The Kinetics and Mechanism of the Oxidation of Chromium (III) by the Peroxodisulphate Ion

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The kinetics of the redox reaction between chromium(III) and the peroxodisulphate ion were investigated at 60°C in an acid perchlorate medium and in a mixed perchlorate-sulphate medium in the pH range 0.5 to 3. At sufficiently high concentrations of chromium(III) and of hydrogen ions, two chromium(III) ions are oxidized to chromium(VI) for every peroxodisulphate ion used up in the decomposition path that is uncatalyzed by hydrogen ions.

A reaction mechanism, consistent with the observed kinetics, is suggested. This involves both the sulphate radical-ion and the hydroxyl radical in the rate-determining step. At acidities high enough for the hydrogen-ion catalyzed decomposition to be appreciable (pH <3), some intermediate from this reaction path, too, is proved to participate in the redox reaction.

Complex formation between chromium(III) and peroxodisulphate ion reduces the over-all rate of decomposition.

The aim of the present investigation is to elucidate the mechanism of the reaction in aqueous solution of chromium(III) and peroxodisulphate ion. Apparently, no detailed study of this reaction has been previously performed, but the kinetics of the corresponding silver(I)-catalyzed reaction has been studied by Yost.[1] This latter reaction follows the general pattern exhibited by silver(I)-catalyzed oxidations involving peroxodisulphate ion (*cf.* Ref. 2, p. 195).

Since Yost's paper, the kinetics and mechanism of the thermal decomposition of peroxodisulphate ion have been extensively investigated.[2,3] The results from these studies are vital to the consideration of oxidation reactions involving peroxodisulphate ions; also, investigations of reactions between peroxodisulphate ions and various species may elucidate the mechanism of the thermal decomposition of the ion. Fronæus and Östman [4] have found that the mechanism for the oxidation of cerium(III) by peroxodisulphate ion has a rate-determining step in the uncatalyzed thermal decomposition of peroxodisulphate ions and this step is probably a bimolecular reaction with water

$$S_2O_8^{2-} + H_2O \xrightarrow{k_1} HSO_4^- + SO_4^- + OH \tag{1}$$
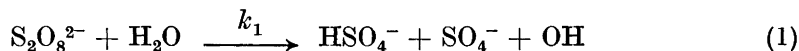
However, most investigators (e.g. Refs. 2, 5, and 6) prefer the alternative mechanism, originally proposed by Bartlett and Cotman [7] and later accepted by Kolthoff and Miller.[3] This has a homolytic dissociation of the peroxodisulphate ion

$$S_2O_8^{2-} \longrightarrow 2\ SO_4^- \tag{2}$$
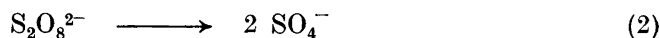
as the primary step. However, this is inconsistent with the aforementioned results,[4] which have been substantiated by recent measurements.[8]

In acid solution, the peroxodisulphate ion decomposes by two competing reaction paths, and the rate law is given by the equation [3,4]

$$-\frac{d\ [S_2O_8^{2-}]}{d\,t} = (k_1 + k_H[H^+])\ [S_2O_8^{2-}] \tag{3}$$

In the present investigation, the self-decomposition of the peroxodisulphate ion, the formation of chromium(VI), and the evolution of oxygen gas, have all been studied separately using the same experimental conditions.

The kinetic measurements may be divided into two Sections;
1. The empirical rate law is studied at a constant pH.
2. The kinetic behaviour is investigated as a function of pH.

EXPERIMENTAL

Chemicals. Chromium(III) perchlorate stock solutions were prepared by precipitating the hydroxide, dissolving in perchloric acid and reprecipitating twice. The perchloric acid ("Baker Analyzed"), sodium perchlorate, sodium sulphate, and peroxodisulphates were of analytical grade.

Analytical methods. The concentration of chromium(VI) was determined spectrophotometrically. Diluted samples of the reaction mixture were tempered at 25°C, after which the absorbance was measured with a Hilger Uvispek spectrophotometer or a Zeiss spectrophotometer (Model PMQ II). The measurements were performed at wavelength 350 nm, where chromium(VI) has an absorption maximum in the pH range covered, and where the absorption of chromium(III) gives a correction term that is almost negligible. Calibration curves were prepared using potassium dichromate solutions of similar ionic strength and hydrogen-ion concentration to the experimental solutions.

Knowing the chromium(VI) concentration, the peroxodisulphate concentration was determined by cerimetric titration. Oxygen was removed by bubbling purified nitrogen gas through the samples for 10 min. A known volume of an iron(II) sulphate solution, acidified with sulphuric acid, was then added. The chromium(VI) was reduced quickly, the peroxodisulphate, more slowly. After 20 min, dilute sulphuric acid was added, and the excess of iron(II) was back-titrated, with an acidified cerium(IV) sulphate solution, to a ferroin endpoint. The cerium(IV) was standardized against oxalate.[9] The titer of the iron(II) solution decreased by *ca.* 0.2 % per day, so it was determined every day by titration against the standard cerium(IV) solution.

Measurements. In Section 1, two solutions in separate vessels, one containing chromium(III) perchlorate and perchloric acid, and the other containing ammonium peroxodisulphate and sodium perchlorate, were brought to 60°C in a paraffin-oil thermostat. The reaction was initiated by mixing equal volumes of the two solutions, as quickly as possible, using a preheated pipette, after which the reaction vessel, a 100-ml glass-stoppered bottle ("Jena Geräteglas"), was shaken vigorously. The zero time was taken when the pipette was half-empty.

