Oxidation of Iodide Ion by Iron(III) Ion in Aqueous Solution

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The kinetics of the redox reaction between Fe^{3+} and I^- ion have been reinvestigated over a wide range of reactant concentrations using the method of initial rates. The first-order dependence on Fe^{3+} and second-order dependence on I^- have been confirmed, the third-order rate constant being $16{\cdot}0 \pm 1{\cdot}0$ l^2 mol^{-2} s^{-1} at 25 °C and ionic strength of 1·0M. In the presence of added ferrous ion, however, the previously derived rate laws do not adequately describe the reaction under all conditions. It is believed that the inner-sphere complex FeI^{2+} does not form to a significant extent, but that an outer-sphere ion-pair between Fe^{3+} and I^- is a likely intermediate. A di-iodo-species may also be involved, and stationary-state assumptions, leading to relatively simple rate expressions, are not valid under all conditions.

THE oxidation of iodide ion by iron(III) ion in aqueous solution is known to occur spontaneously according to equation (1). Although there have been several

$$Fe^{3+} + I^- \longrightarrow Fe^{2+} + \tfrac{1}{2}I_2 \qquad (1)$$

studies of the kinetics of this reaction,[1-4] complete agreement on the interpretation of the results has not been reached, and it is felt that this may be due, in part, to inadequate control of ionic strength, the presence of other complexing species, and perhaps to the indirect means of measurement used. The purpose of this study was two-fold. Using the stopped-flow technique, it was possible for us to cover a much larger range of concentrations and to measure the initial rate of production of I_2 more directly by observing the increase in optical density due to the species I_3^-. It was hoped that this would lead to an evaluation of all terms in the rate law. In addition, the technique enabled us to investigate the possibilities of transient-intermediate formation.

EXPERIMENTAL

Materials.—All solutions were prepared from demineralised water which was distilled successively from alkaline $KMnO_4$ and acidified $K_2Cr_2O_7$ in an all-glass apparatus. Iron(III) solutions were prepared from iron(III) perchlorate (G. Frederick Smith) which had been thrice recrystallised from AnalaR $HClO_4$, and were analysed by tin(II) chloride reduction and titration with $KMnO_4$. Stock $HClO_4$ solutions were standardised against disodium tetraborate, and the acid present in iron(III) solutions determined by titrating to pH 9 with freshly prepared NaOH. Sodium perchlorate solutions, used to adjust the ionic strength, were prepared from B.D.H., low in chloride, $NaClO_4$.

All iodide solutions were freshly prepared from Unilab sodium iodide. Stock solutions of *ca.* 0·2M were prepared by dissolution of accurately weighed quantities of solid; accurate dilution of this gave solutions of lower concentration. Occasional potentiometric titration with silver nitrate showed the concentrations to be reproducible to within ±1%.

Iron(II) solutions, containing very small amounts of iron(III) ion, were prepared by the electrolytic reduction of iron(III) perchlorate. The cell used was designed to maintain an oxygen-free atmosphere and possessed a fine sintered-glass junction to the anodic half-cell containing 1M-$HClO_4$. With large platinum-gauze electrodes and current (*ca.* 200 mA) from a 25 V D.C. power supply, a 0·2M solution (500 ml) of iron(III) ion in 0·5M-$HClO_4$ could be reduced in 24 h. Analysis of the product by the iron(III) thiocyanate method showed the remaining iron(III) concentration to be approximately 3×10^{-6}M, *i.e.* only $1{\cdot}5 \times 10^{-3}$% of the total iron. The iron(II) concentration in these solutions was determined by titration with $KMnO_4$, and the hydrogen-ion concentration by titration to pH 10 with freshly prepared NaOH.

Methods.—Kinetic runs were carried out both on the stopped-flow apparatus, previously described,[5] and an SP 800 recording spectrophotometer. In the latter case, a simple device consisting of two 1 ml tuberculin syringes with linked plungers made it possible to mix accurately equal quantities of two reactants into a standard 2, 10, or 40 mm cuvette placed in the thermostatted cell block, and to begin recording 3—4 s after mixing.

The rate of reaction was measured by observing the increase in optical density (O.D.) at 370 nm. Since the total change was often of the order of 10—100 O.D. units

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[1] A. Schukarew, *Z. phys. Chem.*, 1901, **38**, 353.

