XL.—*The Reaction between Ferric Salts and Thiosulphates.*

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AMONGST the comparatively few quadrimolecular reactions which have been studied, reference may be made to the reduction of chromic acid by phosphorous acid (G. Viard, *Compt. rend.*, 1897, **124**, 148), the interaction of hydrobromic and bromic acids (W. Judson and J. W. Walker, T., 1898, **73**, 410), the bromination of benzene (L. Bruner, *Zeitsch. physikal. Chem.*, 1902, **41**, 513), and the decomposition of potassium chlorate at 395° (J. Scobai, *Zeitsch. physikal. Chem.*, 1903, **44**, 319). Of these reactions the first and second appear to be fairly straightforward, although it should be noted that the decomposition of hydrochloric and chloric acids appears to be of the eighth order, which is to be explained on the assumption that the reaction depends on the ions of the respective acids (R. Luther and F. H. MacDougall, *Zeitsch. physikal. Chem.*, 1908, **62**, 199):

The bromination of benzene and the decomposition of potassium chlorate are attended by side-reactions, so that an addition to the known number of quadrimolecular reactions appears desirable.

Our attention was called to the reaction between ferric salts and sodium thiosulphate in working out a method for estimating the relative amounts of ferrous and ferric iron present in a solution containing considerable quantities of organic matter (*Analyst*, 1912, **37**, 179). The presence of organic matter precluded the use of permanganate or dichromate for oxidation of the ferrous iron; reduction of the ferric iron with stannous or titanous chlorides was equally undesirable on account of the well-known behaviour of these reagents towards easily reducible organic substances. The use of sodium thiosulphate as a reducing agent for the ferric salts offered a possible solution of the difficulty, and eventually satisfactory results were obtained in so far as the estimation of the iron in the two states of oxidation was concerned. At the same time our attention was drawn to the slowness of the reaction between certain ferric compounds and thiosulphates, so that we considered it advisable to measure the rate of reaction and determine the velocity constants in certain cases.

A ferric salt on reduction with a thiosulphate ought to behave as if the reaction were of the fourth order in accordance with the equation:

although the possibility of an apparently bimolecular reaction is not excluded if the reaction takes place in two successive stages:

the second stage being more rapid than the first.

Anomalies are occasionally found in reduction by thiosulphates; thus the reaction between hydrogen peroxide and thiosulphates in acid solution:

is apparently bimolecular; as an explanation the separation of electrically neutral S_2O_3 has been given (Emil Abel, *Monatsh.*, 1907, **28**, 1239).

Whilst the reduction of salts like ferric chloride is too rapid for determination of the velocity of the reaction, ferric alum and solutions containing thiocyanates, phenol, etc., were found to be measurable; the reactions were always of the fourth order, and consequently one may conclude that it is necessary that four molecules or ions react simultaneously and the transient existence of ions, $\text{S}_2\text{O}_3'$, is excluded. The constancy of the "constants" determined leaves much to be desired, but when it is borne in mind that the reaction between *N*/80-solutions of iron (as ferric alum) and sodium thiosulphate is half completed in about eleven minutes at 0°, it will be seen that the experimental work is not of the easiest; whilst the choice of 0° instead of 25° for carrying out the reaction, and the abandonment of attempts to measure the velocities of the reactions between sodium thiosulphate and ferric chloride or of ferric solutions to which only 3 molecules of potassium thiocyanate had been added per atom of iron, will occasion no surprise. The velocities actually determined were those of the reactions between *N*/80-sodium thiosulphate and *N*/80-ferric alum alone or with addition of 4 or 12 molecules of potassium thiocyanate, 4 molecules of phenol, or 4 molecules of ethyl acetoacetate. In all these cases there was no doubt that the reaction was of the fourth order; calculation showed that any other order of reaction was excluded.

EXPERIMENTAL.

Stock solutions were made of ammonia iron alum and sodium thiosulphate. The former contained 2.7925 grams of iron per litre, and was made by weighing out an exact amount of the alum in which the iron had been gravimetrically estimated. (Found, 11.65 and 11.62. Theory, 11.58.) The sodium thiosulphate was *N*/40 (6.2055 grams per litre). In carrying out a measurement, all solutions were cooled to 0°, 25 c.c. of the iron solution were trans-

ferred to a flask previously cooled, 25 c.c. of water or of a solution of thiocyanate, phenol, etc., added; then 50 c.c. of the thiosulphate solution, and the time noted. Samples of 10 c.c. were withdrawn at intervals of about 2 minutes, and transferred to flasks containing excess of solution of disodium phosphate and sodium acetate; both ferrous and ferric salts were thus precipitated, and further reaction of the ferric salt with the thiosulphate prevented. After addition of starch the remaining thiosulphate was titrated with $N/80$ -iodine; the number of c.c. used, subtracted from 10, gave the number of c.c. of thiosulphate which had already reacted with the ferric solution. No inconvenience was caused by the presence of the phosphates of iron. The units employed in calculating the reaction constants from the formula for a quadrimolecular reaction:

$$k = \frac{1}{t} \cdot \frac{1}{3} \left\{ \frac{1}{(a-x)^3} - \frac{1}{a^3} \right\}$$

are arbitrary. $a=10$ (that is, the number of c.c. of reacting mixture withdrawn for each titration); $a-x$ is then given directly by the number of c.c. of iodine used in titrating the unused thiosulphate. The constants recorded must be multiplied by 80^3 if the results are desired for normal solutions (1 c.c. being still the unit of volume).

