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A Kinetic Study of the Aquation of Sulfitoiron(III) Ion[1]

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Received September 10, 1970

Iron(III) forms a sulfite complex, $FeSO_3^+$, that is probably sulfur bonded. The aquation of the complex conforms to the rate law $-d[FeSO_3^+]/dt = (k_1 + k_2[H^+] + k_3[HSO_3^-])[FeSO_3^+]$. The values of the rate constants are 1.1 sec^{-1}, 3.7 M^{-1} sec^{-1}, and 1100 M^{-1} sec^{-1}, respectively, at 25°, $I = 1.00$. The activation parameters are $\Delta H_1^{\ddagger} = 8.4$, $\Delta H_2^{\ddagger} = 10.4$, and $\Delta H_3^{\ddagger} = 12.3$ kcal/mol; $\Delta S_1^{\ddagger} = -30$, $\Delta S_2^{\ddagger} = -21$, and $\Delta S_3^{\ddagger} = -3.2$ eu. An upper limit of 0.4 has been established at 25°, $I = 1.00\ M$, for $Q_1 = [FeSO_3^+][H^+]/[Fe^{3+}][HSO_3^-]$.

Introduction

Hexaaquoiron(III) is both coordinated by sulfite ion[2–4] and reduced by sulfite ion.[2–8] Each of these processes can be observed visually; iron(III) solutions become brown-red upon addition of sulfite solution and then slowly fade.

Iron(III) substitution reactions have been studied extensively[9–21] and apparently occur by similar mechanisms.[9] One of the purposes of this particular study was to gain preliminary data pertaining to the oxidation–reduction reaction between iron(III) and sulfur(IV). The other purpose was to discover whether the reaction is a conventional substitution on iron(III) or a substitution on the very labile[22] sulfur(IV), as in the formally similar chromium(III)–sulfur(IV) system.[23] The results of the study indicate that substitution probably occurs on iron, but not all the reaction paths are conventional.

The net reaction that was studied is given by[24]

$$Fe^{3+} + HSO_3^- = FeSO_3^+ + H^+ \qquad Q_1 \qquad (1)$$

Experimental Section

Reagents.—Iron(III) perchlorate was prepared from the reagent grade oxide or chloride. The oxide was first dissolved in hydrochloric acid solution. The iron chloride solutions were boiled in perchloric acid until chloride could not be detected in a test with silver ion, and iron(III) perchlorate was crystallized and then recrystallized from perchloric acid solution. Iron(III) solutions were analyzed by reduction with sodium sulfite, followed by titration with chromium(VI) or cerium(IV). Perchloric acid in iron(III) stock solutions was analyzed by titration with standard base, after exchange of iron for acid with columns of Dowex 50W-X8 cation-exchange resin in the hydrogen ion form.

Aqueous sulfur dioxide solutions were prepared from sodium or potassium sulfite, different preparations using reagent grade material from one of three different manufacturers. The solid salt was sealed in a screw-neck bottle, capped with a rubber disk; water was sealed in a second such bottle. Both bottles were purged with argon; additions and withdrawals were made by syringe. Gaseous sulfur dioxide was formed by addition of sulfuric acid to the solid sulfite. (*Caution!* Acid must be added in small increments to avoid dangerous pressures in the bottle.) Gaseous sulfur dioxide was transferred to the second bottle, leaving behind any nonvolatile impurities. Sulfur(IV) solutions, used only in preliminary experiments and in some equilibrium measurements, were prepared by dissolution of reagent grade sodium sulfite directly in water or perchloric acid solution. Sulfur(IV) solutions were analyzed iodometrically,[25] using potassium iodate as the primary standard.

Iron(II) perchlorate solutions were prepared by reduction of iron(III) perchlorate with amalgamated zinc. Iron(II) was analyzed by titration with cerium(IV).

Sodium perchlorate was prepared by neutralization of sodium carbonate with perchloric acid. The solution was treated as described by Earley[26] and then crystallized and recrystallized. Sodium perchlorate solutions were analyzed by titration of the acid displaced by aliquots from ion-exchange columns in the hydrogen ion form. Reagent grade perchloric acid was used directly. Water used in all solutions was redistilled from laboratory distilled water.