[2] C. Wagner, *Z. phys. Chem.*, 1924, **113**, 269.

[3] A. V. Hershey and W. C. Bray, *J. Amer. Chem. Soc.*, 1936, **58**, 1760.

[4] A. J. Fudge and K. W. Sykes, *J. Chem. Soc.*, 1952, 119.

[5] G. S. Laurence and K. J. Ellis, *J.C.S. Dalton*, 1972, 1667.

and the governing rate law complex, only the first few percent of the reaction was studied, the method of initial rates being used to determine the various dependences. Oscilloscope traces from the stopped-flow experiments were converted to optical density *vs.* time curves as described previously.[5] By using appropriately expanded time and sensitivity scales, it was a simple process to observe only 1—2% of reaction.

Calculations.—At 370 nm, the light absorption is due to the oxidised iodine species I_2 and I_3^-, and the proportion of these species in solution is governed by the equilibrium (2). We have found the value of K_I to be 720 l mol⁻¹ at

$$I_2 + I^- \overset{K_I}{\rightleftharpoons} I_3^- \qquad (2)$$

25 °C, compared with literature values [6] in the range 630—780 l mol⁻¹. The data of Awtrey and Connick [7] show that the extinction coefficient of I_2 in aqueous solution is only of the order of 1% of that for I_3^-, and it is reasonable to assume that, provided $[I^-] > [I_2]$, all of the light absorption is due to the species I_3^-. By measuring the optical densities of a series of solutions of known I_2 and I^- concentrations under conditions similar to those for the Fe^{3+}–I^- kinetic measurements, and using $K_I = 720$ l mol⁻¹, we have found the extinction coefficient of I_3^- ($\varepsilon_{I_3^-}$) at 370 nm to be 19,420 ± 400 l mol⁻¹ cm⁻¹, which is in good agreement with the value of 20,000 l mol⁻¹ cm⁻¹ extrapolated from the data of Awtrey and Connick.

Although equilibrium (2) is attained rapidly ($k_f \simeq 10^{10}$ l mol⁻¹ s⁻¹) [8] and does not interfere with the overall rate of the Fe^{3+}–I^- reaction, allowance must still be made for the different ratio $[I_3^-] : [I^0_{tot}]$ (I^0_{tot} = total iodine in zero oxidation state) which exists [equation (3)] for different iodide concentrations. This is described by equation (3)

$$[I_3^-] = \frac{K_I[I^-]}{1 + K_I[I^-]}[I^0_{tot}] \qquad (3)$$

provided $[I^-] \gg [I^0_{tot}]$. Since little iodine(0) was formed and the concentration of I^- did not change significantly during the first few percent of reaction, equation (3) was used in converting optical density changes to rates of production of zero valent iodine, *i.e.* $d[I_2]/dt$. All rates are the average of at least five kinetic runs.

RESULTS AND DISCUSSION

In the most recent work, Fudge and Sykes [4] discussed the results of previous studies and reinvestigated the kinetics of the Fe^{3+}–I^- reaction at constant ionic strength. Using two sampling techniques, both involving titration of liberated iodine with thiosulphate, they were able to study the rate dependences over a range of initial rates of iodine production of *ca.* 0·3 × 10⁻⁶—8 × 10⁻⁶ mol l⁻¹ s⁻¹. The reaction scheme they proposed is as in equations (4)—(6), which, on applying the stationary-state assumption to FeI^{2+} and I_2^-, gives rise to the rate expression (7). This scheme is in

$$Fe^{3+} + I^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} FeI^{2+} \qquad (4)$$

$$FeI^{2+} + I^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Fe^{2+} + I_2^- \qquad (5)$$

$$Fe^{3+} + I_2^- \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Fe^{2+} + I_2 \qquad (6)$$

$$-d[Fe^{3+}]/dt = 2d[I_2]/dt = \frac{2k_1k_3}{k_2}\frac{[Fe^{3+}][I^-]^2}{(1 + R)} \qquad (7)$$

$$\text{where} \qquad R = \frac{k_4[Fe^{2+}]}{k_5[Fe^{3+}]} + \frac{k_3}{k_2}[I^-]$$

