

CHROMATOGRAPHIC STUDIES ON THE OXIDATION OF SULPHUROUS ACID BY FERRIC IRON IN AQUEOUS ACID SOLUTION

F. H. POLLARD, P. HANSON AND G. NICKLESS

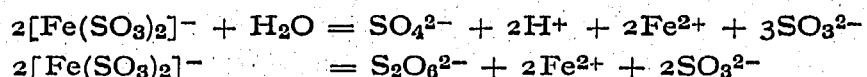
Department of Physical and Inorganic Chemistry, The University, Bristol (Great Britain)

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We have previously indicated¹ that chromatographic procedures can be of great value in kinetic studies, and in this paper which discusses the oxidation of sulphurous acid by ferric iron, the ferrous and ferric iron is separated and estimated by chromatography whilst dithionate is isolated from cations which would otherwise have interfered with its estimation.

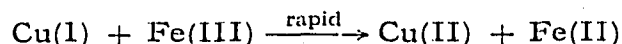
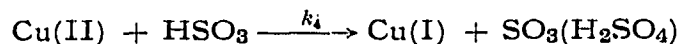
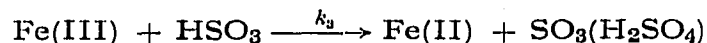
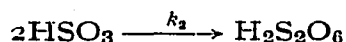
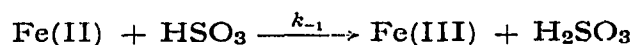
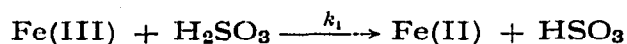
Using non-chromatographic techniques, BASSETT^{2,3} showed that dithionate is formed in a number of reactions where sulphurous acid is oxidized, thus:

(a) Metal ions, easily reducible to a lower valency state or the metal itself, yield dithionate as a result of complex-ion formation with sulphite ion followed by auto-oxidation or reduction of the complex. With ferric chloride solution, the complex-ion FeCl_4^- is sufficiently stable to prevent the formation of the ferrisulphite anion and consequently little dithionate is formed, whereas with sulphate and nitrate no stable complex-ion is formed so that in the presence of sulphurous acid, the ferrisulphite is formed with ease. The auto-oxidation of the latter leads to dithionate, *viz*:



(b) Both sulphate and dithionate can be formed in the oxidation of sulphurous acid by the oxides of manganese. Dithionate can only be formed when an oxide is reduced in one-electron steps. In either the first step $\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}$ or in the second step $\text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$, a single electron would be adsorbed from a SO_3^{2-} ion which could then lose its second electron, giving sulphate, or combine with another singly charged SO_3^- ion to give $\text{S}_2\text{O}_6^{2-}$. The reaction probably occurs on the surface of the oxide and depends on the structure and the location of the active centres.

Some kinetic aspects and stoichiometries of the oxidation of sulphurous acid are described by HIGGINSON AND MARSHALL⁴ and the results are compared with those obtained in the oxidation of hydrazine. The results discussed are almost identical to those of BASSETT and co-workers³ in that all oxidizing agents should lead to the formation of sulphate, but dithionate should only be formed in oxidations with one-equivalent reagents. The copper-catalysed reaction between ferric iron and sulphurous acid⁵ was studied, being more suitable for accurate kinetic interpretation. The following mechanism was postulated:



EXPERIMENTAL SECTION

Reagents

1. A stock solution of iron (III) sulphate, (0.4 *M* with respect to iron) was prepared by oxidation of the corresponding iron (II) sulphate with "100 volume" hydrogen peroxide. Sufficient sulphuric acid was added to make the hydrogen-ion concentration 1.0 *M* and the iron was estimated gravimetrically as the oxide.

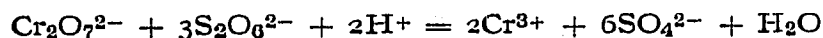
2. A 0.2 *M* solution of sodium sulphite was prepared before each run and standardized using iodine (acid conditions).

3. A 0.2 *M* solution of ferrous sulphate in 1.0 *M* sulphuric acid was prepared by weighing the AnalaR salt.

4. A stock solution of 1.0 *M* sulphuric acid, AnalaR grade. The final reaction mixture was so arranged to be of constant hydrogen-ion concentration, 0.5 *M*, by the addition of sulphuric acid. All reactions were carried out in a thermostat at $25.0 \pm 0.1^\circ$ and solutions were allowed to equilibrate overnight before reaction was started by the addition of sulphite.