Kinetics Experiments.—All kinetics measurements were done with a stopped-flow apparatus; the apparatus has been described.[10,27] Rate measurements were initiated by mixing iron(III) solution with sulfur(IV) solution (formation experiments) or by diluting an equilibrium[28] iron(III)–sulfur(IV) mixture with perchloric acid solution (dilution experiments). In formation experiments, the stopped-flow reservoir for iron(III) solution consisted of an open volumetric flask, continuously purged with

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[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. (b) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

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[28] The word equilibrium in this paper will mean equilibrium with respect to complexation; the system was not at equilibrium with respect to oxidation–reduction in any of the experiments reported here.

argon. The sulfur(IV) reservoir was a small-necked, stoppered bottle. Glass tubes through the stopper permitted purging and addition of sulfur dioxide solution. Prior to addition of aqueous sulfur dioxide, the reservoir was charged with the appropriate quantities of water, perchloric acid, and sodium perchlorate and was bubbled with argon. Bubbling was stopped when sulfur dioxide was added, but a small argon pressure was maintained, and additional argon entered the reservoir above the surface of the solution whenever solution was withdrawn. The total sulfur(IV) concentration in the reservoir was normally calculated from the dilution of the stock solution; a few preliminary analyses of solution in the reservoir gave values in agreement with the calculated concentrations.

The equilibrium mixture used in the dilution experiments had to be prepared seconds before use, owing to the competing oxidation-reduction reaction. In these experiments, the perchloric acid reservoir was an open volumetric flask. Two reservoirs were provided for components of the equilibrium mixture; each was a stoppered bottle identical with that described above. The reservoirs, one for iron(III) and the other for sulfur(IV), were purged separately. Upon addition of sulfur(IV), the argon inlets of the two reservoirs were connected to a common source and the withdrawal tubes were connected to a T leading into the stopped-flow syringe. Thus, the iron(III)-sulfur(IV) equilibrium mixture was formed as it entered the syringe; the dilution experiment was then done immediately.

The various kinetics experiments were monitored at wavelengths ranging from 355 to 470 nm. Three to six measurements were done with each set of reactant solutions; within each such group of measurements, the average deviation from the mean rate constant was typically 4-8%.

Equilibrium Measurements.—Absorbances of equilibrium iron(III)-sulfur(IV) solutions were measured with a Cary Model 14 recording spectrophotometer. The spectrophotometer cells were sealed with serum caps and were purged with argon before addition of sulfur(IV). Hydrogen ion and bisulfite ion concentrations were calculated from the quantities of reagent added and from[29] $Q_a = [HSO_3^-][H^+]/[SO_2] = 0.043$ at 25°, $I = 1.00$. Iron(II) was added to the cells to retard the reduction of iron(III),[3-6] but reduction was still moderately fast, and the measured absorbances were extrapolated to zero time.

Results

Equilibrium Measurements.—Reasonable formulations for iron(III)-sulfur(IV) complexes include the series $Fe(SO_3)_n{}^{3-2n}$,[2,4] and possibly the series $Fe(HSO_3)_n{}^{3-n}$.[3] In addition, species containing more than one iron(III) could exist, as in the chromium(III)-sulfur(IV) system.[23,30] The equilibrium data obtained in this study are consistent with the formation of a single species $FeSO_3^+$, as described by eq 1. Plots (not shown) of $\bar{a}$ = (absorbance/cm)/[Fe(III)] *vs.* $[HSO_3^-]/[H^+]$ are linear, within the scatter, up to $[HSO_3^-]/[H^+]$ ratios of 4. Some of the measured absorbances are presented in Table I.

Comparison of the fourth and fifth experiments listed in Table I shows clearly that $Fe(HSO_3)_n{}^{3-n}$ complexes are not the absorbing species. Comparison of the second and third experiments similarly indicates that polynuclear iron complexes are not the absorbing species. This evidence, together with the linearity of the $\bar{a}$ *vs.* $[HSO_3^-]/[H^+]$ plots, suggests that the only complex observed is $FeSO_3^+$.[31]

TABLE I

MEASURED ABSORBANCES OF EQUILIBRIUM IRON(III)-SULFUR(IV) SOLUTIONS AT 25.0° AND 1.00 *M* IONIC STRENGTH

$10^2[HSO_3^-]$, *M*	$[HSO_3^-]/[H^+]$	$10^3[Fe(III)]$, *M*	$10^3[Fe(II)]$, *M*	λ, nm	$\bar{a}$[a]
0.700	0.088	1.00	5.0	360	74
0.700	0.088	1.00	10	360	79
0.700	0.088	2.00	15	360	76
1.0	0.023	0.394	6.7	370[b]	0.0
0.43	0.10	0.788	3.4	370	72
6.88	0.80	0.197	6.7	370	430

[a] The $\bar{a}$ values were calculated after extrapolation of the absorbance to the time of mixing (see text); small corrections for the absorbance of uncomplexed species were applied. [b] All experiments at 370 nm were done with purified sulfur(IV) solutions (see text).

