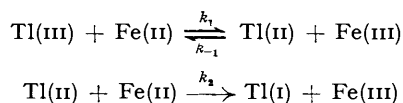


605. *The Kinetics of the Reaction between Thallium(III) and Iron(II) in Aqueous Perchloric Acid.*

By K. G. ASHURST and W. C. E. HIGGINSON.

Contrary to previous work it is shown that iron(III) retards the rate of oxidation of iron(II) by thallium(III) in aqueous perchloric acid. This is consistent with the mechanism:



The significance of the dependence of  $k_1$  and  $k_2/k_{-1}$  (reaction velocity constants) upon the hydrogen-ion concentration is discussed.

JOHNSON (*J. Amer. Chem. Soc.*, 1952, **74**, 959), investigating the kinetics of the reaction  $\text{Tl(III)} + 2\text{Fe(II)} \longrightarrow \text{Tl(I)} + 2\text{Fe(III)}$ , in dilute perchloric acid solution, showed that initially the reaction is of first order with regard to both thallium(III) and iron(II); a falling off apparent in the second-order rate plots after 60% reaction was attributed to small errors in the analytical method. The dependence of the rate upon the hydrogen-ion concentration was interpreted in terms of reaction between  $\text{TlOH}^{++}$  and  $\text{Fe}^{++}$ , and between  $\text{TlO}^+$  and  $\text{Fe}^{++}$ . Forchheimer and Epple (*ibid.*, p. 5772) used somewhat different conditions, in particular higher thallium(III) and iron(II) concentrations, in most of their experiments, and their method of analysis was different; they too noticed a decrease in

the rate of reaction after 60% reaction, but, unlike Johnson, they ascribed this effect to the presence of atmospheric oxygen, for in experiments in the absence of oxygen the effect was not observed. It is to be noted that all Johnson's experiments were done under nitrogen. In both these papers the authors concluded that the products, thallium(I) and iron(III), have no influence upon the rate of reaction, but they were unable to decide between the two most probable reaction schemes: in (i) the initial oxidation-reduction step is the 1-electron transfer reaction  $Tl(III) + Fe(II) \rightarrow Tl(II) + Fe(III)$ , followed by  $Tl(II) + Fe(II) \rightarrow Tl(I) + Fe(III)$ ; in (ii) the 2-electron transfer reaction  $Tl(III) + Fe(II) \rightarrow Tl(I) + Fe(IV)$  is the first step, followed by  $Fe(IV) + Fe(II) \rightarrow 2Fe(III)$ .

We now find that air has no significant effect upon the rate of reaction; we also conclude that in most of our experiments errors in the analysis of reaction samples are unimportant up to 90–95% reaction, and that the analytical accuracy is unaffected by alteration of the concentration of iron(III) present. Our kinetic results are summarised in the annexed Tables; the experiments in Tables 2 and 3 were performed after publication of Johnson's results, and to make comparison possible we used the same ionic strength as in his experiments.

TABLE 1.

Expt.	Initial concentrations, $M \times 10^3$				Best values, linear for ca. 93% :		With $k_2/k_{-1} = 27.0$ :		Simple plot : $k_1$ (initial % linear gradient)	
	Fe(II)	Fe(III)	Tl(I)	Tl(III)	$k_1$	$k_2/k_{-1}$	$k_1$	% linear	$k_1$	% linear
A	2.33	0.065	0.85	32.6	0.95	27.0	0.95	98	0.95	65
B	2.34	4.84	0.85	32.6	0.95	27.0	0.95	97	0.90	50
C	2.32	12.05	0.85	32.6	0.92	30.7	0.97	94	0.79	45
D	2.32	19.24	0.85	32.6	0.81	41.7	0.98	92	0.69	40
E	2.29	0.098	11.82	32.6	0.96	19.9	0.96	95	0.96	60
F	2.29	0.102	23.66	32.6	0.96	18.3	0.94	96	0.94	60
G	2.15	12.20	22.25	32.6	0.99	21.8	0.92	86	0.78	35
H	7.34	0.643	71.1	8.15	0.96	21.2	0.95	87	0.94	65
I	7.34	0.643	0.242	8.15	0.99	23.6	0.97	94	0.99	65
J	7.30	48.57	47.5	8.15	0.89	22.7	0.83	85	0.67	35
K	7.30	48.57	0.242	8.15	0.80	32.8	0.86	85	0.67	35

$[H^+] = 1.00M$ ; ionic strength = 1.60.