As the reaction proceeded, samples were withdrawn for analysis at convenient intervals (usually every 3 h). Iron (II) and iron (III) analyses were carried out as described in a previous paper⁶ using anion-exchange techniques to separate iron (II) from iron (III). Ferrous iron was first eluted with 4 *M* hydrochloric acid followed by ferric iron using 0.5 *M* hydrochloric acid. Colorimetric estimation then followed using 2-nitroso-1-naphthol-4-sulphonic acid.

The analysis of dithionate presents a somewhat different problem than that used for dithionic acid or dithionate alone. In the aliquot taken from the reaction mixture, the estimation is rendered impossible by the presence of ferrous iron and sulphurous acid. HIGGINSON AND MARSHALL⁴ used a titration technique followed by an oxidation of dithionate with dichromate⁷.



In order to avoid this procedure for the oxidation of ferrous iron to ferric iron, all interfering cations were removed from the aliquot of the reaction mixture with a cation exchange resin Zeo-Carb 225. The column technique was used with a 14 cm bed of resin in the hydrogen form. A 10.0 ml aliquot of the reaction mixture was

adsorbed on the top of the column and elution commenced with distilled water until approximately 120 ml of eluant had been collected. This procedure effectively arrested reaction and left the dithionate, sulphate and sulphite as the free acids. The solution was made acid by the addition of 5 ml of concentrated sulphuric acid and the sulphur dioxide was removed with a stream of carbon dioxide. Excess $M/300$ potassium dichromate was added and the solution boiled for 30 min. A further 50 ml of $2 N$ sulphuric acid was added and the solution boiled for 30 min. After cooling, excess ferrous iron was added and the excess was estimated volumetrically with potassium dichromate.

Several determinations were carried out on synthetically prepared mixtures similar to those to be analysed from the reaction mixture. Varying amounts of $1.06 \cdot 10^{-2} M$ dithionate were used (Table I).

TABLE I

Sample number	ml of $S_2O_8^{2-}$ taken	ml of $K_2Cr_2O_7$ used	Molarity of $S_2O_8^{2-} \times 10^2$
1	2.5	2.70	1.08
2	2.5	2.80	1.12
3	5.0	5.48	1.09
4	5.0	5.27	1.05
5	5.0	5.37	1.07
6	10.0	10.58	1.06
7	10.0	11.01	1.10
8	10.0	11.30	1.13

RESULTS AND DISCUSSION

The advantage of using chromatographic methods of analysis in the $Fe(III)-H_2SO_3$ reaction is that unfavourable ratios of $Fe(III)$ to $Fe(II)$ may be measured more accurately than by standard estimations. Also the cation exchange treatment prior to the estimation of dithionate effectively arrests the reaction and leaves the dithionate in a suitable form for analysis. It was for these reasons that the copper was omitted from the reaction.

A plot of reaction rate showed that initially the reaction was bimolecular, but as more ferrous iron was formed, deviation from bimolecularity occurred. Fig. 1 shows a plot of

$$\log_{10} \frac{[Fe(III)]_0 [H_2SO_3]_t}{[H_2SO_3]_0 [Fe(III)]_t}$$

against time in hours for a reaction mixture of $[Fe(III)]_0 = 0.200 M$ and $[H_2SO_3]_0 = 0.0468 M$. The initial reaction velocity k_1 was obtained from the log plot (cf. Table II). Assuming that the mechanism postulated by HIGGINSON AND MARSHALL⁴ for the

