THE REACTION OF POTASSIUM PERSULPHATE WITH THIOGLYCOLIC ACID IN AQUEOUS SOLUTION[1]

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ABSTRACT

The oxidation of thioglycolic acid to dithiodiglycolic acid by potassium persulphate in aqueous solution in the absence of iron did not yield reproducible results, but satisfactory data were obtained when ferrous or ferric ions were added to the system. The catalyst cycle appears to be that ferrous ion is oxidized by persulphate to ferric ion, and the ferric ion is reduced back to ferrous ion by thioglycolic acid. In the absence of persulphate, the reaction of ferric ion with thioglycolic acid in acid solution ($pH < 3$) was second order in both ferric ion and thioglycolic acid concentrations and was markedly inhibited by hydrogen ion.

INTRODUCTION

The rate-controlling step in the thermal decomposition of persulphate ion in aqueous solution has been postulated to be the first-order homolytic dissociation of persulphate to yield sulphate ion radicals (1, 2, 3).

$$S_2O_8^{=} \rightarrow 2SO_4^{\overset{.}{-}}$$

The addition of organic compounds to solutions of persulphate in general increases the rate of decomposition of the persulphate ion, but the mechanisms of many of these reactions are not well understood (2, 4, 5, 6, 7).

The reactions of potassium persulphate with alkyl mercaptans in glacial acetic acid – water solution have been discussed in a previous paper from this laboratory (4). Secondary salt effects were observed which tended to make interpretation of the results difficult, but it seemed that persulphate decomposed unimolecularly to yield two sulphate ion radicals which either reacted with the mercaptan or recombined in a solvent "cage".

For the decomposition of persulphate ion in the presence of certain other organic compounds, e.g. methanol and hydrazobenzene, no evidence for the existence of a solvent cage has been found (2, 5, 6). Furthermore, it has been postulated that the sulphate ion radicals in these reaction mixtures were produced by direct reaction between persulphate ion and the organic compound rather than by unimolecular decomposition of persulphate ion (2, 5), though for the persulphate–methanol reaction there is now doubt that this view is correct (6).

The present investigation was planned originally with the intention of obtaining more information about the reactions of persulphate ion with organic compounds, particularly those containing the sulphydryl group. Thioglycolic acid was chosen to permit experiments in aqueous solution, hence avoiding the difficulties encountered in the earlier investigation (4).

Preliminary experiments (8), which will not be described, indicated that 2 moles of thioglycolic acid were oxidized by 1 mole of persulphate to yield 1 mole of dithiodiglycolic acid, but measurements of the reaction rate were quite erratic. Reproducible data were obtained, however, in the presence of soluble iron salts as catalyst, and it was decided to investigate this catalyzed reaction.

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EXPERIMENTAL

Fisher "purified" thioglycolic acid was distilled rapidly at 8 mm Hg and 95° C, and the distillate was stored at 0° C under an atmosphere of nitrogen (9). Its purity was estimated to be 99.5% by diluting weighed quantities with water and titrating these with standard iodine solution, using starch as the indicator.

The other materials employed in this investigation, which were supplied by Brickman and Company, Montreal, were of reagent grade and were used as received.

Either ferrous or ferric ammonium sulphate was used to catalyze the reaction. The ionic strength of the reaction mixture was adjusted by adding potassium sulphate, sulphuric acid, or mixtures of the two. In calculating the ionic strength, allowance was made for the incomplete dissociation of KSO_4^- and HSO_4^- ions (10, 11).

Both the standardized solutions of the reactants and the reaction mixtures were prepared with laboratory distilled water. Prior to mixing, the reactant solutions were swept with nitrogen (99.9%) which was saturated with water vapor and used without further purification. The reaction mixtures were swept with moist nitrogen while experiments were in progress at 24.8±0.02° C.

The progress of the reaction was determined by transferring aliquots from the reaction mixture to 25 ml of approximately 20% phosphoric acid and estimating the thioglycolic acid content by titration with a standard solution of iodine in a solution of potassium iodide. The phosphoric acid, by complexing the ferric ion, served to slow the reaction and to prevent possible complications in the subsequent titration with iodine. Reaction of persulphate with iodide ion during the iodimetric titration was found to be negligible.