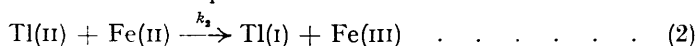
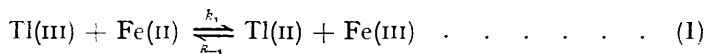
TABLE 2.

Expt.	Initial concns., $M \times 10^3$		Best values, linear for ca. 93% :		With $k_2/k_{-1} = 19.4$ :		Simple second-order plot :	
	Fe(II)	Fe(III)	$k_1$	$k_2/k_{-1}$	$k_1$	% linear	$k_1$	% linear
L	5.96	0.018	1.80	19.4	1.80	98	1.80	60
M	5.96	0.192	1.78	19.4	1.78	97	1.74	50
N	5.74	0.237	1.83	19.4	1.83	96	1.79	70
O	5.54	10.10	1.74	27.6	1.84	83	1.67	45
P	5.59	28.05	1.65	25.6	1.84	88	1.34	35
Q	5.59	48.80	1.51	28.9	1.70	84	1.14	25

$[H^+] = 0.668M$ ; ionic strength = 3.00;  $[Tl(I)] = 1.65 \times 10^{-4}M$ ;  $[Tl(III)] = 6.12 \times 10^{-3}M$ .

The results in Tables 1 and 2 show that the reaction velocity constant, obtained from the initial gradient of the simple first- or second-order plot, decreases as the initial concentration of iron(III) is increased, and the curvature of these plots becomes more pronounced. This can be seen in Fig. 1, which shows the simple second-order plots,  $\log [Fe(II)]_t/2[Tl(III)]_t$ , against  $t$ , for experiments in Table 2. The experimental conditions were similar, except that the initial concentrations of iron(III) were increased from L to Q. Increases in the initial concentration of thallium(I) have no effect on the initial gradient, but cause a small alteration in the curvature of the simple plots towards the end of the reaction. As discussed on p. 3049, this effect is due to a side-reaction affecting the accuracy of the analytical procedure, and we conclude that, over the concentration range studied, thallium(I) has no significant effect upon the rate of reaction.

Accordingly, we suggest that the overall reaction must involve the following steps :



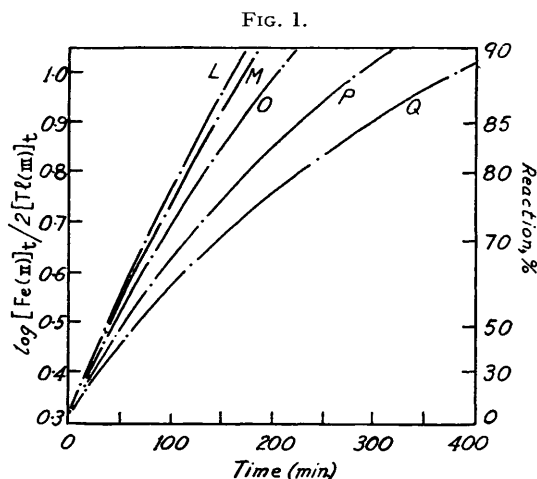
The retarding effect of iron(III) is ascribed to the reversal of reaction (1). From this reaction scheme the expression

$$d[\text{Fe(II)}]/dt = -2k_1k_2[\text{Fe(II)}]^2[\text{Tl(III)}]/\{k_2[\text{Fe(II)}] + k_{-1}[\text{Fe(III)}]\} \quad (i)$$

can be deduced by making the stationary-state assumption  $d[\text{Tl(II)}]/dt = 0$ . If  $a = [\text{Fe(II)}]_{\text{initial}}$ ,  $b = 2[\text{Tl(III)}]_{\text{initial}}$ , and  $c = [\text{Fe(III)}]_{\text{initial}}$ , integration gives:

