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Monobromoiron(III) Ion. Equilibrium Studies on the Complex and on the Ion Pair and Kinetic Studies on the Substitution and Reduction Reactions[1]

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Studies on iron(III)–bromide complexes reveal two species—an inner complex $FeBr^{2+}$ and an ion pair Fe^{3+},Br^-—whose stabilities have been separately evaluated. At 1.6°, $\mu = 1.00\ M$, $Q_i = 0.034 \pm 0.003\ M^{-1}$, and $Q_o = 0.20\ M^{-1}$. The substitution rate constants for $FeBr^{2+}$ at 1.6° and $[H^+] = 1.00\ M$ are: aquation, 10.7 sec^{-1}; formation, $0.34 \pm 0.03\ M^{-1}\ sec^{-1}$. The reduction reactions of $FeBr^{2+}$ and Fe^{3+},Br^- by Cr^{2+} and Eu^{2+} have been studied. The values of k_{FeBr} are $\geq 2 \times 10^7\ M^{-1}\ sec^{-1}$ for Cr^{2+} and $1.3 \times 10^6\ M^{-1}\ sec^{-1}$ for Eu^{2+} at 1.6° and $\mu = 1.00\ M$. The third-order rate constants under the same conditions are $3.9 \times 10^3\ M^{-2}\ sec^{-1}$ for Cr^{2+} and $5.8 \times 10^3\ M^{-2}\ sec^{-1}$ for Eu^{2+}. The mechanisms of the various reactions are discussed. The third-order reactions are best understood as reactions of the ion pair and the reducing agents.

Introduction

The rate of reduction of the monobromoiron(III) complex $(H_2O)_5FeBr^{2+}$ by Cr^{2+} and Eu^{2+} is of considerable interest as one of a series of similar reactions.[2–4] The net equations for these two processes are

$$(H_2O)_5FeBr^{2+} + Cr(H_2O)_6^{2+} = Fe(H_2O)_6^{2+} + (H_2O)_5CrBr^{2+} \quad (I)$$

$$(H_2O)_5FeBr^{2+} + Eu_{aq}^{2+} = Fe(H_2O)_6^{2+} + Eu_{aq}^{3+} + Br^- \quad (II)$$

One question of obvious interest in the latter reaction is whether electron transfer occurs by an inner-sphere mechanism involving a bridging bromide ion. We note that "direct" evidence of bridging is not likely, however, since either of the potential products resulting from Br^- bridging, $(H_2O)_5Fe^{II}Br^+$ or $Eu^{III}Br^{2+}$, would dissociate essentially upon its formation following electron transfer.

The study of reactions I and II was complicated by the existence of two monobromo cations, the inner complex cited above and an ion pair, or outer-sphere complex, $Fe(H_2O)_6^{3+},Br^-$. The formation and aquation of the inner complex, shown in reaction III, competed

$$Fe(H_2O)_6^{3+} + Br^- = (H_2O)_5FeBr^{2+} + H_2O \quad (III)$$

with reaction II. Rate measurements under the conditions of interest were carried out for reaction III, which had been studied previously by Matthies and Wendt.[5]

The stability quotients for the inner complex, reaction III, and the ion pair, reaction IV, are designated

$$Fe(H_2O)_6^{3+} + Br^- = Fe(H_2O)_6^{3+},Br^- \quad (IV)$$

Q_i and Q_o, respectively. The spectrophotometric study of Lister and Rivington[6] on equilibrium solutions yielded a single equilibrium quotient Q, the sum of Q_i and Q_o.[7]

In this study we have evaluated the following quantities pertaining to the iron(III) complexes: (a) the separate equilibrium quotient Q_i for $(H_2O)_5FeBr^{2+}$ by two independent methods, (b) the value of Q_o by difference, after a value comparable to that of Lister and Rivington[6] was obtained for the sum, (c) some uv–visible spectral data for both complexes, from measurements on solutions in which ion-pairing reaction IV was at equilibrium, but where significant inner complex had not yet formed, (d) the aquation and formation rates of the inner complexation reaction, eq III, (e) kinetic studies of the rates of reduction of the inner complex by Cr(II) and Eu(II) as in reactions I and II, and (f) kinetic studies on the rates of reduction of the Fe^{3+},Br^- ion pair by the same reducing agents, as shown in the reactions

$$Fe(H_2O)_6^{3+},Br^- + Cr(H_2O)_6^{2+} = Fe(H_2O)_6^{2+} + (H_2O)_5CrBr^{2+} + H_2O \quad (V)$$

$$Fe(H_2O)_6^{3+},Br^- + Eu_{aq}^{2+} = Fe(H_2O)_6^{2+} + Br^- + Eu_{aq}^{3+} \quad (VI)$$

Experimental Section

Materials.—The preparation, storage, transfer, and analysis of chromium(II), europium(II), lithium, and iron(III) perchlorate solutions have been described.[2,4] The source of bromide ion was reagent grade hydrobromic acid. Traces of bromine were removed by treating HBr stock solutions with a small concentration of iron(II) perchlorate, the latter prepared by reducing a solution of the iron(III) salt with amalgamated zinc. The HBr stock solutions to be mixed with Cr^{2+} or Eu^{2+} solutions were not pretreated with Fe^{2+}, but the concentration of each diluted Cr^{2+} or Eu^{2+} solution was always analyzed after mixing with HBr. Reagent grade perchloric acid was used without purification. The water used throughout was prepared by twice redistilling laboratory distilled water from alkaline permanganate solution in a tin-lined Barnstead still.