accord with current theories, since it consists of a series of bimolecular reactions between oppositely charged ions; the species FeI^{2+} could well be expected to exist by analogy with $FeBr^{2+}$ and $FeCl^{2+}$, and the existence of the radical anion I_2^- in aqueous solution is now well established.[9] However, agreement between experiment and theory was not complete, and Fudge and Sykes [4] have had to rely, not unreasonably, on the assumption that $k_3[I^-[\ll k_2$, and that I_2^- can react more rapidly with FeI^{2+} than with Fe^{3+}. There was also the possibility of interference from an iron(III) nitrate complex, and of some systematic error due to the indirect method of measuring rates.

By using the techniques described we have been able to study the effect of much larger changes in reactant concentrations and have measured initial rates ranging from 14,000 × 10⁻⁶ to 0·05 × 10⁻⁶ mol l⁻¹ s⁻¹. Our results confirm those of Fudge and Sykes in the concentration ranges they studied, but it is clear that the rate expression (7) does not represent the course of reaction over all concentration ranges. We have used a computer program to vary continuously the terms k_4/k_5 and k_3/k_2 (k_1k_3/k_2 can be evaluated unambiguously, see below) in an attempt to correlate such values obtained from equation (7) with the experimentally observed rates, but have found this to be possible only over narrow concentration ranges. In general, the discrepancy in rates was many times greater than the possible experimental uncertainty, and in some instances only negative values for the rate constants gave reasonable agreement.

A likely source of error in the derivation of equation (7) is in making the stationary-state assumption about the species FeI^{2+}. Perhaps an equally reasonable assumption to make is that k_1 and k_2 are very large compared with k_3 and k_4, and the redox reaction [(equation (5)] is preceded by the equilibrium (4) ($K_1 = k_1/k_2$). This results in equation (8), which is

$$d[I_2]/dt = k_3K_1[Fe^{3+}][I^-]^2/\{(1 + k_4[Fe^{2+}]/k_5[Fe^{3+}])\} \qquad (8)$$

equivalent to the assumption of Fudge and Sykes that ($k_3[I^-] \ll k_2$) and so does not constitute anything new, except perhaps to confirm that the stationary-state assumption is not necessarily correct.

We suggest (see below) that equation (4) does not

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[6] 'Stability Constants,' Chem. Soc. Special Publ. No. 17, **1964**.

[7] A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, 1951, **73**, 1842.

[8] M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, 1962, **84**, 1355.

[9] J. H. Baxendale and P. L. T. Bevan, *J. Chem. Soc.* (*A*), 1969, 2240.

consist of the formation of the complex FeI^{2+}, but of an outer-sphere ion-pair between Fe^{3+} and I^- [equation (9)]. In view of the second-order iodide dependence

$$Fe^{3+} + I^- \longrightarrow Fe^{3+},I^- \qquad (9)$$

for the overall redox reaction, it is apparent that the transition state must contain two iodide ions, and it is thought that the ion-pair is a precursor to a species of the type I^-,Fe^{3+},I^- which undergoes a relatively rapid electron-transfer reaction in competition with formation of the inner-sphere complex [equation (10)].

$$Fe^{3+},I^- \rightleftharpoons FeI^{2+} \qquad (10)$$

It might also be possible for the ion-pair to react with I_2^- as in equation (11).

$$Fe^{3+},I^- + I_2^- \longrightarrow Fe^{2+} + I_3^- \qquad (11)$$

If one is to consider fast equilibrium formation of the ion-pair, there is little reason why the possible formation of a di-iodo ion-triplet species (as distinct from the transition state discussed above) and its subsequent reactions should not be considered also. Two possibilities are shown in equations (12) and (13). Hershey

$$FeI_2^+ \text{ (ion triplet)} \longrightarrow Fe^{2+} + I_2^- \qquad (12)$$

$$FeI_2 \text{ (ion triplet)} + Fe^{3+} \longrightarrow 2Fe^{2+} + I_2 \qquad (13)$$

and Bray[3] also suggest the formation of tetravalent iron but this seems unlikely.