For experiments in 0.15 *M* sulphuric acid, both the progress of reaction and the concentration of ferric ion were determined by periodically removing aliquots from the reaction mixture and recording their ultraviolet spectra for wavelengths up to 400 mμ. From the data in Table I it may be inferred that appreciable complex formation did not occur between any of the components present in the reaction mixtures. The concentration of ferric ion in reaction mixtures was estimated from the optical density measured at 325 mμ. The optical densities at lower wavelengths were then corrected for the contri-

TABLE I

Optical density of aqueous solutions of the components and of various mixtures of the components present in the iron-catalyzed persulphate - thioglycolic acid reaction mixtures (sulphuric acid 0.15 M/l. (mole/liter))

Composition of solution	Optical density						
	D330	D310	D290	D270	D250	D230	D210
A. Pure components							
8.02×10^{-4} *M* $S_2O_8^=$				0.005	0.026	0.089	0.367
0.955×10^{-3} *M* TSH				0.005	0.088	0.250	0.722
1.00×10^{-3} *M* TSH				0.005	0.075	0.240	0.783
1.91×10^{-3} *M* TSH				0.012	0.162	0.479	
1.00×10^{-4} *M* TSST				0.024	0.098	0.189	0.331
4.00×10^{-4} *M* Fe^{++}					0.010	0.018	0.020
4.45×10^{-5} *M* Fe^{+++}	0.069	0.110	0.102	0.087	0.157	0.235	0.230
8.00×10^{-5} *M* Fe^{+++}	0.134	0.199	0.185	0.160	0.276	0.408	0.415
B. Mixtures of components							
8.02×10^{-4} *M* $S_2O_8^-$ and 1.91×10^{-3} *M* TSH				0.022	0.190	0.572	
8.02×10^{-4} *M* $S_2O_8^-$ and 4.45×10^{-5} *M* Fe^{+++}	0.069	0.113	0.109	0.098	0.185	0.330	0.630
4.00×10^{-4} *M* Fe^{+++} and 0.955×10^{-3} *M* TSH				0.005	0.103	0.272	0.754
1.00×10^{-4} *M* TSST and 1.00×10^{-3} *M* TSH				0.035	0.184	0.450	
1.00×10^{-4} *M* TSST and 4.00×10^{-4} *M* Fe^{++}				0.028	0.118	0.219	0.364
1.00×10^{-4} *M* TSST and 8.00×10^{-5} *M* Fe^{+++}	0.134	0.199	0.209	0.185	0.386	0.830	0.827

bution by ferric ion and, by using this corrected value, the concentrations of the remaining components in the reaction mixture at any time were calculated using the following equation,

$$[\mathrm{TSST}] = \frac{D-\epsilon_{\mathrm{TSH}}[\mathrm{TSH}]_0-\epsilon_{\mathrm{S_2O_8^=}}[\mathrm{S_2O_8^=}]_0}{\epsilon_{\mathrm{TSST}}-2\epsilon_{\mathrm{TSH}}-\epsilon_{\mathrm{S_2O_8^=}}}$$

where D represents the corrected optical density, ϵ the respective extinction coefficients, and $[\mathrm{TSH}]_0$ and $[\mathrm{S_2O_8}]_0$ the initial concentrations of thioglycolic acid and persulphate respectively. The results obtained using the spectrophotometric method were in excellent agreement with those obtained using the volumetric method (Fig. 4).

RESULTS

Experiments at a pH of approximately 2 showed the reaction to be first order in the persulphate concentration and zero order in the thioglycolic acid concentration. The first-order rate constant for persulphate disappearance, k_1' in Table II, was directly proportional to the concentration of iron in the system, which indicates that, in the presence of added iron, direct reaction between persulphate and thioglycolic acid was negligible. The effect of ionic strength on the calculated second-order rate constant, $k_1 = k_1'/[\mathrm{Fe}]$, is shown in Fig. 1, and it is apparent that the rate-controlling step of the reaction consists of interaction between doubly charged ions of the opposite sign.

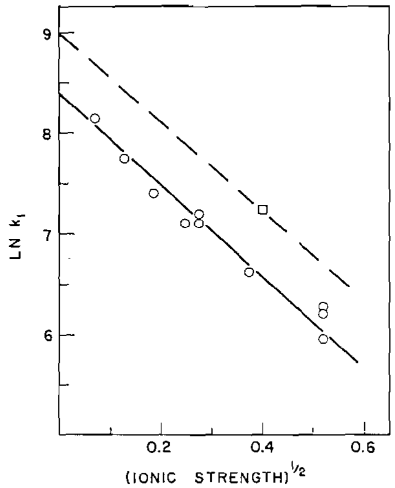


FIG. 1. Variation of the second-order rate constant, k_1, with the ionic strength: —□— see ref. (16, 17).