Measurements.—A Cary Model 14 recording spectrophotometer with a thermostated cell holder[8] was used for spectral measurements. The rates of rapid reactions were measured using the stopped-flow apparatus described previously.[9] In experiments where product analyses were to be made, the eight-jet mixing

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[1] (a) Work was performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission; Contribution No. 2398. (b) Based on the Ph.D. thesis of D. W. C., Iowa State University, May 1968. (c) Fellow of the Alfred P. Sloan Foundation.

[2] D. W. Carlyle and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 2272 (1968).

[3] G. Dulz and N. Sutin, *ibid.*, **86**, 829 (1964).

[4] D. W. Carlyle and J. H. Espenson, *ibid.*, **91**, 599 (1969).

[5] P. Matthies and H. Wendt, *Z. Physik. Chem.* (Frankfurt), **30**, 137 (1961).

[6] M. W. Lister and D. W. Rivington, *Can. J. Chem.*, **33**, 1603 (1955).

[7] Only one value is obtained, and it is the unweighted sum indicated, irrespective of the relative abundances of the two complexes or of the contribution each species makes to the property measured: E. L. King, J. H. Espenson, and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).

[8] J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

[9] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).

chamber and syringe assembly of the flow instrument was used. This procedure was found to be essential for obtaining reproducible product distributions from very rapid reactions. All of the rate and equilibrium studies described here were carried out at ionic strength 1.00 *M*, maintained with $LiClO_4$.

The substitution rates of the inner complex were studied using the stopped-flow technique in experiments at 4050 Å, by mixing Fe^{3+} with Br^-. These experiments measured the approach to equilibrium in reaction III and in principle would allow evaluation of the forward and reverse rate constants. In fact, the reverse (aquation) rate so dominated the experiment, as it did also in the earlier work of Matthies and Wendt[5] on the same reaction under different conditions, that the forward (formation) rate was not evaluated by such measurements.

An indirect approach to measure the formation rate was employed, by making that step a major rate-determining component upon mixing a solution of Fe^{3+} (in $HClO_4$) with one containing Cr^{2+} and Br^-. The $FeBr^{2+}$ so formed was quantitatively converted to $CrBr^{2+}$, which was separated by ion exchange using Dowex 50W-X8 resin according to the procedure described.[4]

The equilibrium quotient for the inner complex, Q_i, was obtained by two methods—the quotient of forward and reverse rate constants for reaction III, and an analysis for the inner complex $FeBr^{2+}$ in *equilibrium* solutions based upon its quantitative conversion to $CrBr^{2+}$ upon reaction with Cr^{2+}. The $CrBr^{2+}$ so obtained was separated and analyzed as before.

The value of the gross formation quotient, Q, was obtained spectrophotometrically under the conditions of interest in a procedure similar to that of Lister and Rivington.[6] The difference of Q and Q_i gave Q_o, the stability quotient for the proposed ion pair. Experiments in which Fe^{3+} and Br^- were mixed using the stopped-flow apparatus revealed considerable uv absorption formed within a time where an inappreciable concentration of the inner complex could have formed (the latter conclusion based upon the rates of reaction III). The instantaneous absorption is attributed to the ion-pairing process, reaction IV.

The rate constants for the Fe^{3+}–Br^- reduction reactions were measured by the stopped-flow procedure by mixing Fe^{3+} solutions with Cr^{2+} or Eu^{2+}, bromide ion being exclusively in the latter solution. For Br^-, unlike other ions,[4] the rates of (III) are sufficiently competitive that corrections for formation of $FeBr^{2+}$ were necessary, but such interference by the inner complex was small.

The reactions of $FeBr^{2+}$ were studied with iron(III) and bromide ions in solution together before mixing with the reducing agents. Competition of the other reactions was quite severe during the study of $FeBr^{2+} + Eu^{2+}$, and three different procedures were used to circumvent these difficulties, as described in a later section.

Results

Aquation Rate of $(H_2O)_5FeBr^{2+}$.—An absorption increase at 4050 Å, λ_{max} for the inner complex, occurred at a rate measurable by the stopped-flow procedure, upon mixing Fe^{3+} and Br^-. The rate of formation of $FeBr^{2+}$ according to reaction III is governed by eq 1,

$$d[FeBr^{2+}]/dt = k'_f[Fe^{3+}][Br^-] - k'_{aq}[FeBr^{2+}] \quad (1)$$

where k'_f and k'_{aq}, which are functions of $[H^+]$, are related to Q_i: $Q_i = k'_f/k'_{aq}$. According to this expression, the approach to equilibrium in reaction III should follow pseudo-first-order kinetics under conditions where $[Br^-]$ remained substantially constant. The expression for the apparent rate constant, derived by the usual procedures,[9,10] is that given by eq 2. The

$$-d \ln \{[FeBr^{2+}]_\infty - [FeBr^{2+}]\}/dt = k_{app} = k'_f[Br^-] + k'_{aq} \quad (2)$$

appropriate rate plots[9-11] followed the expected first-order behavior as evidenced by linear rate plots to at least 90% completion. Repetitive measurements on the same set of solutions generally agreed to within 2%. Also in accord with eq 2, the values of k_{app} were not dependent on the iron(III) concentration. The values of k_{app}, covering the range $0.014 \leq [Br^-] \leq 0.50$ *M*, are summarized in Table I. Over the entire range of bromide concentrations k_{app} remained constant within experimental error, indicating $k'_f[Br^-]$ was very small relative to k'_{aq}. These results give $k'_{aq} = 10.7 \pm 0.5$ sec^{-1} (1.6°, 1.00 *M* H^+, $\mu = 1.00$ *M*), and in a single experiment at 15.8°, $k'_{aq} = 55.6$ sec^{-1}.