With these additional reactions to consider, it is not feasible to derive mathematically a simple overall rate law without making considerable assumptions concerning rates of attainment of equilibria, steady states, *etc.* It would be expected, however, that the effect of these reactions would be most noticeable at high concentrations of iodide ion, where the assumptions made in deriving equation (7) would be invalid. It is in fact seen experimentally (see below) that the marked deviations from equation (7) occur at high concentrations, particularly when $[I^-] > [Fe^{3+}]$.

It would appear then that reactions (4)—(6) do play important parts (where FeI^{2+} represents the outer-sphere ion-pair), but that further reactions of higher order species would have also to be considered in order to arrive at a rate law covering the complete range of reactant concentrations.

The Nature of the Intermediate FeI^{2+}.—The stopped-flow technique has been used successfully to show the existence of transient intermediates,[5,10] and a systematic 'search' was undertaken in the present system. Reactions were monitored at wavelengths from 350 to 650 nm using solutions ranging from 10^{-4} to 10^{-1}M-Fe^{3+}, 10^{-4} to 10^{-1}M-I^-, and 0·01 to 0·5M-H^+ at temperatures of 0 and 25 °C. In view of the known retardation of the overall redox reaction by Fe^{2+}, several runs were also performed in the presence of high concentrations of Fe^{2+}.

The only optical density change noted during the course of reaction was an increase at wavelengths below 400 nm and the spectrum of this species, compiled from stopped-flow measurements,[5] was identical to the u.v. spectrum of I_3^-. In some instances, due to the instrument dead-times, the solution showed some light absorption at the commencement of observations, but this was much less than 1% of that of the total reaction and extrapolation back for the appropriate time showed that the O.D. at the time of mixing was due only to the reactant absorbances, and that no other light-absorbing species was formed during the instrument dead-time. The non-detection of an intermediate however, does not alone rule out the possibility of the transient formation of, for example, the FeI^{2+} species, since it may be that its concentration is always too low to be detectable. In view of the second-order iodide dependence for the overall redox reaction, the rate-determining step must be reaction (5) and, therefore, the low optical absorption of the intermediate might be due either to its rapid dissociation or low extinction coefficient.

An estimate of the maximum possible formation constant K_1 ($= k_1/k_2$) can be made from the available data. Thus a theoretical treatment of charge-transfer spectra[11,12] allows us to predict confidently that the complex species FeI^{2+} would have a charge-transfer absorption within the wavelength range studied and, assuming it to have an extinction coefficient of only 500 l mol^{-1} cm^{-1} (c.t. absorptions are generally 2—20 times more intense), a concentration of as little as 10^{-5}M-FeI^{2+} could be detected since O.D. changes down to 0·001 could be measured in the 2 mm cell of the stopped-flow apparatus. There was no evidence for the species even at the highest reactant concentrations used (0·1M) and K_1 therefore could not have a value greater than 10^{-3} l mol^{-1}. Comparison with similar complexes ($FeCl^{2+}$, $K = 2{\cdot}89$ at 1·0M ionic strength;[13] $FeBr^{2+}$, $K = 0{\cdot}61$ l mol^{-1} at ionic strength 1·2M[14]) shows this value to be lower than might be expected. Furthermore, on substituting a value of 10^{-3} for k_1/k_2 in the measured value of k_1k_3/k_2, a minimum value for k_3 of 16×10^3 l mol^{-1} s^{-1} is obtained, and since k_3 must be rate-limiting, k_1 would need to be even greater than 16×10^3 l mol^{-1} s^{-1}. A comparison with the rates of formation of similar iron(III) complexes ($FeCl^{2+}$, $k = 9{\cdot}4$ at ionic strength 1·0M, 25 °C[15]; $FeBr^{2+}$, $k = 20$ at ionic strength 1·7M, 22 °C;[16] $FeNCS^{2+}$, $k = 127$ l mol^{-1} s^{-1} at ionic strength 0·4M, 25 °C[17]) suggests that this is unlikely to be a valid estimate for the FeI^{2+} complex.

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[11] J. N. Murrel, *Quart. Rev.*, 1961, **15**, 191.

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[13] M. J. M. Wood, P. K. Gallagher, and E. L. King, *Inorg. Chem.*, 1962, **1**, 55.