For reaction mixtures in which the concentration of sulphuric acid was 0.15 M and in which the iron was initially in the ferrous state, the initial rates of reaction and the first-order rate constants at zero time were functions of the initial concentrations of both the persulphate and the thioglycolic acid (Table III). Furthermore, the concentration of ferric ion reached a stationary value which increased with increasing persulphate concentration and decreased with increasing thioglycolic acid concentration (Figs. 2 and 3). Division of the rate of disappearance of persulphate in these reaction mixtures by the product of the persulphate and ferrous ion concentrations at a given instant of time yielded a second-order rate constant corresponding to k_1 which was independent of the reaction mixtures, and for which the average value (651 l. mole^{-1} min^{-1}) was in reasonable agreement with that shown in Fig. 1 at the same ionic strength. As observed

TABLE II

The effect of different initial concentrations of ferric ion, persulphate, and thioglycolic acid on the rate of disappearance of persulphate at pH $\simeq$ 2

Initial $[Fe^{+++}]$ $(\times 10^5)$	Initial $[S_2O_8^=]$ $(\times 10^3)$	Initial [TSH] $(\times 10^3)$	$[K_2SO_4]$	$[H_2SO_4]$	Ionic strength (μ)	k_1' (min^{-1})	$k_1 = k_1'/[Fe]$ $(l.\ M^{-1}\ min^{-1})$
10.0	1.60	4.50	0.00	0.10	0.269	0.0492	492
10.0	3.20	9.00	0.00	0.10	0.269	0.0492	497
10.0	6.40	13.50	0.00	0.10	0.269	0.0492	460
10.0	6.40	4.50	0.00	0.10	0.269	0.0380	380
4.0	3.19	9.72	0.0057	0.010	0.038	0.066	1650
4.0	3.19	4.86	0.0057	0.010	0.038	0.066	1650
4.0	3.19	14.94	0.0057	0.010	0.038	0.066	1650
2.0	8.00	9.40	0.0095	0.10	0.272	0.00782	391
2.0	4.00	9.40	0.0095	0.10	0.272	0.00794	397
2.0	2.40	9.40	0.0095	0.10	0.272	0.00782	391
2.0	1.60	9.40	0.0095	0.10	0.272	0.00794	397
0.8	4.00	9.35	0.0095	0.10	0.272	0.00329	410
4.0	4.00	9.35	0.0095	0.10	0.272	0.01640	410
10.0	4.00	9.35	0.0095	0.10	0.272	0.0398	398

TABLE III

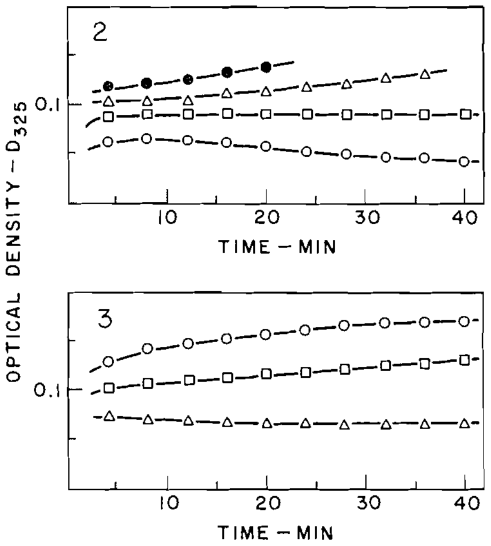
The effect of different initial concentrations of ferrous ion, persulphate, and thioglycolic acid on the rate of disappearance of persulphate in 0.15 *M* sulphuric acid (ionic strength = 0.224)