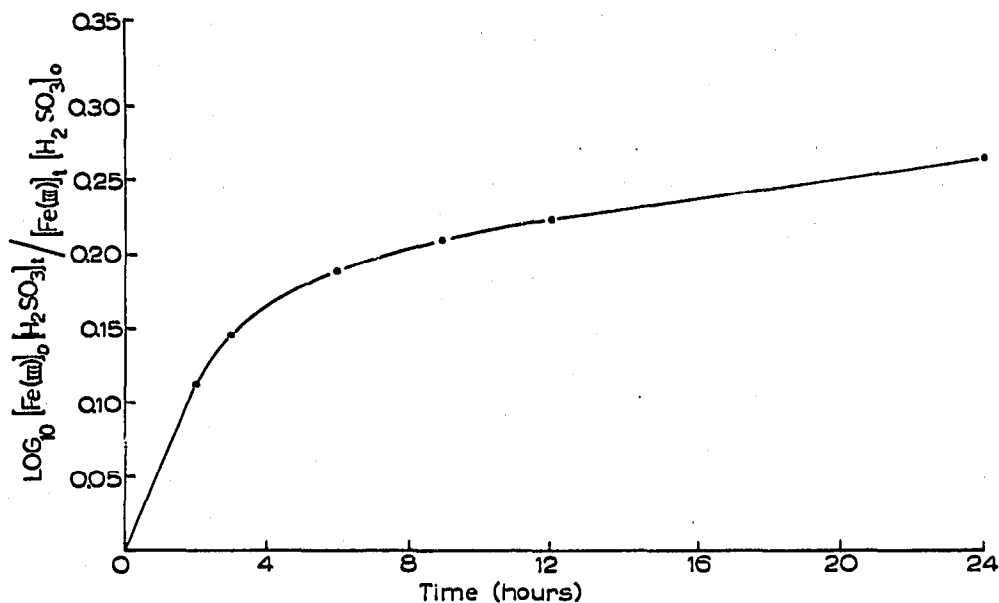


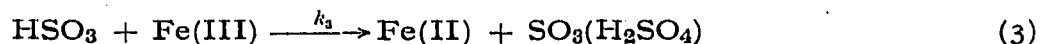
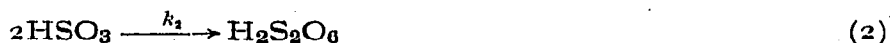
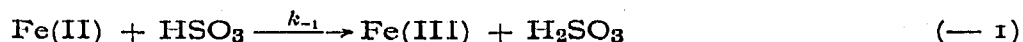
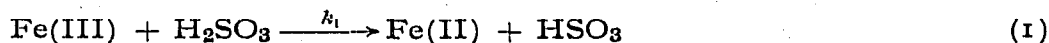
Fig. 1. The effect of time upon the initial reaction rate.

 TABLE II
 $[\text{Fe(II)}]_0 = 0$

Run number	$[\text{Fe(III)}]_0$ mole.l ⁻¹	$[\text{H}_2\text{SO}_3]_0$ mole.l ⁻¹	$R(\text{Fe})$ $\times 10^2$ mole.l ⁻¹ .h ⁻¹	$R(\text{H}_2\text{S}_2\text{O}_8)$ $\times 10^2$ mole.l ⁻¹ .h ⁻¹	Value of slope	k_1 l.mole ⁻¹ .h ⁻¹
1	0.0400	0.0850	0.42	0.20	0.0240	1.23
2	0.0200	0.0895	0.22	0.11	0.0403	1.33
3	0.2000	0.0468	0.85	0.35	0.0565	0.85
4	0.2000	0.0189	0.45	0.16	0.0680	0.87
5	0.2000	0.0915	1.40	0.65	0.0330	0.70
6	0.1000	0.0920	0.85	0.40	0.0030	0.86

Average value $k_1 = 0.97 \pm 0.20$ l.mole⁻¹.h⁻¹.

copper-catalysed reaction between sulphurous acid and ferric iron is correct



For convenience, all sulphur species are shown as uncharged molecules or radicals.

It was found that, on adding increasing amounts of ferrous iron to the reaction mixture deviation from bimolecularity occurs very quickly after the initial rate. From the suggested mechanism and making the usual stationary-state assumption that $R(\text{HSO}_3) = 0$, an equation relating the products and reactants with the initial velocity constant k_1 may be derived:

$$\frac{[\text{Fe(III)}] [\text{H}_2\text{SO}_3]_0}{R(\text{Fe})} = \frac{1}{2k_1} + \frac{k_{-1}}{2k_1k_3} \frac{[\text{Fe(II)}]_0}{[\text{Fe(III)}]_0} \quad (4)$$

as long as $R(\text{Fe}) \gg R(\text{H}_2\text{S}_2\text{O}_6)$. This equation did not hold, particularly where $[\text{H}_2\text{SO}_3]_0 > [\text{Fe(III)}]_0$ when almost quantitative oxidation of sulphurous acid to dithionate occurred (Table III).

TABLE III

Run number	11	12	7	8	9	10
$[\text{Fe(III)}]_0$ mole·l ⁻¹	0.1049	0.1026	0.1008	0.1010	0.0433	0.0417
$[\text{H}_2\text{SO}_3]_0$ mole·l ⁻¹	0.0425	0.0460	0.0895	0.0900	0.0860	0.0860
$[\text{Fe(II)}]_0$ mole·l ⁻¹	0.04523	0.01740	0.04920	0.01900	0.04671	0.01835
$[\text{Fe(II)}]_0/[\text{Fe(III)}]_0$	0.4311	0.1695	0.4882	0.1881	1.078	0.440
$R(\text{Fe}) \times 10^3$ mole·l ⁻¹ ·h ⁻¹	1.75	3.15	3.50	5.67	1.9	2.5
$R(\text{H}_2\text{S}_2\text{O}_6) \times 10^4$ mole·l ⁻¹ ·h ⁻¹	8.0	13.5	10.5	24.0	8.5	12.5
$\frac{[\text{Fe(III)}]_0 [\text{H}_2\text{SO}_3]_0}{R(\text{Fe})}$	2.548	1.498	2.577	1.603	1.960	1.434
$\frac{[\text{Fe(III)}]_0^2 [\text{H}_2\text{SO}_3]_0^2}{[\text{Fe(II)}]_0^2 \times 10^3}$	9.72	73.62	33.60	228.8	6.36	38.18