TABLE I

RATE CONSTANTS FOR APPROACH TO EQUILIBRIUM IN REACTION III[a]

Temp, °C	$10^3[Fe(III)]_0$, *F*	$10^3[Br^-]_0$, *M*	k_{app}, sec^{-1}
1.6	14.2	14.2	10.4
1.6	25.6	25.6	11.3
1.6	3.00	133	10.9
1.6	2.00	200	10.7
1.6	1.00	400	11.1
1.6	0.800	500	10.5
15.8	51.2	80.0	55.6

[a] Conditions: $[H^+] = 1.00$ *M*, $\mu = 1.00$ *M*, λ 4050 Å.

The time needed to reach a stable absorption spectrum in Fe^{3+} solutions containing bromide ions was *ca.* 0.5 sec; subsequent to this no spectral changes were noted over the entire uv–visible regions even on standing several days. The rate constants are typical[6,9,10,12] of substitution in the inner coordination sphere of $Fe(H_2O)_6^{3+}$ and can be assigned to the inner complex, which is an assignment consistent with the kinetic derivations outlined above.

Formation Rate of $(H_2O)_5FeBr^{2+}$.—The very low stability of $FeBr^{2+}$ prevented a direct evaluation of the formation rate constant k'_f from the rate of approach to equilibrium. The following indirect procedure was devised.

The complex $FeBr^{2+}$ oxidizes Cr^{2+} far more rapidly than does either of the species Fe^{3+} or Fe^{3+},Br^-. An appropriate choice of concentration conditions permits the following sequence of reactions to be studied

$$Fe^{3+} + Br^- \xrightarrow{k'_f} FeBr^{2+} \xrightarrow[\text{fast}]{Cr^{2+}} CrBr^{2+}$$

The rate of Fe^{3+} loss by this sequence accounts for an appreciable portion of the total when a solution of Fe^{3+} (containing no bromide) is mixed with a solution containing Cr^{2+} and Br^-. Competing with this pathway are three additional reactions consuming iron(III): $Cr^{2+} + Fe^{3+}$, $Cr^{2+} + FeOH^{2+}$, and $Cr^{2+} + Fe^{3+} + Br^-$. The total rate of disappearance of iron(III) is given by

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(10) D. R. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

(11) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 137 (1926).

(12) F. P. Cavasino, *J. Phys. Chem.*, **72**, 1378 (1968).

$$-\mathrm{d}[\mathrm{Fe}^{3+}]/\mathrm{d}t = k'_{\mathrm{f}}[\mathrm{Fe}^{3+}][\mathrm{Br}^-] + [\mathrm{Fe}^{3+}][\mathrm{Cr}^{2+}]\{k_1 + (k_2/[\mathrm{H}^+]) + k_{\mathrm{Br}}[\mathrm{Br}^-]\} \quad (3)$$

in which k_1 and k_2, representing the respective reductions of Fe^{3+} and $FeOH^{2+}$ by Cr^{2+}, are known from previous studies,[3,4] and k_{Br} is derived from experiments to be presented subsequently in this paper. At 1.6° and $\mu = 1.00$ *M* (with $LiClO_4$) the values are[4] $k_1 = 250$ M^{-1} sec^{-1}, $k_2 = 800$ sec^{-1}, and $k_{Br} = 3.9 \times 10^3$ M^{-2} sec^{-1}.

The first term in eq 3 was made as appreciable as possible in these experiments by maintaining a low Cr^{2+} concentration. The iron(III) concentration was lower still, however, so that $[Cr^{2+}]$ remained essentially constant. Under such conditions the disappearance of iron(III) is expected to follow pseudo-first-order kinetics. According to eq 3 the rate constant so evaluated ($-\mathrm{d}\ln[\mathrm{Fe}^{3+}]/\mathrm{d}t$) should be the quantity given by

$$k = k'_{\mathrm{f}}[\mathrm{Br}^-] + [\mathrm{Cr}^{2+}]_{\mathrm{av}}\{k_1 + (k_2/[\mathrm{H}^+]) + k_{\mathrm{Br}}[\mathrm{Br}^-]\} \quad (4)$$

Experiments under four sets of concentration conditions were carried out and each gave the linear first-order plot predicted. Table II summarizes the results of the experiments. A rearrangement of eq 4 yields an expression for k'_f; with k measured and the other quantities known, a value of k'_f can be calculated. The measured rate constant k is higher than the value computed were $k'_f = 0$ by 17, 37, 20, and 37%, respectively, in the four experiments. Thus the first term in eq 3 can be made quite significant, but it was not so large as to predominate in the entire experiment. Table II summarizes the values found for k'_f, the average being 0.34 ± 0.03 M^{-1} sec^{-1} (1.6°, $[H^+] = 1.00$ *M*, $\mu = 1.00$ *M*).