$$\frac{k_{-1}(a+c)}{k_2 - k_{-1} \left(1 + \frac{a+c}{b-a}\right)} \cdot \frac{1}{[\text{Fe(II)}]_t} - \log_e \frac{[\text{Fe(II)}]_t}{2[\text{Tl(III)}]_t} = \frac{k_2(b-a)}{k_2 - k_{-1} \left(1 + \frac{a+c}{b-a}\right)} k_1 t + M \quad (ii)$$

a second-order kinetic equation modified by the term  $1/[\text{Fe(II)}]_t$ ,  $M$  being a constant. In first-order conditions, with thallium(III) in considerable excess over iron(II),  $(b-a)$  and  $2[\text{Tl(III)}]$  are both replaced by  $b$ . For first- or second-order conditions, if the appropriate value of  $k_2/k_{-1}$  is known, the plot of the left-hand side of (ii) against  $t$  will be linear for the whole reaction, and  $k_1$  can be found. For each experiment, a value of  $k_2/k_{-1}$  was selected



to give the best linear plot; in practice, linearity could be achieved up to about 95% of reaction. It can be seen from Tables 1 and 2 that there is much better constancy in the  $k_1$  values obtained in this way than in those obtained from the initial gradients of simple first- or second-order plots. If the reaction scheme proposed is correct, the  $k_2/k_{-1}$  value should be constant at a given temperature, hydrogen-ion concentration, and ionic strength, but the variations in this ratio from one experiment to another are fairly large. However,  $k_2/k_{-1}$  values obtained in this way appear to be very sensitive to small errors in finding the reactant concentrations towards the end of the reaction. We have therefore assumed that the  $k_2/k_{-1}$  value found at low initial concentrations of iron(III) should hold at higher concentrations, and we record for each experiment the  $k_1$  value found with this assumption, and the percentage of reaction for which the corresponding plots are linear. The constancy of the  $k_1$  values is further improved, and even in the most unfavourable cases linear plots are obtained up to 83% reaction. As examples of the various types of plot, Fig. 2 shows for experiment  $Q$  the simple second-order plot, the best straight line obtained by using the full equation (ii), and the plot obtained by using the  $k_2/k_{-1}$  value found at low initial concentrations of iron(III) (curve I).

In Fig. 3 are plotted iron(II) concentrations at different times for  $Q$  and  $Q'$ ; these experiments were similar in all respects except that one was carried out with de-aerated solutions under nitrogen, and the other in air. The corresponding reaction curve for experiment  $L$ , with a much lower initial concentration of iron(III), is also plotted. From the  $k_1$  and  $k_2/k_{-1}$  values deduced from  $L$ , the iron(II) concentrations at different times in

the first two experiments can be calculated, and the corresponding reaction curve is shown as the full line in Fig. 3. This agreement between the experimental and the calculated reaction curves for experiments Q and Q' is also found for other experiments at high initial concentrations of iron(III). This gives further indication that, within experimental error, single values of  $k_1$  and  $k_2/k_{-1}$  hold for all experiments at a given temperature, hydrogen-ion concentration, and ionic strength.

The alternative mechanism involving a 2-electron transfer first step with the formation of iron(IV) as an intermediate leads to a dependence of rate upon concentrations of the form :

$$-d[\text{Fe(II)}]/dt = 2k_3k_4[\text{Fe(II)}]^2[\text{Tl(III)}]/\{k_4[\text{Fe(II)}] + k_{-3}[\text{Tl(I)}]\} \quad \text{(iii)}$$

where  $k_3$  and  $k_{-3}$  are respectively the velocity constants for the forward and reverse reactions  $\text{Fe(II)} + \text{Tl(III)} \rightleftharpoons \text{Fe(IV)} + \text{Tl(I)}$ , and  $k_4$  is the velocity constant for the reaction  $\text{Fe(IV)} + \text{Fe(II)} \rightarrow 2\text{Fe(III)}$ .