If the rate of disappearance of HSO_3 radicals by reaction (—1) is sufficiently greater than the sum of the rates of reaction (2) and (3), we have as an approximation

$$[\text{HSO}_3] = K \frac{[\text{Fe(III)}] [\text{H}_2\text{SO}_3]}{[\text{Fe(II)}]}$$

where

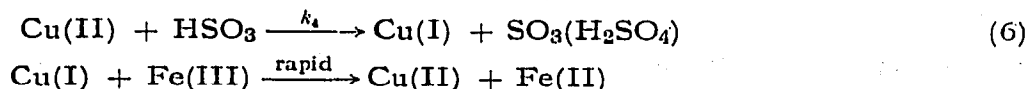
$$K = k_1/k_{-1}$$

From reaction (2):

$$R(\text{H}_2\text{S}_2\text{O}_6) = \frac{1}{2} k_2 K^2 \frac{[\text{Fe(III)}]^2 [\text{H}_2\text{SO}_3]^2}{[\text{Fe(II)}]^2} \quad (5)$$

and a plot of $R(\text{H}_2\text{S}_2\text{O}_6)$ against $[\text{Fe(III)}]^2 [\text{H}_2\text{SO}_3]^2/[\text{Fe(II)}]^2$ should be a straight line and pass through the origin. This is not the case in Fig. 2 and it may be that dithionate is formed in some other way.

From the scheme suggested⁴, copper salts should speed up the reaction with the production of more ferrous iron and less dithionate



The initial rate was obtained for an equal stoichiometric mixture of ferric iron and sulphurous acid with 0.01 M, 0.005 M and 0.002 M copper sulphate solution and, as expected, less HSO_3 radicals were available for dimerisation with the production of less dithionate and more ferrous iron.

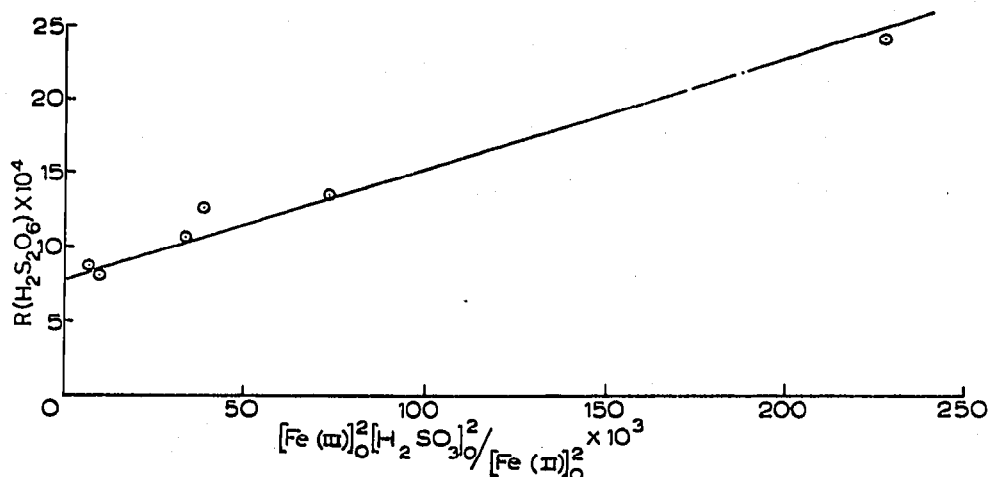


Fig. 2. The test of equation (5).

SUMMARY

Chromatographic techniques have been employed for the separation of ferrous and ferric iron and also in the isolation of dithionate prior to analysis.

The mechanism postulated by HIGGINSON AND MARSHALL⁴ has been used to explain the results obtained in the reaction between sulphurous acid and ferric iron in the absence of copper. Almost quantitative oxidation of sulphurous acid to dithionate occurred with increasing $\text{H}_2\text{SO}_3/\text{Fe}^{3+}$ ratios.

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