TABLE II

RATE CONSTANT k'_f FROM $Cr^{2+} + Br^- + Fe^{3+}$ STUDIES[a]

$[Br^-]$, *M*	$10^4[Cr^{2+}]_0$, *M*	$10^4[Fe^{III}]_0$, *F*	k_{obsd}, sec^{-1}	k'_f, M^{-1} sec^{-1}
0.150	1.66	0.200	0.307	0.35
0.300	0.925	0.150	0.30	0.37
0.350	1.80	0.200	0.515	0.30
0.500	1.15	0.200	0.497	0.364
			Av	0.34 ± 0.03

[a] Conditions: 1.6°, $[H^+] = 1.00$ *M*, $\mu = 1.00$ *M*.

Stability Constant of $(H_2O)_5FeBr^{2+}$.—One value of Q_i is calculable from the measured k'_f and k'_{aq} values: $Q_i = k'_f/k'_{aq}$. The results obtained above give $Q_i = 0.032 \pm 0.003$ M^{-1} at 1.6° and $\mu = 1.00$ *M*.

The value of Q_i was also determined under the same conditions by a completely independent technique. Solutions of $FeBr^{2+}$, in equilibrium with Fe^{3+} and Br^-, were mixed (using the stopped-flow mixing chamber) with excess Cr^{2+}. The resulting $CrBr^{2+}$ was quantitatively separated by ion-exchange chromatography.[4] These experiments always had $[Fe(III)]_0 > [Cr^{2+}]_0 > [FeBr^{2+}]_0$, so that no Cr^{2+} remained unoxidized. (This is an important point, since the reaction $Cr^{2+} + O_2$ in the presence of Br^- produces $CrBr^{2+}$, in amounts sufficient to vitiate such results.)

The total $[CrBr^{2+}]$ in the product solution was assumed to form, quantitatively, in the following ways: (1) very rapid oxidation of Cr(II) by the $FeBr^{2+}$ present at the instant of mixing, (2) oxidation of excess Cr(II) by the third-order k_{Br} path (described later in this paper), and (3) oxidation of excess Cr(II) by $FeBr^{2+}$ formed after the initial $FeBr^{2+}$ was reduced. The concentration of $FeBr^{2+}$ present at the instant of mixing was computed by an iterative procedure, as follows. A value for Q_i was assumed permitting calculation of the concentrations of all of the species in the mixed solution immediately after reduction of the $FeBr^{2+}$ initially present. These concentrations, together with the previously measured rate constants—k_1, k_2, k_{Br}—and the value for k'_f consistent with $k'_{aq} = 10.7$ sec^{-1} and the assumed value for Q_i, were used to calculate the concentration of each species as a function of time, until the Cr^{2+} was consumed. A Runge–Kutta numerical method similar to that described by Espenson and Parker[13] was used to solve the differential equations involved in this computation.

The yield of $CrBr^{2+}$ so calculated was compared to the observed, a new Q_i was selected, and the computation was repeated until the two concentrations agreed. Three experiments were performed. The data together with the Q_i values so computed are summarized in Table III. On the basis of the sensitivity of the convergence, we estimate the precision of Q_i by this method at roughly 10–20%. The average of these three experiments gives $Q_i = 0.039 \pm 0.006$ M^{-1}, which can be compared with $Q_i = 0.032 \pm 0.003$ M^{-1} computed from the rate constants.

Spectrophotometric Measurements on $Fe^{3+} + Br^-$ Solutions.—Absorbance measurements on solutions of iron(III) containing various high bromide concentrations, with 1.00 *M* H^+, were made at 4050 Å, the reported [5] maximum wavelength for the bromo complex. The absorbance values (*D*) for an optical path of *b* cm were converted to an apparent molar absorptivity of iron(III), $\bar{\epsilon}$, by the relation $\bar{\epsilon} = (D - D_0)/b[\mathrm{Fe(III)}]$, where D_0 represents the absorbance with $HClO_4$ in place of HBr. The values of $\bar{\epsilon}$ observed as a function of bromide ion concentration and temperature are summarized in Table IV.

Were a single iron(III) bromide complex formed, eq 5 would apply,[14] where ϵ_1 represents the molar absorptivity of the presumed single complex and *Q* represents its stability constant. Linear plots were obtained when the data of Table IV were fit to eq 5. The very small degree of association did not permit a very severe test, nor were the parameters very precise. The values at each temperature are: $10^{-2}\epsilon_1$ (M^{-1} cm^{-1}) = 7.0, 8.7, and 7.9 at 1.6, 15.8, and 25.0°, respectively; $Q = 0.23$, 0.26, and 0.37 M^{-1} at the same three temperatures.

$$\bar{\epsilon} = \epsilon_1 - (1/Q)(\bar{\epsilon}/[\mathrm{Br}^-]) \quad (5)$$

The direct evaluations of Q_i described above gave $Q_i = 0.032 \pm 0.003$ and 0.039 ± 0.006 M^{-1} at 1.6° com-

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(13) J. H. Espenson and O. J. Parker, *J. Am. Chem. Soc.*, **90**, 3689 (1968).

(14) T. W. Newton and G. M. Arcand, *ibid.*, **75**, 2449 (1953).

