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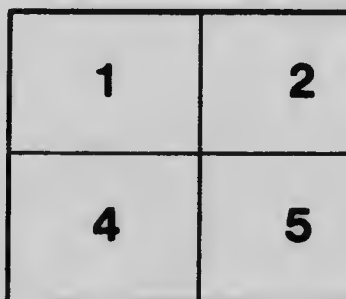to the generosity of:

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ERRIC SALTS ON THE RATE
US SALTS, by W. F. Green

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THE EFFECT OF FERRIC SALTS ON THE OXIDATION OF FERROUS SALTS AND THE CATALYTIC ACTION OF THIS

BY W. F. GREEN

Experiments carried out in this laboratory by Benson in 1902–1904[1] showed that the oxidation of ferrous sulphate by chromic acid is much retarded by the presence of ferric salts, and that the catalytic action of iron salts on the oxidation of iodides by chromic acid is likewise diminished by the same reagent.

In the hope of throwing light on this phenomenon of negative catalysis, I have studied the effect of ferric salts on the rate of oxidation of ferrous salts by chlorates and by oxygen and on the rate of oxidation of iodides by chlorates and by bromic acid in the presence of ferric salts.

I. Oxidation of ferrous chloride by potassium chlorate

The rate of this reaction has been measured, since no effect of the ferric salt on the rate is indicated by theory; direct measurements, however, were necessary to make sure.

The measurements were carried out in glass vessels, under carbon dioxide, in a thermostat at the temperature used by Noyes. The volume of the reacting solution was 100 cc in each case. The solution of ferrous chloride originally used contained 0.4148 equivalent (52.60 grams of FeCl₂) per liter, the potassium chlorate 0.500 equivalent (per liter, while the hydrochloric acid per liter, and the permanganate used in titration was per liter.

The reagents were present in almost equivalent quantities, and from the results of the measurements the "constant" K of the kinetic equation dx/dt

[1] Jour. Phys. Chem., **7**, 1, 356 (1903).
[2] Zeit. phys. Chem., **22**, 210 (1897).

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tion of iodides by chloric acid
ce of ferrous salts.

hloride by chloric acid

as been studied by Noyes;[2]
e rate is apparent in his re-
ver, were undertaken to make

ried out in stoppered bottles,
nostat at 30° C. as described
acting solution was 250 cc in
rous chloride, free of ferric,
2.60 grams $FeCl_2$) per liter;
uivalent (10.21 grams $KClO_3$)
ic acid was 1.022 normal,
itration was 0.122 normal.

in almost equivalent quan-
the measurements the "eon-
tion $dx/dt = K(A - x)^2$ was

3).

calculate., in which A represents the geometrical mean of
the numbers of equivalents of the three reagents present at
the moment $t = 0$. In order to avoid "initial disturbances,"
the time of the first analysis was taken as zero for t and for x,
the composition of the solution at that moment being calcu-
lated from the known quantities of the stock solutions used in
making it up, and the result of the first analysis.

At the head of each table is given the number of equiva-
lents of each reagent per liter at $t = 0$; under t the time from
the first titration in minutes; under "titration" the number of
cubic centimeters of permanganate used in titrating 25 cc of
the reacting solution; under D the differences from the last
column; under $x = \dfrac{0.122\ D}{25}$ the equivalents of ferrous salt
oxidized per liter; and under K the constant calculated as
explained above.

The reacting solution of Table 1 contained initially only
the trace of ferric salt forme. in the two minutes which elapsed
between the time of mixing and the first titration. The
solutions of Table 2 contained 20 grams ferric ammonium
alum per liter; that of Table 3, 40 grams of the alum; and
that of Table 4, 64 grams. The values of K are practically
the same for all; in other words the ferric salt exerts no ap-
preciable retarding influence on the rate.