Since we observed no retarding effect of thallium(I) upon the rate of reaction,  $k_4$  must

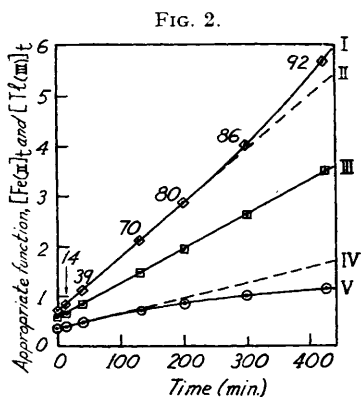


FIG. 2.  
Curve II,  $k_1 = 1.70$ ,  $k_2/k_{-1} = 19.4$ .  
Curve III,  $k_1 = 1.51$ , best line.  
Curve IV,  $k_1 = 1.14$ . Curve V,  
simple second-order plot. The  
numbers above curve I represent  
reaction, %.

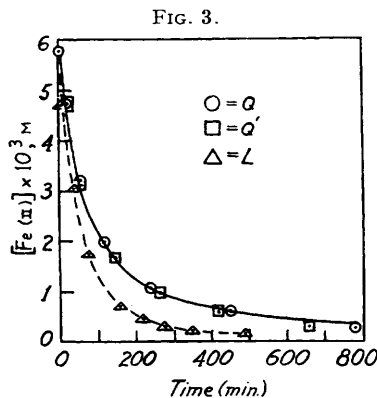


FIG. 3.

be very much larger than  $k_{-3}$  if this mechanism occurs to any extent, and in this case its contribution to the rate of removal of iron(II) would be :

$$-d[\text{Fe(II)}]/dt = 2k_3[\text{Fe(II)}][\text{Tl(III)}] \quad \text{(iv)}$$

We conclude, however, that equation (ii) without an extra term in  $k_3$  is in accord with the experimental results, and therefore we consider that these results provide good evidence that reaction proceeds through steps (1) and its reverse and (2), and that the alternative mechanism is unimportant.

*Dependence of the Velocity Constants on Hydrogen-ion Concentration.*—In Table 3 we list data from experiments at various hydrogen-ion concentrations between 0.4M and 2.8M. The concentrations of reactants are about twice as large as generally used in Johnson's experiments. Our values for  $k_1$  have been analysed in the same way as his  $k$  values, and we conclude, similarly, that this constant can be expressed by

$$K_1(k_1' + k_1''K_2/[\text{H}^+])/(K_1 + [\text{H}^+])$$

Here  $k_1'$  and  $k_1''$  correspond to Johnson's  $k_1$  and  $k_2$ , respectively,  $K_1$ , the first hydrolysis constant of  $\text{Tl}^{+++}$ , is taken as 6.4 mole l.<sup>-1</sup>, and  $K_2$  is its second hydrolysis constant (see Johnson, *loc. cit.*). We find  $k_1' = 0.85 \pm 0.02$  mole<sup>-1</sup> l. min.<sup>-1</sup> (Johnson finds  $k_1 = 0.84$ ), and  $k_1''K_2 = 0.82 \pm 0.02$  min.<sup>-1</sup> (Johnson finds  $k_2K_2 = 0.74$ ). At the low initial concentrations of iron(III) in these and Johnson's experiments there is not more than

2% difference between corrected  $k_1$  values and those taken from the initial slope of the simple second-order plot; hence the reasonable degree of agreement found between his values and ours. Since curvature was only apparent in his simple second-order plots after 60–70% of reaction, it is probable that under conditions where we have not done parallel experiments the values of  $k$  found from the initial gradients of his plots are also good values for  $k_1$ .

With regard to Johnson's conclusions about the nature of the reacting species, the form of the variation of  $k_1$  with the hydrogen-ion concentration indicates only that the reaction between thallium(III) and iron(II) can take two paths involving the formation of two transition complexes, the one including  $\text{Tl}^{+++}$ ,  $\text{Fe}^{++}$ , and  $\text{OH}^-$ , and the other including  $\text{Tl}^{+++}$ ,  $\text{Fe}^{++}$ , and  $2\text{OH}^-$ . Thus, for example, reaction between  $\text{Tl}^{+++}$  and  $\text{FeOH}^+$  cannot be distinguished from that between  $\text{TlOH}^{++}$  and  $\text{Fe}^{++}$ , and it is incorrect therefore to identify  $k_1'$  and  $k_1''$  with reactions between specific ions.