[14] M. W. Lister and D. E. Rivington, *Canad. J. Chem.*, 1955, **33**, 1603.

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

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

[17] J. F. Below, R. E. Connick, and C. P. Coppel, *J. Amer. Chem. Soc.*, 1958, **80**, 2961.

It is clear then that the intermediate in this reaction is not an inner-sphere 'charge-transfer complex' analogous to $FeCl^{2+}$. However, outer-sphere ion-pairs between Fe^{3+} and halide ions can exist in aqueous solution [18] and the rates of attainment of equilibria are fast.[19] If the intermediate was of this form, it is not surprising that it could not be observed since, even though K_1 might be much larger than predicted above (and k_1 proportionally smaller), the extinction coefficient of any absorption band would be much less than that assumed as the transition involved would merely be a perturbation of the *d–d* transition for Fe^{3+}. We believe therefore that the equilibrium, which must occur prior to reaction (5), involves the formation of the outer-sphere ion-pair, FeI^{2+}.

Iron(III) *and Iodide-ion Dependences.*—Previous investigations have been limited to reactant concentrations which yield low rates, because of the mode of measurement. In addition, many measurements have been at high conversions of Fe^{3+} to Fe^{2+}, requiring allowance for the known retardation by Fe^{2+}. In this study we have measured the initial rates in the absence of Fe^{2+} at 25 °C, and acid and ionic strengths of 0·25 and 1·0M respectively. The reactant concentrations and measured rates are listed in Table 1 from which it can be seen that the reaction is first order in Fe^{3+} and second order in iodide over the complete range studied. The third-order rate constant k_1k_3/k_2 is $16{\cdot}0 \pm 1{\cdot}0$ l^2 mol^{-2} s^{-1} under these conditions.

TABLE 1

Rate dependence on Fe^{3+} and I^- concentrations. $[H^+] = 0{\cdot}25$M; Ionic strength = 1·0M; temp. = 25 °C

Run	$10^3[Fe^{3+}]$ (M)	$10^3[I^-]$ (M)	10^4 Initial rate (mol l^{-1} s^{-1})	Rate/$[Fe^{3+}][I^-]^2$ (l^2 mol^{-2} s^{-1})
1	99·00	96·0	137·58	15·1
2	49·45	96·0	73·19	16·1
3	19·80	96·0	30·14	16·5
4	9·90	96·0	15·02	16·4
5	3·95	96·0	6·09	16·7
6	1·18	96·0	1·75	16·0
7	99·00	9·6	1·32	14·7
8	49·45	9·6	0·68	14·9
9	19·80	9·6	0·30	16·3
10	9·90	9·6	0·15	15·9
11	3·95	9·6	0·06	16·2
12	1·18	9·6	0·02	17·0
13	99·00	86·0	113·15	15·5
14	99·00	74·4	88·36	16·1
15	99·00	60·7	60·60	16·6
16	99·00	43·1	29·78	16·1
17	1·18	86·0	1·36	15·5
18	1·18	74·4	1·08	16·5
19	1·18	60·7	0·70	16·1
20	1·18	43·1	0·35	16·0

Although it is difficult to make accurate adjustments to allow for ionic strength differences, it is possible to compare this value for the rate constant with data from previous studies. Thus Hershey and Bray [3] obtained values at 25 °C of 87 and 810 l^2 mol^{-2} s^{-1} at ionic strengths of 0·09 and 0·0M respectively and a value of the order of 10 l^2 mol^{-2} s^{-1} at an ionic strength of 1·0M is not unreasonable. From the data of Fudge and Sykes,[4] one can calculate a value of 19 l^2 mol^{-2} s^{-1} at ionic strength 0·602M and 20 °C.