TABLE III

EVALUATION OF Q_i BY $CrBr^{2+}$ YIELD EXPERIMENTS[a]

$[Fe(III)]$,[a] *F*	$[Br^-]$,[b] *M*	$10^4[Cr^{2+}]_0$,[b] *M*	$10^4[CrBr^{2+}]$, *M* (obsd)	Q_i, M^{-1}	$10^4[FeBr^{2+}]_0$,[b,c] *M* (calcd)
0.0300	0.111	5.75	3.60	0.032	2.13
0.0250	0.133	3.85	3.59	0.047	3.14
0.0300	0.111	3.89	3.18	0.037	2.47

[a] Conditions: 1.6°, 1.00 *M* H^+, $\mu = 1.00$ *M*. [b] Concentrations after mixing but before reaction. [c] Computed using the value of Q_i given for each experiment.

TABLE IV

APPARENT MOLAR ABSORPTIVITY OF IRON(III) AS A FUNCTION OF BROMIDE CONCENTRATION AND TEMPERATURE[a]

$10^3[Fe(III)]$, *F*	$[Br^-]$, *M*	$\bar{\epsilon}$, M^{-1} cm^{-1}		
		1.6°	15.8°	25.0°
50.0	0.0200	7.52	10.88	14.0
7.28	0.0799	13.2	18.2	23.6
7.28	0.133	21.1	29.1	37.6
7.28	0.173	26.9	37.4	48.2
7.28	0.200	30.4	42.6	54.6
3.64	0.533	77.7	107	131
3.64	0.800	109	150	181

[a] Conditions: $[H^+] = \mu = 1.00$ *M*, λ 4050 Å.

pared with $Q = 0.23\ M^{-1}$ from the spectrophotometric data. This discrepancy suggested that a second species, a labile ion pair, was important under the conditions of this study, as described in reaction IV. In this event the appropriate relation for $\bar{\epsilon}$ is

$$\bar{\epsilon} = \frac{\epsilon_i Q_i + \epsilon_o Q_o}{Q_i + Q_o} - \frac{1}{Q_i + Q_o}\,\frac{\bar{\epsilon}}{[Br^-]} \qquad (6)$$

Independent evidence was obtained for a species formed immediately upon mixing Fe^{3+} and Br^- by stopped-flow measurements at 1.6°. In the wavelength range 2500–3300 Å, the absorbance of the solution freshly mixed in the flow apparatus was notably higher than that computed for the separate components Fe^{3+} and Br^-. The immediate absorbance was, however, lower than the equilibrium value reached after occurrence of inner complexation reaction III. The data were not very precise, but they did serve to establish the presence of a species other than $FeBr^{2+}$, which had a strong uv absorption.

No such instantaneous absorbance enhancement was noted at 4050 Å, making it possible to reconsider the data of Table IV. In the limit where $\epsilon_o \ll \epsilon_i$, the intercept is $\epsilon_i Q_i/(Q_i + Q_o)$. The intercept at 1.6° is 702 M^{-1} cm^{-1}, whence, from the values $Q_i = 0.034\ M^{-1}$ and $Q_i + Q_o = 0.23\ M^{-1}$, ϵ_i is 4750 M^{-1} cm^{-1} at 4050 Å and 1.6°.

Under the further assumption that ϵ_i is independent of temperature from 1.6 to 25.0°, the intercepts at 15.8 and 25.0° lead to the values $Q_i = 0.048$ (15.8°) and 0.062 (25.0°) and (by difference) $Q_o = 0.21$ (15.8°) and 0.31 (25.0°). The uncertainties in the experimental data and the assumptions involved cause us to estimate that these values probably are reliable to within only 20%.

Oxidation of Eu^{2+} and Cr^{2+} by Fe^{3+}, Br^- (Reactions V and VI).—We shall first consider the evaluation of the third-order rate constant k_{Br} as given by eq 7.

$$-d[Fe^{3+}]/dt = k_{Br}[Fe^{3+}][M^{2+}][Br^-] \qquad (7)$$

For this purpose bromide ion was added to only the reducing agent, with perchlorate being the only anion in the Fe(III) solutions. The paths for Fe(III) disappearance in these circumstances are the normal two paths in perchlorate solution: the path considered above for k_{Br} and a two-step sequence involving formation of $FeBr^{2+}$ followed by its reduction. The total rate of loss of Fe^{3+} is represented by eq 8, which incorporates

$$-d[Fe^{3+}]/dt = (k_1 + k_2[H^+]^{-1} + k_{Br}[Br^-])[Fe^{3+}][M^{2+}] + k'_f[Fe^{3+}][Br^-] \qquad (8)$$

the valid assumption that $FeBr^{2+}$ is reduced as rapidly as it is formed. In these experiments the concentration of Eu^{2+} or Cr^{2+} was considerably higher than that of Fe^{3+}. The known values of k_1, k_2, and k'_f established that the last term in eq 8 made a rather unimportant contribution to the total rate. For these reasons, an attempt was made to fit the rate data to the usual second-order expression. The concentration conditions were as follows: Eu^{2+} at 1.6°, 2.4–5.2 × 10^{-3} *M* Eu^{2+}, 0.2–1.0 × 10^{-3} *M* Fe^{3+}, 0–0.64 *M* Br^-; Eu^{2+} at 15.8°, 0.5–5 × 10^{-4} *M* Eu^{2+}, 2–4 × 10^{-4} *M* Fe^{3+}, 0–0.50 *M* Br^-; Cr^{2+} at 1.6°, 4.4–5.0 × 10^{-3} *M* Cr^{2+}, 1.3–1.4 × 10^{-3} *M* Fe^{3+}, 0–0.40 *M* Br^-. All experiments had $[H^+] = 1.00$ *M*.