TABLE 3.

Expt.	Initial concns., $\text{M} \times 10^3$			Best values,			Simple second-order plot:	
	Fe(II)	Fe(III)	$[\text{H}^+]$ , M	$k_1$	$k_2/k_{-1}$	% linear	$k_1$	% linear
R	8.62	1.357	0.40	2.74	16.2	96	2.80	45
S	9.06	0.913	0.668	1.89	23.6	98	1.86	60
T	9.06	0.913	1.00	1.45	30.8	98	1.43	60
U	9.06	0.913	1.50	1.10	45.2	98	1.10	65
V	8.73	1.245	1.50	1.09	45.2	96	1.09	70
W	9.06	0.913	2.00	0.94	50.0	98	0.92	75
X	8.62	1.357	2.40	0.86	58.2	95	0.86	60
Y	8.73	1.245	2.80	0.82	63.8	98	0.82	55

ionic strength = 3.00;  $[\text{Tl(I)}] = 2.95 \times 10^{-4}\text{M}$ ;  $[\text{Tl(III)}] = 1.018 \times 10^{-2}\text{M}$ .

In Table 3, values of  $k_2/k_{-1}$  are also tabulated for each experiment. The accuracy of these values is about  $\pm 6\%$ ; within this limit the dependence upon hydrogen-ion concentration can be expressed as  $k_{-1}/k_2 = 0.0215/[\text{H}^+] + 0.0090$ . If it is assumed that  $k_{-1}$  is likely to show a similar type of dependence on the hydrogen-ion concentration to  $k_1$ , since both apply to reaction between a trivalent and a bivalent metal ion, then

$$k_{-1} = (k_{-1}' + k_{-1}''/[\text{H}^+]) / (K_3 + [\text{H}^+])$$

$K_3$ , by analogy with the forward reaction, is the first hydrolysis constant of  $\text{Fe}^{+++}$ , and if it is small compared with the hydrogen-ion concentration, the above equation becomes  $k_{-1} = (k_{-1}' + k_{-1}''/[\text{H}^+]) / [\text{H}^+]$ . The form of the experimental dependence of  $k_{-1}/k_2$  on the hydrogen-ion concentration can now be obtained if it is assumed that the rate of the reaction between thallium(III) and iron(II) depends inversely on the hydrogen-ion concentration, *i.e.*, if  $k_2 \propto 1/[\text{H}^+]$ . There are of course numerous ways in which  $k_{-1}$  and  $k_2$  can vary with  $[\text{H}^+]$  and give the observed dependence of  $k_{-1}/k_2$ ; the above assumptions seem to be the most reasonable. The accuracy with which the values of  $k_2/k_{-1}$  have been determined is such that it is permissible to neglect  $K_3$  compared with  $[\text{H}^+]$  provided  $K_3 \gg 0.1$  mole  $\text{l}^{-1}$ . This constant was determined by a spectrophotometric method at  $25^\circ$  and ionic strength 3.00, and shown to be approximately 0.003 mole  $\text{l}^{-1}$ .

#### EXPERIMENTAL

*Stock Solutions.—Thallium(III) perchlorate.* Thallium(I) chloride was precipitated from "AnalaR" thallium(I) sulphate, and recrystallised from water. It was oxidised in suspension in dilute hydrochloric acid by potassium bromate, the solution filtered, and thallium(III) oxide precipitated with ammonia. This precipitate was washed free from chloride ions, and dissolved in excess of 60% "AnalaR" perchloric acid, and the solution filtered and diluted with water to 2M with respect to acid. Total thallium in the solution was determined by reduction of thallium(III) by sulphur dioxide to thallium(I), followed by titration against potassium iodate in 6M-hydrochloric acid solution. Thallium(I) present initially was found by a similar titration on the original solution; thallium(III) was found by difference. The solution was standardised at intervals, but was fairly stable.

