paths may also obtain in reaction 7. However, it is necessary to consider an additional mechanism for reaction 7, namely, the inner-sphere, hydroxide-bridged path producing $FeCl^+$ and $FeOH^{2+}$. This is probably the preferred path for reaction 7 for the following reasons. Since it is likely that $K_{2h} \leq K_{1h}$, $k_4' \geq 8 \times 10^3$ M^{-1} sec^{-1}; *i.e.*, we estimate that k_4' is larger than k_3 by more than three orders of magnitude. The relatively rapid rate of reaction 7 implies a pathway for this reaction which does not operate in reaction 6. This could be the hydroxide-bridged path since hydroxide is known to be a good bridging group in the iron(II)–iron(III) sys-

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 4591 (1964).

(3) T. J. Conocchioli and N. Sutin, *ibid.*, **89**, 282 (1967).

(4) D. E. Pennington and A. Haim, *ibid.*, **88**, 3450 (1966).

(5) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(6) The value of $(1 + \alpha)$ is 1.04 under the conditions used in these studies.

(7) R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959).

(8) We have assumed that $Fe(OH)Cl^+$ and Fe^{2+}, rather than $FeCl^{2+}$ and $FeOH^+$, are the reactants in the acid-dependent path. Either formulation is consistent with the rate law. The first pair of reactants is preferred, however, since $Fe(OH)Cl^+$ has already been implicated in the inverse-acid, iron(II)-independent path. Moreover, the hydrolysis constant of $FeCl^{2+}$ is very probably greater than that of Fe^{2+} and consequently $(Fe(OH)Cl^+)(Fe^{2+}) >> (FeCl^{2+})(FeOH^+)$; *i.e.*, the rates are written in terms of the concentrations of the predominant species in the solution.

tem.[9,10] Moreover, since $K_4 = K_3K_{1h}/K_{2h}$, it follows that $k_{-4}'/k_{-3} = k_4/K_{1h}k_3$. The values of k_3 and k_4 have been determined in the present study and $K_{1h} = 1.28 \times 10^{-3}$ M at 25.0° and ionic strength 3.0 M.[11] Consequently $k_{-4}'/k_{-3} = 1.9 \times 10^3$ under the above conditions. This ratio may be compared with 1.1×10^3 for the ratio of the rates of the Fe^{2+}–$FeOH^{2+}$ and Fe^{2+}–Fe^{3+} reactions,[9] and 1.4×10^3 for the ratio of the rates of the Cr^{2+}–$FeOH^{2+}$ and Cr^{2+}–Fe^{3+} reactions.[12] The similarity of the ratios is quite striking and their magnitude provides further evidence for the view that the $FeCl^{+}$–$FeOH^{2+}$, Fe^{2+}–$FeOH^{2+}$, and Cr^{2+}–$FeOH^{2+}$ reactions proceed *via* inner-sphere, hydroxide-bridged transition states.

Finally, regardless of the detailed mechanisms of reactions 6 and 7, these studies have important implications for the mechanism of the chloride-catalyzed iron(II)–iron(III) exchange reaction. The results obtained in this work are in agreement with the conclusion reached previously, namely, that the chloride-bridged path provides the major pathway for the $FeCl^{2+}$–Fe^{2+} reaction.[2,13] A new feature provided by the present studies is that the rate law for the iron(II)–iron(III) exchange reaction in the presence of chloride ions should contain an additional term of the form $k(FeCl^{2+})(Fe^{2+})/(H^+)$ arising from reaction 6. This term should be revealed by studies of the chloride dependence of the iron(II)–iron(III) exchange reaction as a function of acidity.[14]

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(9) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(10) B. Baker and N. Sutin, to be published.

(11) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

(12) G. Dulz and N. Sutin, *ibid.*, **86**, 829 (1964).

(13) The rate constant for the chloride-bridged $FeCl^{2+}$–Fe^{2+} reaction determined in the present studies is 28.8 M^{-1} sec^{-1} at 25.0° and ionic strength 3.0 M, in good agreement with the value previously reported.[2]

(14) This term did not show up in previous studies[9] of the iron(II)–iron(III) exchange reaction because the acid dependence of the exchange reaction was determined in the absence of chloride ions, while the chloride dependence was determined at constant acidity.

Correspondence

Correlation of Force Constants with Bonding in the Dichalcogenides of Carbon[1]

Sir:

There are ten possible species in the series of linear XCY molecules with X, Y = O, S, Se, Te. For the mixed species with X ≠ Y, there are four general quadratic valence force constants to be determined from only three fundamental frequencies. Therefore, one must have more information than the three frequencies to solve the normal coordinate problem for a general quadratic valence force field. As noted by Wentink[2] there is a remarkable constancy of the CO and CS distances in the molecules CO_2, OCS, OCSe, CS_2, SCSe, and SCTe. This implies that the CX and CY bonding is similar in structure in all ten XCY species. Hopefully we can use this constancy of bond structure to evaluate the force constants.

Wentink[3] has observed the vibrational spectra of some of the more unusual of these compounds and has discussed[2] the fundamental frequencies and force constants. He showed that the data could be explained by a Lennard-Jones type of potential for essentially van der Waals interaction of the two end atoms as developed by Duchesne and Monfils.[4]

It is the opinion of this author that, in contrast to the above, the van der Waals forces should be relatively small between the end atoms of a linear triatomic molecule and that so-called resonance effects[5] are much more important in contributing to the interaction constant. For CO_2 the carbon atom π bonds to the two oxygens, sharing its two valence π orbitals with four oxygen π orbitals. If one CO bond is stretched, its CO π bonding is weakened. This makes the carbon π orbitals more available to π bond with the other oxygen tending to shorten its CO bond. We can define an interaction displacement coordinate, $(S_{\mathrm{CO}})_{\mathrm{CO'}} = -\beta$, as the change in length of one CO bond to minimize the energy after unit positive change in length of the other CO bond.[6] It is easily shown[5,7] that

$$F_{\mathrm{CO,CO'}} = -(S_{\mathrm{CO}})_{\mathrm{CO'}}F_{\mathrm{CO}} = \beta F_{\mathrm{CO}} \qquad (1)$$

With the similarity in bonding mentioned in paragraph 1 in mind, the following hypotheses are reasonable.

(*1*) *For XCY any change in CX bond order*[8] *gives rise to a proportional change of opposite sign for CY bond order, independent of Y. The proportionality constant, γ, is the same for all X.*

(*2*) *A small change in bond order causes a proportional change of opposite sign in bond length and vice versa. The proportionality constant, P_{CX}, depends on the atoms involved.*

Using these hypotheses (or approximations) we can

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(1) This work was sponsored by the U. S. Atomic Energy Commission.

(2) T. Wentink, Jr., *J. Chem. Phys.*, **30**, 105 (1959).

(3) T. Wentink, Jr., *ibid.*, **29**, 188 (1958).

(4) J. Duchesne and A. Monfils, *ibid.*, **17**, 586 (1949).

(5) C. A. Coulson, J. Duchesne, and C. Manneback, "Victor Henri Memorial Volume," Maison Desoer, Liege, 1948, p 33.

(6) The work of S. F. A. Kettle [*Spectrochim. Acta*, 1388 (1966)] indicates that changes in σ bonding are relatively negligible for this system.

(7) L. H. Jones, *J. Mol. Spectry.*, **8**, 105 (1962).

(8) By bond order is meant a measure of the degree of bonding. The bond order can range continuously from 0 to 3.