Initial $[Fe^{++}]$ $(\times 10^5)$	Initial $[S_2O_8^=]$ $(\times 10^3)$	Initial [TSH] $(\times 10^3)$	Initial $\frac{d[S_2O_8^=]}{dt}$ $(M\ l.^{-1}\ min^{-1} \times 10^5)$	Initial k_1' (min^{-1})
10.0	2.00	10.95	7.1	0.0368
10.0	4.00	10.95	15.5	0.0359
10.0	6.00	10.95	20.0	0.0320
10.0	8.00	10.95	24.0	0.0299
10.0	2.00	4.38	7.0	0.0347
10.0	4.00	4.38	12.7	0.0304
10.0	8.00	4.38	20.0	0.0253
10.0	4.00	2.18	12.1	0.0285
10.0	4.00	7.63	13.0	0.0331
10.0	4.00	15.30	13.0	0.0370
5.0	4.00	10.95	7.5	0.0161
15.0	4.00	10.95	22.0	0.0630

previously for pH$\sim$2, the initial rate of reaction extrapolated to zero when the initial concentration of ferrous ion was decreased to zero indicating that direct reaction between persulphate ion and thioglycolic acid was negligible.

When the added iron was initially in the ferric state, the reaction was preceded by an induction period, but following this induction the rate of reaction was the same as for experiments in which the iron was initially in the ferrous state (Fig. 4). The stationary-state concentration of ferric ion was independent of the valence state of the iron at zero time, although it was not attained for several minutes when the iron was initially in the ferric state. The rate of disappearance of ferric ion during the greater part of the induction period, i.e. before its concentration reached a stationary value, was not influenced by the presence of persulphate (Fig. 5).

To study the reaction between ferric ion and thioglycolic acid in sulphuric acid solutions, the disappearance of ferric ion was followed by the change in optical density at 305 mμ. The thioglycolic acid concentration was in sufficient excess over that of ferric ion to be considered independent of time. The slopes of the straight lines in Fig. 6, which show the second-order dependence of the reaction rate on the ferric ion concentration, are



FIGS. 2 AND 3. Effect of different initial concentrations of persulphate and of thioglycolic acid on the optical density at 325 mμ. Initial concn. Fe^{++} 10.0×10^{-5} M/l. Concn. H_2SO_4 0.15 M/l.

FIG. 2. Initial concn.	TSH	0.01095 M/l.
Initial concn. $S_2O_8^=$	○	0.00200 M/l.
	□	0.00400 M/l.
	△	0.00600 M/l.
	●	0.00800 M/l.

FIG. 3. Initial concn.	$S_2O_8^=$	0.00400 M/l.
Initial concn. TSH	○	0.00218 M/l.
	□	0.00763 M/l.
	△	0.01530 M/l.

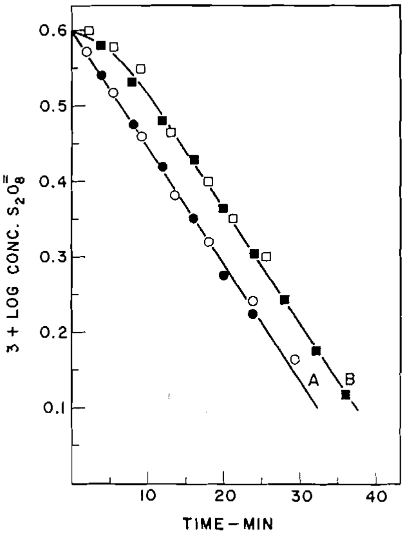


FIG. 4. Effect of the initial oxidation state of the dissolved iron on the rate of disappearance of persulphate.

A	Iron initially ferrous
B	Iron initially ferric
○, □	Iodimetric analysis
●, ■	Spectrophotometric analysis

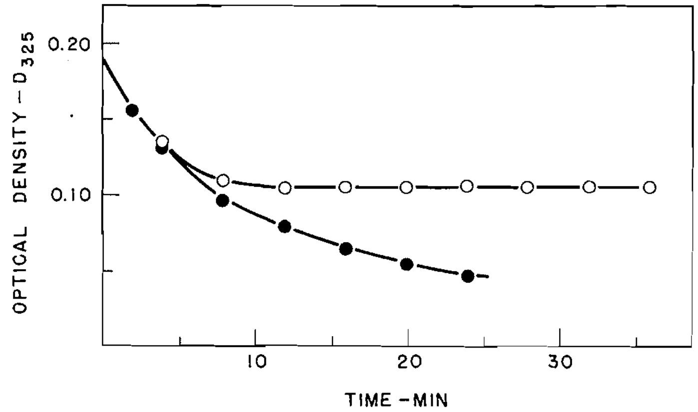


FIG. 5. The variation of optical density at 325 mμ with time when the iron was initially in the ferric state.