Thallium(I) perchlorate was obtained from pure thallium(I) nitrate by fuming with excess of 60% perchloric acid, and recrystallised three times from water. A stock solution was made up by weight, and checked by titration against potassium iodate.

Iron(II) perchlorate solution in dilute perchloric acid was prepared by dissolving Hilger's "H.H.P." iron turnings in excess of dilute perchloric acid. The solution was frequently standardised against potassium dichromate, with *N*-phenylanthranilic acid as indicator. Iron(III) present was obtained by subtracting the iron(II) concentration from that of total iron, calculated from the weight of metal used.

Iron(III) perchlorate solution was prepared from the iron(II) perchlorate solution by oxidation with excess of concentrated hydrogen peroxide solution.

Sodium perchlorate solution was prepared by neutralising "AnalaR" perchloric acid with "AnalaR" sodium hydroxide and filtering.

*Procedure.*—The reaction was followed by determining the iron(II) concentration in the reaction mixture at intervals. Samples of the reaction mixture were quenched in excess of cerium(IV) ammonium sulphate solution, followed by back-titration to the ferroin end-point with iron(II) ammonium sulphate solution. 0.01M- and 0.004M-Solutions of these reagents were used as required and were prepared by dilution from 0.1M-stock solutions. The diluted iron(II) solutions were standardised potentiometrically against a standard potassium dichromate solution, and the corresponding cerium(IV) solutions were then standardised against these iron(II) solutions by use of ferroin. These diluted iron(II) and cerium(IV) solutions slowly decreased in strength and were frequently restandardised.

The accuracy of the determination of iron(II) in the reaction samples was determined in independent experiments under similar experimental conditions. It was shown that the presence of thallium(I) and thallium(III) does not affect the ferroin end-point when the excess of cerium(IV) is titrated with iron(II). The end-point was improved by addition of sulphuric acid to make the solution 0.5M in this acid before commencement of the back-titration; the ferroin indicator also seemed to be more stable when this amount of sulphuric acid was used. In such solutions a very slow oxidation of thallium(I) by cerium(IV) occurs. The excess of cerium(IV) was therefore kept small, and the reaction sample back-titrated within 10 min. of being quenched. Under these conditions errors were as stated below except in experiments at high ( $>10^{-2}$ M) thallium(I) concentrations, where the appropriate first- or second-order plots were similar to those for the corresponding experiments at low thallium(I) concentrations but showed an apparent decrease in rate after 85–90% of reaction. This was consistent with the expected over-consumption of cerium(IV) owing to the oxidation of thallium(I). It was concluded that, with the exception mentioned, the concentration of iron(II) in the reaction solution could be determined to  $\pm 10^{-5}$ M, an error of about  $\pm 20\%$  of the total iron(II) concentration at 98% reaction. Systematic errors, if present, were within these error limits. In most kinetic experiments a titration was taken at 98–100% reaction. Even in the presence of large concentrations of the products the reaction appeared to go to completion.

All kinetic experiments were done at  $25.0^\circ \pm 0.05^\circ$  in 500-ml. glass-stoppered flasks. The initial volume of the reaction solutions was from 100 to 250 ml., and 10, 20, or 25 ml. samples were taken as appropriate. Several experiments were repeated under nitrogen, de-aerated solutions being used; no significant difference was observed between these experiments and duplicates carried out in air. An experiment in absence of light gave results identical with those of a duplicate in daylight. Most experiments were therefore done in air and without precautions to keep out light. In all cases sodium perchlorate solution was used to make up the ionic strength to the values quoted. The amount of chloride ion in the reaction solutions at ionic strength = 3.00 was not greater than  $2.5 \times 10^{-4}$ M; experiments showed that concentrations of chloride ion of this magnitude have negligible effects on the rate of reaction. At chloride-ion concentrations of the same order as the reactant concentrations we observed similar retardation phenomena to those described by Forchheimer and Eppe (*loc. cit.*), and we believe their explanation to be essentially correct.

We thank Mr. J. C. Stocks for assistance in the early stages of this investigation.