The kinetic data followed the anticipated second-order rate expression, as evidence by linear rate plots. The values in different runs at constant $[Br^-]$ were in agreement within the experimental error of *ca.* 7%. The second-order rate constants increased regularly with increasing $[Br^-]$. According to eq 8 the apparent second-order rate constant, $-(d[Fe^{3+}]/dt)[Fe^{3+}]^{-1}\cdot[M^{2+}]^{-1}$, is the composite

$$k = k_1 + k'_2[H^+]^{-1} + k_{Br}[Br^-] + k'_f[Br^-][M^{2+}]_{av}{}^{-1} \qquad (9)$$

The last term was treated as a correction to k, which averaged 2.2% in the Eu^{2+} runs and 1% in the Cr^{2+} runs. For each experiment a value of k_{cor} was computed according to

$$k_{cor} = k - k'_f[Br^-][M^{2+}]_{av}{}^{-1} = k_1 + k_2[H^+]^{-1} + k_{Br}[Br^-] \qquad (10)$$

The values of k_{cor} for Eu^{2+} at 1.6° varied with $[Br^-]$ between 7.0 × 10^3 and 9.0 × 10^3 M^{-1} sec^{-1}, compared to 5.69 × 10^3 M^{-1} sec^{-1} with $[Br^-] = 0$. Similar increases were noted at 15.8° for Eu^{2+} and at 1.6° for Cr^{2+}. The plots of k_{cor} *vs.* $[Br^-]$, as suggested by eq 10, are shown in Figure 1. The slopes of these plots give the following values: Eu^{2+}, $k_{Br} = (5.8 \pm 0.6) \times 10^3$ at 1.6° and $(1.2 \pm 0.4) \times 10^4$ M^{-2} sec^{-1} at 15.8°;

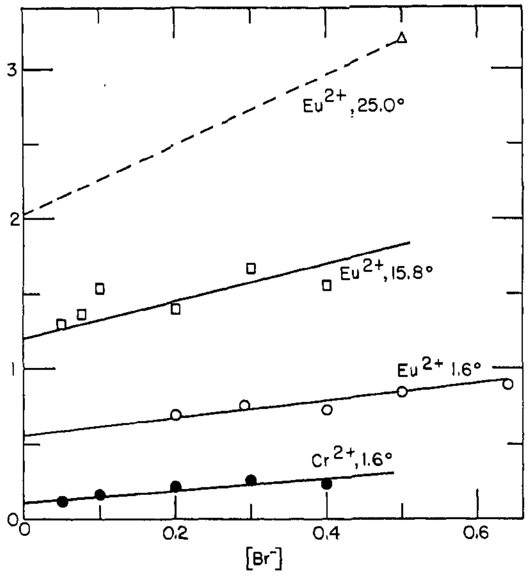

Figure 1.—A plot of the apparent second-order rate constant *vs.* $[Br^-]$ to evaluate k_{Br} for Eu^{2+} and Cr^{2+} reactions. The intercepts correspond to the values obtained in the absence of bromide, as given in ref 2 (Eu^{2+}) and ref 4 (Cr^{2+}). One 25.0° point for Eu^{2+}, $10^{-4}k = 4.6\ M^{-1}\ sec^{-1}$, was omitted from the graph (see text).

Cr^{2+}, $k_{Br} = (3.9 \pm 0.5) \times 10^3\ M^{-2}\ sec^{-1}$ at 1.6°. Two experiments were done with Eu^{2+} at 25.0°, with $[Br^-] = 0.500\ M$; values of $10^{-4}k_{cor}$ were 3.2 and 4.6 $M^{-2}\ sec^{-1}$. The former is consistent with the values at the lower temperatures assuming a normal Arrhenius relation. Also, the second value was based on a run with $[Eu^{2+}]$ and $[Fe^{3+}]$ nearly 10 times lower than in most other experiments and as such it was a run in which the correction term contributed 15%, a factor of 10 greater than in most other runs. The activation parameters for k_{Br} applying to the reaction of Eu^{2+} are $\Delta H^{\ddagger} = 3.2 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -30 \pm 6$ eu.

Oxidation of Eu^{2+} and Cr^{2+} by $FeBr^{2+}$ (Reactions I and II).—The total rates of loss of $FeBr^{2+}$ and Eu^{2+} upon mixing iron(III) + bromide with europium(II) solutions are given by eq 11 and 12. In the general

$$-d[FeBr^{2+}]/dt = k_{FeBr}[FeBr^{2+}][Eu^{2+}] - k'_f[Fe^{3+}][Br^-] + k_{aq}[FeBr^{2+}] \quad (11)$$

$$-d[Eu^{2+}]/dt = k_{FeBr}[FeBr^{2+}][Eu^{2+}] + (k_1 + k_2[H^+]^{-1} + k_{Br}[Br^-])[Fe^{3+}][Eu^{2+}] \quad (12)$$

procedure used for other complexes,[2,4] concentration conditions were chosen to make the first term be the only contribution of consequence. The reaction of $FeBr^{2+}$ and Eu^{2+}, eq II, occurs too slowly for this to be a useful procedure.

Three different methods, all giving data of low accuracy, were employed to measure the rate of reduction of $FeBr^{2+}$ by Eu^{2+}. The results are as follows.