TABLE I

Fe″ = 0.1169, Chl = 0.0925, Ac = 0.0947, (A = 0.1008), Fe‴ = 0

Number	T	Titration	D	x	K
1	0	23.95	—	—	—
2	13	19.10	4.85	0.0237	0.054
3	30	15.90	8.05	0.0393	0.056
4	45	14.22	9.73	0.0475	0.056
5	60	13.05	10.90	0.0532	0.058
6		11.45	12.50	0.0610	0.060

TABLE 2

$Fe'' = 0.1179$, $Chl = 0.0935$, $Ac = 0.0957$, $(A = 0.1018)$, $Fe''' = 0.0416$

Number	T	Titration	D	*r*	K
1	0	24.15	—	—	—
2	12	20.10	4.05	0.0198	0.045
3	30	16.65	7.50	0.0366	0.048
4	45	14.77	9.38	0.0458	0.051
5	60	13.48	10 67	0.0521	0.053
6	90	11.80	12.	0.0603	0.056

TABLE 3

$Fe'' = 0.1152$, $Chl = 0.0908$, $Ac = 0.0930$, $(A = 0.091)$, $Fe''' = 0.0832$

Number	T	Titration	D	*i*	K
1	0	23.60	—	—	
2	31	16.15	7.45	0.0364	0 048
3	60	13.50	10.10	0.0493	0.049
4	93	11.50	12.10	0.0591	0.057

TABLE 4

$Fe'' = 0.1145$, $Chl = 0.0901$, $Ac = 0.0923$, $(A = 0.0984)$, $Fe''' = 0.1330$

Number	T	Titration	D	*r*	K
1	0	23.45	—	—	
2	31	15.85	7.60	0.0370	0.051
3	60	13.00	10.45	0.0510	0.055
4	93	11.00	12.45	0.0608	0.063

II. Oxidation of ferrous sulphate by oxygen

This reaction was studied here by Mr. J. W. McBain in 1901.[1] I used the method of working and of analysis described by him, and his apparatus for the preparation and storage of the solution of oxygen, which was saturated with the gas at $15.5°$ C and 758 mm barome.er. The ferrous sulphate solution was freed from ferric salt by barium carbonate

[1] Jour. Phys. Chem., **5**, 623 (1901).

as described by Miss Benson;[1] it was kept under carbon dioxide and gave no red color with potassium sulphocyanate.

In every case the reacting solution contained 200 cc of 1.05 normal sulphuric acid[2] and 200 cc oxygen water per liter; the amounts of ferrous sulphate and ferric chloride in mols per liter are given at the head of each table. All experiments were carried out at 30° C.

The standard solution used for comparison in the colorimeter was made up fresh for each experiment, by mixing a solution containing 0.0966 gram $FeCl_3$ per liter of normal sulphuric acid, with its own volume of an aqueous solution of ammonium sulphocyanate containing 47.5 grams of the salt per liter.

In making an analysis, 25 cc of the reacting mixture were added to 12.5 cc of the ammonium sulphocyanate, and to this (except in the case of Table 5) 50 cc of water were added; 15 cc of the colored solution so prepared were placed in the colorimeter tube. Twenty-five cc 0.00459 normal ferric chloride thus treated matched 14 mm of the standard color if the 50 cc water had been added, 52.5 mm if it had not. In Tables 5 and 6 each analysis was made from the contents of a separate stoppered bottle; in Tables 7 and 8 samples were pipetted from a larger quantity.

In Tables 5 and 6 the differences are entered under "amount oxidized" in the last column. Their equality shows that the ferric salt has no influence on the rate. In the experiments of Tables 7a and 8a, immediately before the second analysis, ferric chloride was added to the reacting solution in such quantity that the amount added per liter was equal to the amount added per liter to the solutions of 7b and 8b respectively at the beginning of the experiment. The agreement between the results of the last three analyses in Tables 7a and b and 8a and b respectively shows that the presence of ferric chloride during the first seventeen hours of the reaction had no effect on the rate.

[1] Jour. Phys. Chem., **7**, 5 (1903).
[2] Except Table 5B where 250 cc acid was used.