(i) *Ferric Alum and Thiosulphate.*

25 C.c. $N/20$ -ferric alum solution, 25 c.c. distilled water,
50 c.c. $N/40$ -sodium thiosulphate.

$$t = \text{seconds, } a = 10, k = \frac{1}{t} \cdot \frac{1}{3} \left\{ \frac{1}{(a-x)^3} - \frac{1}{a^3} \right\}.$$

I.			II.		
t .	$a-x$.	k .	t .	$a-x$.	k .
133	7.69	0.3007×10^{-5}	113	7.95	0.2920×10^{-5}
279	6.50	0.3156	248	5.78	0.2970
402	5.82	0.3375	374	5.93	0.3382
529	5.58	0.2997	516	5.40	0.3457
646	5.02	0.3563	663	5.00	0.3511
804	4.69	0.3603	819	4.69	0.3539
954	4.39	0.2385	1017	4.23	0.4005
1078	4.14	0.4047	1128	4.18	0.3646
1257	3.95	0.4039			
Mean.....		0.3365×10^{-5}	Mean.....		0.3419×10^{-5}

Mean of both series, 0.3392×10^{-5} .

(ii) *Ferric Alum, Potassium Thiocyanate, and Thiosulphate.*

In the first experiments made on the rate of reaction of solutions of ferric thiocyanate (iron alum and potassium thiocyanate), an

attempt was made to follow the course of the reaction colorimetrically. Although the results obtained furnished no useful constants, it was found that whilst the reaction proceeded rapidly when only three molecular proportions of potassium thiocyanate were added per atom of ferric iron, the rate of reduction by sodium thiocyanate was greatly reduced when the potassium thiocyanate was added in considerable excess to the ferric solution. The results obtained with 4 and 12 molecules of potassium thiocyanate per atom of iron are recorded.

(iia) $1\text{Fe}:4\text{KCNS}:1\text{Na}_2\text{S}_2\text{O}_3$.

25 C.c. $N/20$ -ferric alum, 25 c.c. $4N/20$ -KCNS,
50 c.c. $N/40$ -sodium thiosulphate.

t .	$a-x$.	k .	t .	$a-x$.	k .	t .	$a-x$.	k .
129	4.66	2.295×10^{-5}	129	4.55	2.485×10^{-5}	144	4.45	2.395×10^{-5}
249	3.65	2.620	265	3.60	2.571	289	3.45	2.693
374	3.05	3.055	402	3.09	2.727	483	2.91	2.731
504	2.86	2.232	534	2.81	2.812	659	2.67	2.608
613	2.67	2.802	649	2.60	2.871	858	2.46	2.572
760	2.43	3.012	783	2.49	2.715	1008	2.26	2.839
907	2.31	2.945	929	2.32	2.837	1174	2.19	2.673
1095	2.19	2.868	1098	2.19	2.860	1388	1.99	3.021
1220	2.19	2.574	1224	2.11	2.938	1550	1.93	2.969
Mean...		2.712×10^{-5}	Mean...		2.757×10^{-5}	Mean ..		2.722×10^{-5}

Mean of three series, 2.730×10^{-5} .

It will be seen that the reaction is half completed in about two minutes, and great constancy of k is not to be expected.

(iib) $1\text{Fe}:12\text{KCNS}:1\text{Na}_2\text{S}_2\text{O}_3$.

25 C.c. $N/20$ -ferric alum, 25 c.c. $12N/20$ -KCNS,
50 c.c. $N/40$ -sodium thiosulphate.

t .	$a-x$.	k .	t .	$a-x$.	k .
109	7.40	0.4492×10^{-5}	268	6.05	0.4438×10^{-5}
262	6.09	0.4262	451	5.35	0.3993
394	5.50	0.3331	563	4.91	0.4211
494	5.22	0.4069	698	4.69	0.4151
613	4.91	0.4056	809	4.42	0.4343
783	4.64	0.3836	958	4.28	0.4092
1019	4.33	0.3707	1090	4.09	0.4165
1124	4.09	0.3622	1225	3.96	0.4110
1270	3.92	0.4096			
Mean.. ..		0.3945×10^{-5}	Mean.....		0.4188×10^{-5}

Mean of both series, 0.4066×10^{-5} .