The failure of the $\bar{a}$ *vs.* $[HSO_3^-]/[H^+]$ plots to show decreasing slope as the abscissa increases to 4 implies that the fraction of iron that is complexed is near zero at $[HSO_3^-]/[H^+] \leq 4$. If it is estimated that the fraction is <0.1 at $[HSO_3^-]/[H^+] = 4$, then $Q_1 \leq 0.4$. This limit does not appear to be inconsistent with the results obtained by Danilczuk and Swinarski.[2] These workers concluded that $Fe(SO_3)_3{}^{3-}$ is the principal species, but they worked with much higher sulfur(IV) concentrations and lower acid concentrations than were used here.

Estimation of Q_a.—Calculation of $[HSO_3^-]$ values at 25° was based on the value $Q_a = 0.043$ at 25°.[29] That value was measured in media identical with those employed in this study. Rate measurements were done during this study at 2.9 and 15.2°, as well as at 25°, and Q_a values were not directly available at these lower temperatures for the media employed. Values of $\Delta H_a°$ at zero ionic strength have been reported,[32] ranging from about −3.8 to −4.3 kcal/mol. A value of −4.0 kcal/mol was chosen for use in this study, although it is recognized that $\Delta H°$ values may be dependent on ionic strength. The value chosen for $\Delta H°$ is not extremely critical; see note *d* for Table III.

Rate Measurements.—The rate of approach to equilibrium by reaction 1 has been studied at $[HSO_3^-]/[H^+] < 0.15$. Since Q_1 is less than 0.4, it can be shown that under these conditions the observed rate constant is essentially the rate constant for aquation (the reverse of reaction 1).[9,10]

Equilibrium was approached by a first-order process in each experiment.[33] The measured rate constant is defined by eq 2.[9,10] The rate constant k' is a function

$$\frac{-d([FeSO_3^+]_{eq} - [FeSO_3^+])}{dt} = k'([FeSO_3^+]_{eq} - [FeSO_3^+]) \quad (2)$$

of both $[H^+]$ and $[HSO_3^-]$, as presented in eq 3. Values of k' were measured under a variety of conditions, as

$$k' = k_1 + k_2[H^+] + k_3[HSO_3^-] \quad (3)$$

described below, and were fitted to eq 3 and to the abso-

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[29] M. Frydman, G. Nilsson, T. Rengemo, and L. G. Sillén, *Acta Chem. Scand.*, **12**, 878 (1958).

[30] G. P. Haight, Jr., E. Perchonock, J. Emmenegger, and G. Gordon, *J. Amer. Chem. Soc.*, **87**, 3835 (1965).

[31] The data do not rule out the presence of other complexes, provided they have small stability quotients and small molar absorbancy coefficients.

[32] K. S. Pitzer, *J. Amer. Chem. Soc.*, **59**, 2365 (1937), and references therein.

[33] In preliminary experiments with $[HSO_3^-]/[H^+]$ ratios greater than about 0.2 at 25° and with no Fe^{2+} added initially, reduction of iron competed significantly with complexation of iron. Each experiment being reported here was done with the ratio less than 0.15.

TABLE II

OBSERVED AND CALCULATED RATE CONSTANTS FOR AQUATION OF SULFITOIRON(III) AT 1.00 *M* IONIC STRENGTH[a]