TABLE 5

	5(a)					5(b)			
	$Fe''' = 0$, $Fe'' = 0.229$					$Fe''' = 0.0119$, $Fe'' = 0.229$			
No.	Time Hrs.	Min.	Reading in mm.	Amount oxidized	No.	Time Hrs.	Min.	Reading in mm.	Amount oxidized
1	0	07	5.0	—	1	0	07	7.5	—
2	3	02	23.5	18.5	2	3	02	27.5	20.0
3	5	33	35.5	30.5	3	5	33	36.5	29.0
4	23	25	60.0	55.0	4	23	25	59.5	52.0
5	28	06	64.0	59.0	5	28	06	68.0	60.5

TABLE 6

	6(a)					6(b)			
	$Fe''' = 0$, $Fe'' = 0.2384$					$Fe''' = 0.0119$, $Fe'' = 0.2384$			
No.	Time Hrs.	Min.	Reading in mm.	Amount oxidized	No.	Time Hrs.	Min.	Reading in mm.	Amount oxidized
1	0	08	0.0	—	1	0	07	12.0	—
2	1	50	5.0	5.0	2	1	50	16.0	4.0
3	20	00	11.0	11.0	3	20	00	21.0	9.0
4	70	25	11.5	11.5	4	70	25	23.5	11.5

TABLE 7

	7(a)				7(b)		
	No. 1, $Fe''' = 0$; No. 2, $Fe''' = 0.0238$; $Fe'' = 0.2384$				$Fe''' = 0.0238$, $Fe'' = 0.2384$		
No.	Time Hrs.	Min.	Reading in mm.	No.	Time Hrs.	Min.	Reading in mm.
1	0	03	0.0	1	0	06	17.0
2	17	30	34.5	2	17	35	34.5
3	22	54	48.5	3	22	54	48.0
4	43	15	88.0	4	43	15	89.0

TABLE 8

8(a)			8(b)		
No. 1, Fe''' = 0; No. 2, Fe''' = 0.0238; Fe'' = 0.1907			Fe''' = 0.0238, Fe'' = 0.1907		

No.	Time Hrs. Min.		Reading in mm.	No.	Time Hrs. Min.		Reading in mm.
1	0	03	0.0	1	0	04	20.0
2	17	50	41.5	2	17	50	42.0
3	22	49	49.5	3	22	49	51.0
4	43	18	68.0	4	43	18	68.0

III. Catalysis of the reaction between chloric and hydriodic acids

This reaction has been studied here by Mr. W. C. Bray in 1902–3.[1]

He found that addition of a little ferrous salt greatly accelerated the rate. I have measured the effect of ferrous and ferric salts on the rate, and also the effect of ferric salt on the catalysis by ferrous.

In my experiments I followed Bray, working in stoppered bottles under carbon dioxide at 30° C. In every case the total volume of the reacting solution was 250 cc, containing initially 50 cc of normal hydrochloric acid, 50 cc of normal potassium iodide, and 10 cc half-normal potassium chlorate (p. 389); the iron is given at the head of the tables, the unit being 55.9 grams iron (ferrous or ferric) per liter. Fifty cc were removed for analysis, and titrated with hundredth-normal thiosulphate. In calculating the constant $K = 1/t \log_{10} (A/A - x)$ the time of the first titration, made within one minute of adding the iodide, was taken as $t = 0$; the amount of this titration was subtracted from all subsequent readings before entering them in the tables, and from 50.00 to give the value of A.

The results show that the reaction is greatly accelerated by both ferrous and ferric salts; that the acceleration is practically equal for equal amounts of iron independent of its

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[1] Jour. Phys. Chem., 7, 92 (1903).

state of oxidation; and that in solutions containing both ferrous and ferric salt, the effects of the two are additive. The presence of ferrous salt in the solution of Table 12, after standing for twenty-four hours, was shown by potassium ferricyanide.