Initial concn. TSH 0.01085 M/l. Initial concn. $S_2O_8^{=}$ ○ 0.00400 M/l.
● 0.00000 M/l.

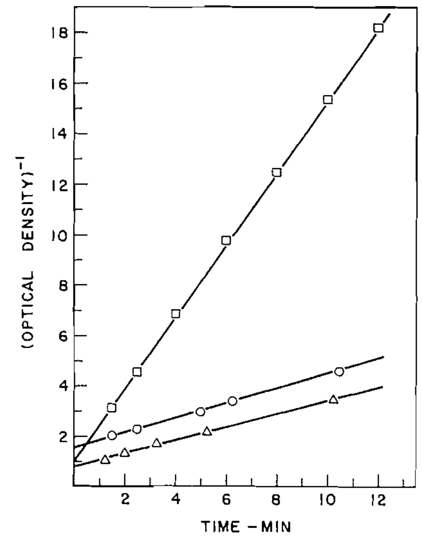


FIG. 6. Effect of different initial concentrations of thioglycolic acid on the rate of reaction between ferric ion and thioglycolic acid.

Initial concn. TSH ○ 0.00488 M/l.
□ 0.01220 M/l.
△ 0.00488 M/l.

proportional to the square of the thioglycolic acid concentration, indicating the over-all reaction to be of the fourth order. The effect of sulphuric acid concentration on the calculated fourth-order rate constant, k_4''', is shown in Table IV.

When the ferric ion and thioglycolic acid were mixed initially in these experiments, a blue complex was formed which faded rapidly as observed in earlier investigations (13, 14). However, extrapolation of the measured optical densities at 305 mμ to zero time indicated that the optical density of ferric ion was not influenced by thioglycolic acid, and hence that ferric ion – thioglycolic acid complexes were highly dissociated.

The dependence of the fourth-order rate constant on hydrogen ion concentration was

TABLE IV

Variation of k_4''', the calculated fourth-order rate constant for the ferric ion – thioglycolic acid reaction, with the concentration of sulphuric acid

$[H_2SO_4]$	k_4''' ($l.^2\ M^{-2}\ min^{-1} \times 10^{-6}$)
0.050	242
0.100	27.6
0.150	10.3

determined more exactly by making experiments at various levels of perchloric acid when the ionic strength of the reaction mixtures was adjusted to 1.00 with sodium perchlorate. The reaction was followed by periodically removing aliquots of the reaction mixture and estimating the ferric ion content colorimetrically as the thiocyanate complex (12). Again the thioglycolic acid concentration was in sufficient excess over that of ferric ion to be effectively independent of time. The fourth-order rate constant, k_4', was found to be inversely proportional to approximately the fourth power of the hydrogen ion concentration (Fig. 7). Low concentrations of sulphate ion in these reaction mixtures also caused inhibition (Table V).

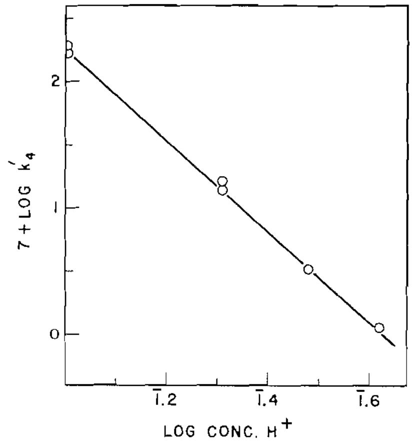


FIG. 7. Effect of perchloric acid concentration on k_4'.

TABLE V

Effect of sulphuric acid concentration on the fourth-order rate constant, k_4'' (ionic strength = 1.00)

$[HClO_4]$	$[H_2SO_4]$	$[SO_4^{=}]$	$[H^+]$	k_4'' ($l.^2\ M^{-2}\ min^{-1} \times 10^{-7}$)	k_4' ($l.^2\ M^{-2}\ min^{-1} \times 10^{-7}$)
0.101	0.0098	0.0070	0.118	63.8	110
0.101	0.0098	0.0070	0.118	71.4	110
0.101	0.0245	0.0170	0.143	22.1	52.5

NOTE: Values of k_4', which were interpolated from Fig. 7, were determined under identical experimental conditions except that sulphate ion was absent.