Iron(II)*-ion Dependence.*—A test of equation (7) was made by measuring the initial rates at fixed Fe^{3+} and I^-, but differing Fe^{2+} concentrations. The pertinent data are listed in Table 2. The values in columns 6 and 7 confirm that, for a given set of Fe^{3+} and I^- concentrations, the retardation term is dependent on the first power of the iron(II)-ion concentration, although there appears to be a slight trend in the values of R/$[Fe^{2+}]$ when the iodide concentration exceeds that of Fe^{3+}. There are also obvious dependences of the term R/$[Fe^{2+}]$ on both Fe^{3+} and I^- concentrations; the term varies approximately inversely with Fe^{3+}

TABLE 2

The retardation effect of iron(II) ion. $[H^+] = 0{\cdot}25$M; Ionic strength = 1·0M; temp. = 25 °C

Run	$10^5[Fe^{3+}]$ (M)	$10^3[I^-]$ (M)	$10^3[Fe^{2+}]$ (M)	10^6 Rate (mol l^{-1} s^{-1})	R	R/$[Fe^{2+}]$
21	99·13	99·77	10·20	14,330	0·104	10·20
22	99·14	99·77	20·40	12,770	0·239	11·72
23	99·17	99·77	51·00	9990	0·584	11·45
24	1·24	99·77	10·20	21·83	8·07	791
25	1·25	99·77	20·40	12·24	15·30	750
26	1·26	99·77	30·60	8·55	22·52	736
27	1·27	99·77	40·80	7·24	26·99	662
28	1·28	99·77	51·00	6·01	33·02	648
29	99·13	9·93	10·20	97·43	0·609	59·7
30	99·14	9·93	20·40	91·45	0·714	35·0
31	99·17	9·93	51·00	41·38	2·790	54·7
32	1·24	9·93	10·20	0·053	36·2	3550
33	1·25	9·93	20·40	0·025	77·0	3780
34	1·26	9·93	30·60	0·019	101·0	3330
35	1·27	9·93	40·80	0·017	115·0	2820
36	1·28	9·93	51·00	0·015	130·0	2540

TABLE 3

Dependence of retardation term on Fe^{3+} and I^- concentrations. $[H^+] = 0{\cdot}25$M; Ionic strength = 1·0M; temp. = 25 °C; $[Fe^{2+}] = 0{\cdot}0502$M

Run	$10^3[Fe^{3+}]$ (M)	$10^3[I^-]$ (M)	10^6 Rate (mol l^{-1} s^{-1})	R/$[Fe^{2+}]$
37	99·30	96·00	8825	13·20
38	49·80	96·00	3737	19·30
39	20·00	96·00	835	50·6
40	10·10	96·00	268	90·8
41	4·20	96·00	589	190
42	1·40	96·00	10·3	382
43	99·30	9·80	32·62	73·5
44	49·80	9·80	9·16	148
45	20·00	9·80	1·70	341
46	10·10	9·80	0·604	493
47	4·20	9·80	0·167	754
48	1·40	9·80	0·050	847
49	99·30	96·00	8825	13·2
50	99·40	86·00	6596	15·7
51	99·40	74·50	5716	10·9
52	99·40	60·65	2973	19·4
53	99·40	43·25	1304	25·6
54	99·30	9·80	32·6	73·5
55	1·40	96·00	10·25	382
56	1·55	86·00	8·44	413
57	1·55	74·50	6·74	387
58	1·55	60·65	4·36	397
59	1·55	43·25	2·92	297
60	1·40	9·80	0·05	847

[18] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, 1969, **8**, 575.

[19] L. de Maeyer and K. Kustin, *Ann. Rev. Phys. Chem.*, 1963, **14**, 1.

concentration, consistent with equation (7), but on increasing the I^- concentration by a factor of 10, the value of $R/[Fe^{2+}]$ is decreased by a factor of only four or five. It is necessary therefore for the term R in equation (7) to be more complex, and to either contain a factor $[I^-]^{-x}$, where x is fractional, or several terms containing $[I^-]$ to different powers. All of these terms in R must contain a power of $[Fe^{2+}]$ also, in order to account for the strict third-order dependence which is found in the absence of Fe^{2+}.

Retardation Dependence of Fe^{3+} *and* I^- *Concentrations.*—The variation of the term R was investigated further by measuring the initial-rate dependences on both $[Fe^{3+}]$ and $[I^-]$ in the presence of high concentrations of Fe^{2+} (Table 3). Once again it can be seen that a simple relationship does not exist between the rates, retardation terms, and concentrations, particularly in the case of iodide variations. It is clear that the term R must contain more factors than exist in equation (7), and these could most likely be obtained by a consideration of higher-order iron(III) iodide species.

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