TABLES 9 AND 10

9 $Fe = 0,$					10 $Fe'' = 0.0005,$			
No.	t	$A-x$	K		No.	t	$A-x$	K
1	0.0	50.0	—		1	0.0	49.75	0 0
2	35.0	0.1	0.000034		2	35.0	48.00	0.00045
3	97.0	0.3	0.000018		3	95.0	45.00	0.00046
4	1200.0	1.52	0.000011		4	116.0	44.20	0.00044
					5	1197.0	13.80	0.00046

TABLES 11 AND 12

11 $Fe''' = 0.0005$					12 $Fe'' = 0\ 0005, \quad Fe'''' = 0\ 0005$			
No.	t	$A-x$	K		No.	t	$A-x$	K
1	0.0	44.30	—		1	0.0	44.4	—
2	30.0	43.00	0.00043		2	15.0	43.0	0 00093
3	77.0	40.30	0.00053		3	30.0	41.5	0.00098
4	90.0	39.65	0.00054		4	45 0	40.2	0.00096
5	1159.0	7.15	0 00060		5	62.0	38.9	0.00091
					6	92.0	36.6	0.00091
					7	105.0	35.3	0.00095
					8	150.0	33.2	0.00085

TABLES 13 AND 14

13 $Fe'' = 0.001$					14 $Fe''' = 0.001$			
No.	t	$A-x$	K		No.	t	$A-x$	K
1	0.0	48.40	—		1	0.0	44.50	—
2	15.0	46.95	0.00087		2	15 0	43.10	0.00093
3	30.0	45.40	0.00092		3	30.0	41.70	0.00094
4	45.0	44.00	0.00092		4	45.0	40.15	0.00100
5	62.0	42.40	0.00093		5	62.0	38 65	0 00099
6	92.0	39 90	0 00091		6	92.0	36.10	0.00099
7	105.0	38.90	0 00090		7	105.0	35.00	0.00099
8	150 0	35.45	0.00090		8	150.0	31.45	0.00101

IV. Catalysis of the reaction between bromic and hydriodic acids

This reaction has been studied here by Mr. Clark[1] in 1904-5, and I followed his method of working, mixing the iron salts with the iodide and acid before adding the bromate.

In each experiment the total volume of the reacting solution was 250 cc, containing 10 cc decinormal potassium iodide, 20 cc decinormal hydrochloric acid, and 10 cc decinormal potassium bromate (one sixtieth formula weight per liter); the iron present is given at the head of each table in formula-weights Fe (ferrous or ferric) per liter. In each experiment the temperature was 30° C, and the duration of the reaction thirty minutes. The numbers in the tables give the volume (cubic centimeters) of hundredth-normal arsenite oxidized in two or four duplicate experiments, the total reduction of the bromate corresponding to 100 cc arsenite.

Except where the presence of large amounts of ferric salt interfere with the titration, the results of the duplicates are in fair agreement; they show that, as in the case of chloric acid, equal weights of ferrous and ferric iron have the same effect on the rate, and that in mixtures as well the acceleration depends only on the total amount of iron present.

TABLE 15

$t = 30$.   Readings in cc. of n/100 sodium arsenite

No.	Fe = 0	$I^{-\prime\prime}=0.0002$ per liter	$Fe^{\prime\prime}=0.0001$ per liter	$Fe^{\prime\prime}=0.0004$ per liter	$Fe^{\prime\prime\prime}=0.0002$ per liter	$Fe^{\prime\prime}=0.0002$ $Fe^{\prime\prime\prime}=0.0001$ per liter
1	4.86	8.92	8.86	11.67	9.80	10.04
2	4.95	8.94	8.83	11.92	11.32	10.83
3	—	—	—	11.65	10.94	10.45
4	—	—	—	11.89	10.24	10.44

Conclusion

The oxidation of ferrous salt by chloric acid, and by oxygen, is not retarded by addition of ferric salt; neither is the catalytic action of ferrous salt on the oxidation of hy-

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[1] Jour. Phys. Chem., 10, 679 (1906).

driodic acid by chloric or bromic acids. The negative catalysis which ferric salts exert on the oxidation of ferrous salts by chromic acid, and on the liberation of iodine in solutions containing ferrous salt, chromic and hydriodic acids, thus stands alone.

Ferric salt is without effect on the rate of oxidation of ferrous salt by chloric acid and by oxygen. Both ferrous and ferric salts accelerate the liberation of iodine in solutions containing chloric or bromic acid and hydrogen iodide, the rate depending merely on the amount of iron present, and not on its state of oxidation.

These measurements were carried out at the suggestion of Prof. W. Lash Miller in the winter of 1904-5.

The University of Toronto,
Chemical Laboratory,
March, 1908.