$10^3[HSO_3^-]$, *M*	$[H^+]$, *M*	10^3[Fe(III)], *M*	k', sec^{-1} Obsd	Calcd
0.09[b,c]	0.500	4.00	0.76	0.77
0.10[b]	0.400	4.00	0.64	0.69
0.18[b]	0.200	4.00	0.54	0.53
0.28[b]	0.100	4.00	0.45	0.47
2.00	0.037	3.20	0.80	0.76
4.00	0.074	3.20	1.8	1.2
4.00	0.074	6.40	0.90	1.2
6.00	0.074	6.40	1.6	1.6
8.00	0.074	6.40	1.8	2.0
10.0	0.148	3.20	2.9	2.5
0.06[b,c]	0.500	4.00	1.8	1.7
0.08[b]	0.400	4.00	1.6	1.5
0.14[b]	0.200	4.00	1.3	1.1
0.23[b]	0.100	4.00	1.2	0.99
2.00	0.054	3.20	1.9	1.9
4.00	0.054	3.20	3.4	3.0
6.00	0.054	3.20	5.2	4.0
8.00	0.054	3.20	6.3	5.1
10.0	0.054	3.20	6.0	6.2
0.06[b,c]	0.520	4.00	3.0	3.1
0.07[b]	0.409	4.00	2.7	2.7
0.12[b]	0.215	4.00	1.9	2.0
0.43	0.043	9.60	1.8	1.8
0.86	0.043	3.80	2.4	2.3
0.86	0.086	6.40	1.9	2.4
1.51	0.0215	3.20	3.6	2.9
2.15	0.043	3.20	3.8	4.1
4.30[d]	0.043	1.90	5.4	6.2
4.30	0.043	1.90	6.1	6.2
4.30	0.043	1.90	6.8	6.2
4.30	0.086	3.20	6.1	6.3
4.30	0.430	9.60	8.6	7.6
5.15	0.043	9.60	8.6	7.6
5.15	0.043	1.30	8.2	7.2
6.01	0.043	1.90	7.5	8.1
6.02	0.086	3.20	7.3	8.3
8.00	0.200	6.40	10.4	11.0
8.00	0.200	3.20	11.3	11.0
8.00[e]	0.200	3.20	11.3	11.0
8.60	0.086	3.80	10.3	11.3
11.0	0.150	3.80	14.5	14.2
11.0	0.200	3.80	14.3	14.4
12.0	0.100	2.60	16.7	15.2
12.0	0.300	6.40	16.3	15.9
16.0	0.200	3.80	22.2	20.1

[a] The first group of 10, the second group of 9, and the last group of 25 experiments listed in the table were done at 2.9, 15.2, and 25.0°, respectively. [b] In these dilution experiments, both $[HSO_3^-]$ and [Fe(III)] were uncertain, owing to the oxidation–reduction reaction. [c] The values used for Q_a at 2.9, 15.2, and 25° were 0.074, 0.054, and 0.043 *M*, respectively. See text. [d] About 1×10^{-6} *M* Pb(II) was in the reaction mixture. [e] The initial iron(II) concentration was 0.0175 *M*.

lute rate theory expression simultaneously. A nonlinear least-squares computer procedure was used.[34] It was assumed that $\kappa = 1$, and the data points were weighted as $1/k'$.[2] The results of the calculation are summarized in Tables II and III.

Measured values of k' were independent of $[SO_2]$ (over the range 4.3×10^{-4}–8.4×10^{-2} *M* at 25°), $[HSO_3^-]/[H^+]$ (over the range 1.0×10^{-2}–1.2×10^{-1} *M* in formation experiments at 25°), [Fe(III)] (over the range 1.9×10^{-3}–9.6×10^{-3} *M* at 25°), and wavelength of monitoring light. It has been demonstrated[35,36] that Fe^{2+} can catalyze iron(III) aquation reactions. Since traces of Fe^{2+} were formed during all experiments reported here, 0.0175 *M* Fe^{2+} was added to one experiment initially. Addition of the Fe^{2+} did not affect the measured value of k'.

TABLE III

CALCULATED RATE PARAMETERS FOR REACTION 1, AT 1.00 *M* IONIC STRENGTH

Path	Value at 2.9°	15.2°	25.0°	$\Delta S^{\ddagger}$, eu	$\Delta H^{\ddagger}$, kcal/mol
k_1[a]	0.33	0.66	1.1	-30 ± 7[b]	8.4 ± 1.9
k_2[c]	0.84	2.0	3.7	-21 ± 9	10.4 ± 2.5
k_3[c]	200[d]	540	1140	-3.2 ± 2.6	12.3 ± 0.8

[a] Sec^{-1}. [b] The indicated uncertainties are the calculated[34] standard deviations. [c] M^{-1} sec^{-1}. [d] The value for k_3 is computed to be 183 or 216 M^{-1} sec^{-1}, if $\Delta H_a°$ is −5.00 or −3.00 kcal/mol, respectively.