Method 1.—Kinetic data were obtained at 1.6, 15.8, and 25.0° in experiments where bromide ion was present in both Fe(III) and Eu(II) solutions, so that no displacement in the equilibria occurred upon mixing the two. The absorbance changes were recorded at 2700–2580 Å, where Eu^{2+}, Fe^{3+}, $FeBr^{2+}$, and Fe^{3+},Br^- absorb. The absorbance changes were compared with those generated by a Runge–Kutta iteration procedure. This latter computation employed the known values of relevant rate constants, k_{Br}, k'_{aq}, and k'_f, known molar absorptivities, and various assumed values of k_{FeBr}. At the three temperatures in question, the values of $10^{-6}k_{FeBr}$ were 1.4, 2.3, and 3.3 $M^{-1}\ sec^{-1}$, respectively ($\mu = [H^+] = 1.00\ M$). The procedure was not very sensitive to changes in k_{FeBr}, however, and the values may be in error by 30%.

Method 2.—In three of the above experiments at 25.0° the concentration of $FeBr^{2+}$ remained nearly constant, owing to a higher activation enthalpy for complexation than for reduction. The computer procedure of method 1 gave the result that in these runs the concentration of $FeBr^{2+}$ never deviated by more than 15% from its average value. That being true, the rates of loss of Eu^{2+} and Fe^{3+} are equal, and eq 13 can be derived for k_{FeBr}. The value used for $[FeBr^{2+}]_{av}$

$$k_{FeBr} = \{k_{app} - (k_1 + k_2[H^+]^{-1} + k_{Br}[Br^-])[Fe^{3+}]_{av}\}/[FeBr^{2+}]_{av} \quad (13)$$

was the average value computed by method 1, using at 25.0° $k_{FeBr} = 3.3 \times 10^6\ M^{-1}\ sec^{-1}$. The three experiments in question gave values of $10^{-6}k_{FeBr} = 4.2$, 3.5, and 3.5 $M^{-1}\ sec^{-1}$.

Method 3.—Experiments in which $FeBr^{2+}$ was mixed with Eu^{2+} (bromide free) were performed at 1.6°, and the absorbance values were measured at 4050 Å. The concentrations of Eu^{2+}, Fe^{3+}, and Br^- were nearly constant during the time of reduction of $FeBr^{2+}$. Assuming this constancy the slope of a pseudo-first-order plot by the method of Guggenheim[11] can be shown to be $k_{FeBr}[Eu^{2+}] + k'_{aq}$. Two such experiments were done, each with $[Br^-] = 0.500\ M$, $[FeBr^{2+}] = 7.0 \times 10^{-6}\ M$, and $[Fe^{3+}] = 2.06 \times 10^{-4}\ M$. The results are given below. The values agree with method 1, but again the precision is quite low.

$10^5[Eu^{2+}]$, M	$k_{FeBr}[Eu^{2+}] + k'_{aq}$, sec^{-1}	$10^{-6}k_{FeBr}$, M^{-1} sec^{-1}
2.85	43.2 ± 6.5	1.3
5.22	81 ± 13	1.4

Attempts made to measure the rate of reaction of $FeBr^{2+}$ and Cr^{2+}, reaction I, were not successful. For example, in one experiment at 1.6°, $[H^+] = 1.00\ M$, with $[Cr^{2+}]_0 = 1.75 \times 10^{-6}\ M$ and $[FeBr^{2+}]_0 = 3.5 \times 10^{-6}\ M$, the reduction was complete before the solution reached the observation point, *i.e.*, within *ca.* 3–4 msec. We set a lower limit of $k_{FeBr} \geq 2 \times 10^7\ M^{-1}\ sec^{-1}$.

Complexation Rates and Equilibria.—The evidence for the existence of two monobromoiron(III) species was (1) the instantaneous uv absorption enhancement that could not have been that of the inner complex and (2) the discrepancy between the gross stability quotient evaluated spectrophotometrically and the value for the inner complex determined directly from the concentration of $FeBr^{2+}$ by either of the two independent methods of analysis for the inner complex involving reaction with Cr^{2+}. The values obtained for the stability constant reveal that the labile ion pair is the more stable of the two, the formation constants at 1.6° being $Q_i = 0.034$ M^{-1} and $Q_0 = 0.20\ M^{-1}$.

The spectrophotometric studies of Lister and Rivington[6] gave a stability constant $Q = 0.63\ M^{-1}$ at $\mu = 1.2\ M$ and 25°. Similar but less extensive studies at ionic strength 1.00 M (with $LiClO_4$) gave the values $Q = 0.20$, 0.26, and 0.37 M^{-1} at 1.6, 15.8, and 25.0°, respectively. Studies such as these on complexes of low stability often agree no better than this, and we do not claim that our value is more reliable than that given by the earlier studies.[6]

Whether the value of Q is 0.2 or 0.6, it provides mild indirect support for the conclusion reached here that a value of Q_i considerably smaller than Q is applicable to the inner complex. Were the larger value applicable to $FeBr^{2+}$, then the rate constant for establishment of equilibrium in reaction III would have been expected to show a considerable variation with $[Br^-]$, according to eq 2, in contrast to the results obtained. For example were $Q = 0.2$ for $FeBr^{2+}$, k_{app} would show a 10% increase over the range of $[Br^-]$ studied, and were $Q = 0.63$, a 24% increase. The constancy of k_{app} with $[Br^-]$ variation (Table I) is consistent with the smaller value $Q_i = 0.034\ M^{-1}$ from which the computed variation in k_{app} was only 1.7% for bromide concentrations up to 0.5 M, which is within the experimental uncertainty.