The fourth-order rate constant, k_4''', for the ferric ion – thioglycolic acid reaction was also determined by dividing the rate of formation of dithiodiglycolic acid in persulphate –

thioglycolic acid reaction mixtures by the product of the square of the ferric ion concentration and the square of the thioglycolic acid concentration. Its value in these reaction mixtures was approximately 100 times greater than that determined in systems which were identical in every way except that persulphate was absent.

A brief investigation of the reaction between persulphate ion and ferrous ion in the absence of thioglycolic acid showed (Table VI) that the reaction was second order, and that the second-order rate constants, k_1, were in good agreement with those interpolated from Fig. 1. The rate of appearance of ferric ion in these reaction mixtures was estimated from the change in optical density at 305 mμ.

TABLE VI

Comparison of second-order rate constants, k_1, for the ferrous ion – persulphate reaction with those interpolated from Fig. 1

Initial $[S_2O_8^=]$	Initial $[Fe^{++}]$	$[K_2SO_4]$	$[H_2SO_4]$	Ionic strength (μ)	k_1 (l. M^{-1} min^{-1})	k_1* (l. M^{-1} min^{-1})
7.88	10.0	0.10	0.0098	0.272	452	448
7.88	10.0	0.00	0.098	0.159	782	730
4.00	10.0	0.00	0.15	0.224	575	513
4.00	20.0	0.00	0.15	0.224	535	513
8.00	20.0	0.00	0.15	0.224	571	513

*See Fig. 1.

DISCUSSION

Thioglycolic acid in no way influenced the rate of the persulphate ion – ferrous ion reaction, whereas the presence of persulphate caused the reaction between ferric ion and thioglycolic acid to occur more rapidly. It is apparent that the catalyst cycle for the reaction between persulphate ion and thioglycolic acid, in the presence of iron, involves persulphate oxidation of ferrous ion to ferric ion, which is then reduced by thioglycolic acid to ferrous ion.

The mechanism for the reaction between persulphate ion and ferrous ion appears to be well established (15, 16, 17).

$$S_2O_8 + Fe^{++} \rightarrow Fe^{+++} + SO_4^{\dot{-}} + SO_4^{=} \qquad [1]$$

$$SO_4^{\dot{-}} + Fe^{++} \rightarrow Fe^{+++} + SO_4^{=} \qquad [2]$$

The calculated second-order rate constant, k_1, obtained in this investigation was approximately one-half that obtained by Williams *et al.* (16, 17). The difference might result from the much larger hydrogen ion concentrations (100- to 1000-fold) in the present experiments.

For the reaction between ferric ion and thioglycolic acid the results may be explained by postulating the existence of a complex containing two ferric ions and two thioglycolic acid molecules, the reaction rate being governed by the first-order decomposition of this complex. That complexes in the ferric ion – thioglycolic acid system do exist is indicated by the blue color that was produced when the two reactants were mixed initially. Lamfrom and Nielsen (14) have shown that the blue complex disappeared by a first-order process at −35° C in a solvent consisting of 6 parts by volume of ethanol to 10 parts by volume of water. It would appear, therefore, that the blue complex might well consist of two ferric ions and two thioglycolic acid molecules.

The inhibition by hydrogen and by sulphate ions suggests that mercaptide and hydrated ferric ions were the reactive species and the proposed mechanism is as follows:

$$Fe^{+++} + SO_4^{=} \rightleftarrows FeSO_4^{+}, \qquad [4]$$

$$FeSO_4^{+} + SO_4^{=} \rightleftarrows Fe(SO_4)_2^{-}, \qquad [5]$$

$$Fe^{+++} + ClO_4^{-} \rightleftarrows FeClO_4^{++}, \qquad [6]$$

$$Fe^{+++} + H_2O \rightleftarrows FeOH^{++} + H^{+}, \qquad [7]$$

$$TSH \rightleftarrows TS^{-} + H^{+}, \qquad [8]$$

$$FeOH^{++} + TS^{-} \rightleftarrows FeOHTS^{+}, \qquad [9]$$

$$2FeOHTS^{+} \rightleftarrows Fe_2(OH)_2(TS)_2^{++}, \qquad [10]$$

$$Fe_2(OH)_2(TS)_2^{++} \rightarrow 2Fe^{++} + {}^{-}TSST^{-} + 2H_2O. \qquad [11]$$