Measured values of k' were dependent on the source of sulfite, unless the purification step was taken. Direct use of reagent grade salts gave irreproducible rates up to 100% larger than are reported in Table II. The cause of the rate increase was not learned, although it was demonstrated in preliminary experiments that addition of small amounts of SO_4^{2-}, $S_2O_6^{2-}$, S^{2-}, or Pb^{2+} to the sulfite reactant solution was without effect.

The k_3 term in eq 3 was dominant under most conditions. In dilution experiments, however, $[HSO_3^-]$ was quite small, owing to conversion of most of the bisulfite to aqueous sulfur dioxide upon dilution with up to 1 *M* perchloric acid. In these experiments the k_3 term contributed only 2–13% of the rate, and both the k_1 and k_2 terms were demonstrated. The bisulfite concentrations in the dilution experiments were admittedly uncertain, owing to the unknown amount of oxidation, but were small and relatively insignificant.

Discussion

Structure Ambiguities.—The sulfitoiron(III) complex can reasonably be expected to adopt one of three basic structures: a bidentate oxygen-bonded, a monodentate oxygen-bonded, or a sulfur-bonded structure. Further, the complex may be of the form $Fe(OH)(HSO_3)^+$, rather than the simpler $Fe(SO_3)^+$. An ion-paired configuration may also exist, but the rates measured here are too low to correspond to ion-pairing processes.

Evidence obtained in this study, as will be discussed, suggests a sulfur-bonded structure. Other considerations, however, point to an oxygen-bonded structure. Empirical hard–soft acid–base concepts[37] suggest oxygen linkage(s), although they also predict an oxygen linkage for sulfitoamminecobalt(III) complexes, which is apparently incorrect.[38,39] Some negative evidence in

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[34] The program is based on Report LASL-2367 + Addenda, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1959.

[35] T. J. Conocchioli and N. Sutin, *J. Amer. Chem. Soc.*, **89**, 282 (1967).

[36] R. J. Campion, T. J. Conocchioli, and N. Sutin, *ibid.*, **86**, 4591 (1964).

[37] R. G. Pearson, *ibid.*, **85**, 3533 (1963).

[38] J. Halpern, R. A. Palmer, and L. M. Blakley, *ibid.*, **88**, 2877 (1966).

[39] R. S. Murray, D. R. Stranks, and J. K. Yandell, *Chem. Commun.*, 604 (1969).

favor of a bidentate complex is the failure to find $Fe(SO_3)_n^{3-2n}$ species with $n > 3$, even though the species $Fe(SO_3)_3^{3-}$ is quite stable at low acidity and high sulfur(IV)[2]. The apparent maximum number of three sulfites per iron may be due to steric crowding; a complex of similar composition, sulfatopentaaquochromium(III), is monodentate.[40]

Mechanisms.—The net activation process[41] corresponding to each term in eq 3 is given in eq 4–6. The net activation process(es) for the reverse of each step is (are) also given in eq 4–6. Solvent molecules that may be involved in the net activation processes are omitted from eq 4–6. These equations completely summarize the information gained solely from the form of the aquation rate law and from the form of the equilibrium constant.

$$\begin{tikzcd} & & FeOH^{2+} + HSO_3^- \arrow[dl, "k_{-1}"'] \\ FeSO_3^+ \arrow[r, "k_1"] & {[FeSO_3^+]^{\ddagger}} & \\ & & Fe^{3+} + SO_3^{2-} \arrow[ul, "k_{-1}'"] \end{tikzcd} \qquad (4)$$

$$FeSO_3^+ + H^+ \xrightarrow{k_2} [FeSO_3H^{2+}]^{\ddagger} \xleftarrow{k_{-2}} Fe^{3+} + HSO_3^- \qquad (5)$$

$$\begin{tikzcd} FeSO_3^+ + HSO_3^- \arrow[r, "k_3"] & {} & \\ & & FeOH^{2+} + 2HSO_3^- \arrow[dl, "k_{-3}"'] \\ & {[FeSO_3(HSO_3)]^{\ddagger}} & \\ & & Fe^{3+} + HSO_3^- + SO_3^{2-} \arrow[ul, "k_{-3}'"] \end{tikzcd} \qquad (6)$$

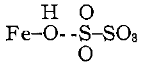
A net activation process identical in form to eq 4 is always observed[9-21] for aquation reactions for FeX^{n+}. In aquation reactions of FeX^{n+} where the ligand is basic, as in the present system, a net activation process identical in form with eq 5 is also usually observed.[9-14] In the two exceptions, $X = CrO_4$[15] and NCO,[16] the k_2 pathway was not observed, probably because it was minor relative to other pathways, rather than because it was absent.[15] Thus, the first two terms in eq 3 are of a usual form.