The kinetic data of Matthies and Wendt on reaction III can be expressed[15] in the form k_{aq} (sec^{-1}) $= 30 + 52[H^+]^{-1}$ at 22 ± 2° and $\mu = 1.7\ M$. The value at $[H^+] = 1.0\ M$ is thus 82 sec^{-1}, which can be compared to the value 105 sec^{-1} at $\mu = 1.00\ M$, extrapolated to 22° from our results at lower temperatures. The agreement appears satisfactory.

Although the present studies were made only at 1.00 M H^+, the earlier work[5] demonstrated the existence of parallel paths. The value $k_f = 8.8\ M^{-1}$ sec^{-1} at 25° can be computed from the values for Q_i and k_{aq} estimated in this study. If the ratio of rate constants under our conditions is assumed to be similar to the published value,[5] then an approximate expression for the forward rate of reaction III at 25°, $\mu = 1.00$, is $k_f = 3.4 + 5.4 \cdot [H^+]^{-1}$. The acid-independent term is of the correct magnitude[9,10,12] for substitution on $Fe(H_2O)_6{}^{3+}$. Assuming the second rate term corresponds to the reaction of $(H_2O)_5FeOH^{2+}$ and Br^-, the rate constant is $3 \times 10^3\ M^{-1}$ sec^{-1} which is also in the accepted range[9,10,12] of values for water elimination from the hydroxo complex.

One might ask whether the inner complex $FeBr^{2+}$ forms from the outer-sphere complex. This detailed mechanism has been proposed, although one cannot state whether the ion pair, which is of substantial stability, is the precursor of $FeBr^{2+}$.

Detailed Mechanisms of the Third-Order Reactions.—The equations written earlier (reactions V and VI) presumed that the third-order rate expression (eq 13) was the reaction of Fe^{3+},Br^- and the reducing agent. Such a process will be designated mechanism A. Two other processes should also be considered: (B) an outer-sphere reaction of $(H_2O)_5CrBr^+$ and $Fe(H_2O)_6{}^{3+}$ and (C) an inner-sphere (water-bridged) reaction of $(H_2O)_5CrBr^+$ and $Fe(H_2O)_6{}^{3+}$. Since both ion-pair formation and Cr(II) substitution are very rapid compared to oxidation–reduction and since both species are very minor components of the solutions in question, all three processes are kinetically equivalent. Since $CrBr^{2+}$ is the product and $CrCl^{2+}$ is in the analogous case of chloride ion,[3] only mechanisms in which Cr(II) is coordinated to the anion are considered; the restriction does not apply for Eu^{2+}.

Since (for Cl^-) the rate constant k_{Cl} was not a function of $[H^+]$, inner-sphere mechanism C appears unlikely. Considerable evidence has been accumulated[2,13] that compared to OH^-, H_2O is an extremely poor bridging ligand. The rate constant for mechanism A is $k_{Br}/Q_o = 2 \times 10^4\ M^{-1}$ sec^{-1} at 1.6°, whereas the value computed[16] for mechanism B is $\geq 4 \times 10^4$ M^{-1} sec^{-1}. The latter value exceeds the rates[4] of many related inner-sphere reactions, including the reduction reactions of $FeCl^{2+}$, FeF^{2+}, $FeOH^{2+}$, $FeNCO^{2+}$, and $Fe(H_2O)_6{}^{3+}$. Were $CrBr^+$ able to react in an outer-sphere reaction at such a high rate, it would be difficult to account for the latter reactions of Cr^{2+} proceeding by an inner-sphere mechanism. To do so would demand, for bromide compared to water, a nonbridging-ligand effect far exceeding the presently accepted values.[17] This is particularly so, since the reaction of Cr^{2+} with Fe^{3+} was so slow[4] as to be indistinguishable from a salt effect. On this relatively indirect basis we postulate that the most plausible mechanism is A, the reaction of Fe^{3+},Br^- and Cr^{2+}.

The halide-bridged reactions of $FeBr^{2+}$ have been discussed in a separate publication.[4]

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(15) The published data[5] are expressed as formation rate constants, the equations having been recast in this form using the published[6] equilibrium quotient. Since this work provides new values for the latter, distinguishing inner and outer complexation processes, and since the actual rate measured is governed nearly entirely by the aquation rate and almost not at all by formation rates (both in ref 5 and in this study), it appeared preferable to express the results as aquation rate constants, which are the quantities governing directly the experimental observation. As noted in the text, our extrapolated value of k_{aq} is not in disagreement with that of Matthies and Wendt;[5] the apparent wide discrepancy in k_f values between this work and the original study[5] originates from Matthies and Wendt's use of a composite equilibrium quotient considerably larger than that measured here directly for the inner complex.

(16) The stability quotient of the Cr(II) complex was taken as ≤10% of the value [J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960)] for the Cr(III) complex $CrBr^{2+}$ for which $Q = 10^{-3}\ M^{-1}$ at 0° and $\mu = 2.0\ M$. The stabilities of iron(III) and iron(III) monochloro complexes differ by at least a factor of 10: H. N. Po and N. Sutin, *Inorg. Chem.*, **7**, 621 (1968); Sr. M. J. M. Woods, P. K. Gallagher, and E. L. King, *ibid.*, **1**, 55 (1962).

(17) D. E. Pennington and A. Haim, *ibid.*, **5**, 1887 (1966).