For the experiments made in the absence of sulphate ion, the following relation is obtained,

$$k_4' \,[\text{ferric}]^2\, [\text{thioglycolic acid}]^2 = \frac{k_{11}K_{10}K_9^{\,2}K_8^{\,2}K_7^{\,2}}{[H^{+}]^4}\, [Fe^{+++}]^2\, [TSH]^2 \qquad \text{(i)}$$

where [ferric] and [thioglycolic acid] represent the total concentrations of ferric ion and thioglycolic acid respectively in the reaction mixture. Owing to the relatively large concentrations of hydrogen ion used in these experiments, the concentrations of $FeOH^{++}$ and TS^{-} ions should be small (18, 19), and since complex formation between ferric and perchlorate ions occurs only to a very limited extent (20), it follows that

$$[\text{ferric}] \simeq [Fe^{+++}]$$

and

$$[\text{thioglycolic acid}] \simeq [TSH].$$

Therefore

$$k_4' = \frac{k_{11}K_{10}K_9^{\,2}K_8^{\,2}K_7^{\,2}}{[H^{+}]^4}. \qquad \text{(ii)}$$

In the presence of low concentrations of sulphate ion

$$[\text{ferric}] = [Fe^{+++}][1+K_4(SO_4^{=})]$$

and

$$k_4'' = \frac{k_{11}K_{10}K_9^{\,2}K_8^{\,2}K_7^{\,2}}{[H^{+}]^4\,[1+K_4(SO_4^{=})]^2}. \qquad \text{(iii)}$$

By combining equations (ii) and (iii),

$$K_4 = \frac{\sqrt{(k_4/k_4'')}-1}{[SO_4^{=}]}. \qquad \text{(iv)}$$

The value of K_4, the association constant of the ferric ion – sulphate complex, calculated in this manner was approximately one-half that determined by Whitekar and Davidson (21).

In the reaction mixtures which were 0.05 to 0.15 *M* in sulphuric acid, the concentration of free ferric ion may be taken as negligible (21), i.e.

$$[\text{ferric}] = [Fe^{+++}][K_4(SO_4^{=})+K_4K_5(SO_4^{=})^2]$$

and

$$k_4''' = \frac{k_{11}K_{10}K_9^{\,2}K_8^{\,2}K_7^{\,2}}{[H^{+}]^4\,[K_4(SO_4^{=})+K_4K_5(SO_4^{=})^2]^2}. \qquad \text{(v)}$$

It is interesting to note that the mechanism for the reaction between ferric ion and thioglycolic acid in weakly acidic and in alkaline solution differs markedly from that suggested here for the reaction in more strongly acidic solution (14, 22, 23).

If no account is taken of the relatively rapid ferric ion – thioglycolic acid reaction which occurred in the presence of persulphate, the following sequence of reactions may be suggested for the iron-catalyzed reaction between persulphate and thioglycolic acid:

$$\mathrm{S_2O_8 + Fe^{++} \rightarrow Fe^{+++} + SO_4 + SO_4} \tag{1}$$

$$\mathrm{SO_4 + Fe^{++} \rightarrow Fe^{+++} + SO_4} \tag{2}$$

$$\mathrm{SO_4 + TSH \rightarrow TS\cdot + HSO_4} \tag{3}$$

$$\mathrm{Fe^{+++} + SO_4^{=} \rightleftarrows FeSO_4^{+}} \tag{4}$$

$$\mathrm{FeSO_4^{+} + SO_4^{=} \rightleftarrows Fe(SO_4)_2^{-}} \tag{5}$$

$$\mathrm{Fe^{+++} + H_2O \rightleftarrows FeOH^{++} + H^{+}} \tag{6}$$

$$\mathrm{TSH \rightleftarrows TS^{-} + H^{+}} \tag{7}$$

$$\mathrm{FeOH^{++} + TS^{-} \rightleftarrows FeOHTS^{+}} \tag{8}$$

$$\mathrm{2FeOHTS^{+} \rightleftarrows Fe_2(OH)_2(TS)_2^{++}} \tag{9}$$

$$\mathrm{Fe_2(OH)_2(TS)_2^{++} \rightarrow 2Fe^{++} + {}^{-}TSST^{-} + H_2O} \tag{10}$$