The rates of formation of FeX^{n+} complexes by net activation pathways corresponding to k_{-1} and k_{-2} are relatively independent of the identity of X.[9,10,19] This independence is accounted for by mechanisms[9] in which the rate-determining step is considered to be elimination of a coordinated water molecule from the outer-sphere complex $HX \cdot FeOH^{2+}$ or from the outer-sphere complex $HX \cdot Fe^{3+}$. Upper limits for the values of k_{-1} and k_{-2} can be calculated from the results of this study and from the value $Q_a' = [FeOH^{2+}][H^+]/[Fe^{3+}] = 1.65 \times 10^{-3}$ at 25°, $I = 1.00$ *M*.[42] The calculated limits for the sulfite system are $k_{-2} < 1.5$ and $k_{-1} < 270\ M^{-1}\ sec^{-1}$ at 25°. Both these calculated limits are lower than previously observed rate constants; the general k_{-2} values lie in the range 2.6–127 $M^{-1}\ sec^{-1}$, and the general k_{-1} values lie in the range 2×10^3–$3 \times 10^5\ M^{-1}\ sec^{-1}$.[9,10,13,19,21]

The calculated values for k_{-1} and k_{-2} are lower for the sulfite system than for other systems. This observation appears to require that substitution be on iron(III), rather than the much more labile sulfur(IV), and thus that the complex be sulfur bonded. Owing to the very large rate at which sulfur(IV)–oxygen bonds can be formed and broken,[22] formation and aquation of oxygen-bonded complexes are expected to be immeasurably fast, by the methods used here.

If the complex is sulfur bonded, however, then k_{-1} and k_{-2} would be expected to fall inside the ranges noted for substitution by other ligands. If the k_{-1} and k_{-2} values for the sulfite system are near the computed upper limits, then they are near the observed ranges and the accepted mechanism[9] is probably adequate to explain the results. The possibility that the formation rate constants are far smaller than the computed upper limits can probably be explained by a modification of the original proposal,[9] so that the normal rate of conversion of the outer-sphere to the stable inner-sphere complex is reduced. Such a reduced conversion rate could possibly occur if the outer-sphere complex is strongly hydrogen bonded or if an oxygen-bonded inner-sphere intermediate is formed.

Observation of the net activation process for aquation described by eq 6 is without precedent. The large effect of bisulfite ion on the aquation rate almost certainly cannot be called general acid catalysis; the stronger acids $SO_2(aq)$ and H_3O^+ are much less effective. If the sulfitoiron(III) species is oxygen bonded or passes through an oxygen-bonded intermediate, then a complex of the form



$$Fe{-}O{\cdot\cdot}\overset{H}{}\!\!\underset{O}{\overset{O}{S}}{-}SO_3$$

involving a pyrosulfite leaving group can reasonably be proposed. If, as is believed, the stable complex is sulfur bonded, an oxygen-bonded transition state of the form $OS(O)O{-}Fe{-}SO_3H$ can be proposed, in which the leaving group is protonated. Similar transition states of the form $OS(O)O{-}Cr{-}X$ have been suggested[23] to account for the sulfite ion catalysis of chromium aquation reactions involving the nonbasic ligands Cl^- and NCS^-. It seems reasonable to suggest that an aquation rate term of the form $k[HSO_3^-][M(H_2O)_5X^{n+}]$ may be observed for other complexes, if X is a basic ligand. A rate law term of this form has been observed in preliminary experiments on the aquation of $Cr(H_2O)_5N_3^{2+}$, and this hypothesis is being tested further.

In summary, the available evidence seems more in accord with a sulfur-bonded $FeSO_3^+$ species than with an oxygen-bonded one, and the data do not require postulation of unusual mechanisms for the k_1 and k_2 rate terms. The unusual k_3 rate term seems most plausibly explained by a transition state in which the catalytic sulfite is oxygen bonded and the leaving group is protonated.

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