(iii) *Ferric Alum, Phenol, and Sodium Thiosulphate.*

25 C.c. *N*/20-ferric alum, 25 c.c. 4*N*/20-phenol solution,
50 c.c. *N*/40-sodium thiosulphate.

<i>t.</i>	<i>a - x.</i>	<i>k.</i>	<i>t.</i>	<i>a - x.</i>	<i>k.</i>
109	7.91	0.3120×10^{-5}	253	6.69	0.3083×10^{-5}
258	6.51	0.3390	398	5.79	0.3477
409	6.17	0.2656	609	5.09	0.3604
533	5.53	0.3074	779	4.71	0.3660
644	5.10	0.3384	933	4.40	0.3835
785	4.71	0.3631	1075	4.35	0.2815
929	4.47	0.3658	1349	3.86	0.4049
1060	4.30	0.3640	1414	3.88	0.3631
1163	4.06	0.4032			
Mean.....		0.3398×10^{-5}	Mean... ..		0.3519×10^{-5}

<i>t.</i>	<i>a - x.</i>	<i>k.</i>	<i>t.</i>	<i>a - x.</i>	<i>k.</i>
194	7.19	0.2906×10^{-5}	132	7.80	0.2796×10^{-5}
332	6.21	0.3189	268	6.55	0.3184
493	5.68	0.2995	407	5.75	0.3488
614	5.12	0.3501	537	5.30	0.3548
738	5.09	0.2974	674	5.00	0.3461
909	4.48	0.3710	823	4.66	0.3602
1038	4.33	0.3634	982	4.46	0.3485
1227	3.96	0.4103	1108	4.28	0.3536
1359	3.85	0.4053	1252	4.03	0.3800
Mean		0.3452×10^{-5}	Mean.....		0.3322×10^{-5}

Mean of four series, 0.3423×10^{-5} .

(iv) *Ferric Alum, Ethyl Acetoacetate, and Sodium Thiosulphate.*

25 C.c. *N*/20-ferric alum, 25 c.c. 4*N*/20-ethyl acetoacetate, and
50 c.c. *N*/40-sodium thiosulphate.

Considerable difficulty was at first experienced in titrating with *N*/80-iodine, probably on account of reaction of the halogen with the acetoacetate. Mr. A. D. Mitchell suggested that considerable dilution and addition of excess of potassium iodide might obviate the difficulty, and, using this suggestion, fair results were obtained.

<i>t.</i>	<i>a - x.</i>	<i>k.</i>	<i>t.</i>	<i>a - x.</i>	<i>k.</i>	<i>t.</i>	<i>a - x.</i>	<i>k.</i>
119	8.44	0.1860×10^{-5}	164	7.31	0.3172×10^{-5}	128	7.78	0.2925×10^{-5}
303	6.45	0.3000	449	5.91	0.2886	302	6.40	0.3106
508	5.47	0.3353	593	5.24	0.3340	444	5.91	0.2886
1025	5.02	0.2694	738	4.99	0.2970	599	5.26	0.3279
1215	4.28	0.3226	1079	4.54	0.2990	952	4.75	0.2918
1408	4.08	0.3244	1255	4.01	0.3854	1322	4.09	0.3434
1644	4.01	0.2943	1395	3.79	0.4248	1457	4.02	0.3293
Mean ..		0.2903×10^{-5}	Mean...		0.3381×10^{-5}	Mean...		0.3120×10^{-5}

Mean of three series, 0.3135×10^{-5} ,

(v) *Other Ferric Compounds.*

Originally it was intended to determine velocity constants for ferric solutions to which other substances than those mentioned above had been added. The homologues of phenol proved to be insufficiently soluble in water and ferric solutions to which four molecular proportions of sodium acetate had been added, whilst reacting slowly, proved quite useless owing to deposition of basic ferric acetate.

The results with acetylacetone were interesting. Solutions containing ferric alum and acetylacetone are very slowly decolorised by sodium thiosulphate; our expectation of measuring the velocity constant with ease was disappointed, for it was found that such solutions were not immediately precipitated by a mixture of sodium phosphate and acetate.

Conclusions.

The comparatively slow reduction of ammonia ferric alum as compared with ferric chloride or solutions of ferric thiocyanate containing only a small excess of potassium thiocyanate, point to the iron being present as part of a complex negative ion in such solutions. These ions might arise by dissociation of the ammonium ferrisulphate in one of the two following ways:

or

Since the reaction is quadrimolecular, two complexes containing iron must react with two thiosulphate ions; hence the second ionisation scheme for the ammonium ferrisulphate appears more probable.

NOTE.—A recent paper by Vorländer (*Ber.*, 1913, **46**, 181) deals with the production of Prussian blue from a ferric salt and ferrocyanide as a time-reaction. The time taken in the production of a precipitate is explained on the ground that ferric salts form incomplete colloidal solutions; whilst this explanation may hold in the case examined by Vorländer, the retardation of many ferric reactions can be explained by the formation of complex negative ions or of very slightly dissociated complexes.

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