$$\mathrm{2TS\cdot \rightarrow TSST} \tag{11}$$

Step [1] was rate controlling in reaction mixtures when the pH was approximately 2, but the reduction of ferric ion by thioglycolic was not rapid relative to step [1] in reaction mixtures 0.15 M in sulphuric acid. If step [2] is assumed negligible relative to [3] because of the large excess of thioglycolic acid over ferrous ion, the steady-state assumption may be applied to the concentrations of ferric and ferrous ions to yield the following relation,

$$\frac{D_{\mathrm{m}}-D}{D^2} = \frac{k_4'''}{\epsilon k_1}\,\frac{[\mathrm{TSH}]^2}{[\mathrm{S_2O_8^{=}}]} \tag{vi}$$

where D represents the optical density of the reaction mixture at 325 mμ, D_{m} the optical density if all the iron had been in the ferric state, and ϵ the extinction coefficient of ferric ion. In actual fact the results from the experiments made in 0.15 M sulphuric acid were found to fit the empirical equation,

$$\frac{D_{\mathrm{m}}-D}{D^2} = \frac{k}{\epsilon k_1[\mathrm{Fe}]^x[\mathrm{TSH}]_0}\,\frac{[\mathrm{TSH}]^2}{[\mathrm{S_2O_8^{=}}]} \tag{vii}$$

where $[\mathrm{Fe}]^x$ represents the concentration of iron in the system raised to some power x and $[\mathrm{TSH}]_0$, the initial concentration of thioglycolic acid.

Furthermore, the values of

$$\frac{k}{k_1[\mathrm{Fe}]^x[\mathrm{TSH}]_0}$$

were of the order of 100 times greater than the value of k_4'''/k_1 (Table VII), owing to the influence of persulphate ion on the ferric ion – thioglycolic reaction.

Additional steps in the reaction sequence already shown are necessary to explain, not only the marked influence of persulphate ion on the over-all rate, but also the induction period when iron was initially in the ferric state, and the lack of influence by persulphate on the rate at which ferric ion concentration is decreased to its stationary value during the induction period. A tentative proposal is that either a sulphate ion radical or a thiyl radical reacts rapidly with a ferric ion – thioglycolic acid complex,

$$SO_4^{\dot{-}} + \text{Fe (III) TSH-complex} \rightarrow Fe^{++} + H^+ + \text{TSST} + HSO_4^- \qquad [12]$$

$$\text{TS}\cdot + \text{Fe (III) TSH-complex} \rightarrow Fe^{++} + \text{TSST} + H^+. \qquad [13]$$

TABLE VII

Comparison of the calculated value of k_4'''/k_1 with the value $\dfrac{k}{k_1[Fe]^x[TSH]_0}$

Initial $[TSH]_0$ $(\times 10^3)$	$\dfrac{k}{k_1[Fe]^x[TSH]_0}$ $(\times 10^{-4})$	k_4'''/k_1 $(\times 10^{-4})$
10.95	92.3	1.85
4.36	333	1.85

In solutions in which the iron is present initially as ferric ion, free radicals will not be produced at zero time, and reactions [12] and/or [13] will not be important. Due to the production of ferrous ion, however, the persulphate – ferrous ion reaction will begin to occur, giving rise to free radicals and hence to the rapid reactions [12] and/or [13]. Therefore, during the early stages of the reaction before ferric ion and in all probability the free-radical concentrations become stationary, the rate of reduction of ferric ion by thioglycolic acid will increase with time causing a corresponding increase in the over-all reaction rate, and an induction period will result. However, when the iron is initially in the ferrous state, the sulphate ion radicals and ferric ion will be produced at zero time, and reactions [12] and/or [13] will assume an important role at the beginning.

A similar mechanism has been suggested for the uptake of oxygen by mixtures of ferric ion and thioglycolic acid in mildly acidic solution (14).

With existing information, it is extremely difficult to determine either the structure of the complex which entered into this reaction or the nature of the radical, whether sulphate ion or thiyl, which reacted with the complex. Because sulphate ion radicals may react with both ferrous ion and thioglycolic acid, the situation is even more complex, since the relative rates of these two reactions are unknown.

In conclusion, it is apparent that to investigate the uncatalyzed persulphate – thioglycolic acid reaction, as was intended originally, the concentration of dissolved iron in the reaction mixtures, and in all probability the concentration of other metallic ions, would have to be very low.

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