In Section 2, a solution containing chromium(III) perchlorate, perchloric acid, sodium perchlorate, and sodium sulphate was tempered in the thermostat. At zero time, a weighed amount of solid potassium peroxodisulphate was added.

At appropriate time intervals, 5-ml samples were withdrawn and added to 5.00 ml (in Section 1), or 15.00 ml (in Section 2 — to avoid precipitation of $KClO_4$), of ice-cooled water. This quenched the reaction. Some of the samples of the run were analysed for chromium(VI), and others for peroxodisulphate.

The experiments for determining the rate of evolution of oxygen gas were carried out using a 200-ml flask, situated in a water thermostat and connected to a water-filled gas burette, maintained at room temperature, $26 \pm 0.5°C$. Immediately prior to each run, the solution and the burette water were saturated with oxygen gas. Magnetic stirring was used throughout the run.

The hydrogen-ion concentrations were determined with a Radiometer PHM 4d and a combined glass-calomel electrode, designed for use in the temperature range $40-120°C$.

RESULTS

1. Kinetics at a constant hydrogen-ion concentration

The following symbols are used.

$b(t)$ = the peroxodisulphate concentration at the time t
c = the initial concentration of chromium(III)
z = the concentration of chromium(VI)

The rate of formation of chromium(VI) and the rate of decomposition of the peroxodisulphate were studied for different values of c and $b(t)$ (cf. Table 1). The composition of the ionic medium was 0.50 M $HClO_4$ + 0.50 M $NaClO_4$.

The peroxodisulphate decomposition. When log $b(t)$ is plotted *versus* t (see Fig. 1), straight lines are obtained. In Table 1 the first-order rate constants [cf. eqn. (3)] are given. The rate constant decreases appreciably, as the ratio $c \cdot b(0)^{-1}$ increases.

Most of the peroxodisulphate in the medium used decomposes by the reaction path catalyzed by hydrogen ions. In a solution containing 1 M $NaClO_4$, but no chromium and no perchloric acid, the rate constant was found to be

Table 1. Rate constants ($k_0 = k_1 + k_H[H^+]$; eqn. (3)) for the decomposition of $S_2O_8^{2-}$ at 60°C in 0.50 M $HClO_4$ + 0.50 M $NaClO_4$. The table gives $k_0 \times 10^3$ in min^{-1} for various initial concentrations of Cr(III) and $S_2O_8^{2-}$. The numbers used in Figs. 1, 2, and 3 are given beside the k_0-value.

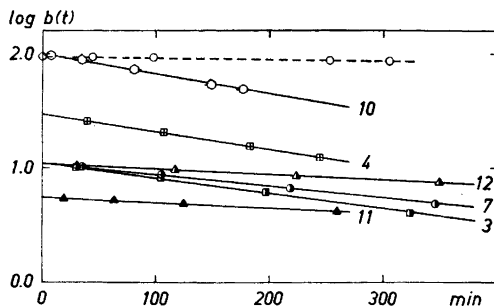| $[S_2O_8^{2-}]_0$ mM	[Cr(III)]$_0$ mM				
	0.22	0.55	1.10	4.40	22.0
5		2.5 (2)	2.0 (6)		1.1 (11)
11		3.2 (3)	2.4 (7)	1.5 (8)	1.1 (12)
30	3.7 (1)	3.6 (4)			
53		4.2 (5)		4.2 (9)	
100				4.2 (10)	

Fig. 1. Representative first-order plots for the decomposition of $S_2O_8^{2-}$. The composition of the solutions is evident from Table 1. The broken curve shows the uncatalyzed decomposition in 1 M $NaClO_4$.

$(2.7 \pm 0.2) \times 10^{-4}$ min^{-1} for the beginning of the decomposition (the broken curve in Fig. 1). The rate constant found is in reasonably good agreement with the data reported by Kolthoff and Miller.[3]

The rate expression for the redox reaction. The measured values of z as a function of t are given in Fig. 2. Application of the initial-rate method clearly shows that the formation of chromium(VI) is a first-order reaction with respect to peroxodisulphate ion. On the other hand, when the initial concentration $b(0)$ is maintained constant, whilst c is increased, the initial reaction rate increases fairly rapidly in the beginning, but at higher chromium(III) concentrations the reaction order, with respect to chromium(III), approaches zero. The initial rate divided by $b(0)$ is about 5.0×10^{-4} min^{-1} for the highest c-values studied.

The experimental data indicate that the oxidation rate may be expressed by the same differential equation as that for the oxidation of cerium(III) [4]

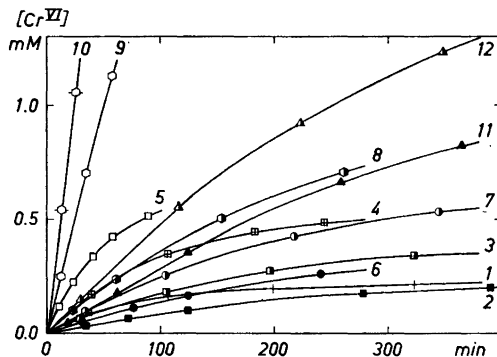$$\frac{dz}{dt} = \beta \cdot b(t) \ \frac{c-z}{1 + \gamma(c-z)} \tag{4}$$

Fig. 2. Kinetics of the redox reaction between Cr(III) and $S_2O_8^{2-}$. Conditions are the same as for Table 1, where the symbols are defined.

where β and γ are constants. The integrated rate law is then given by eqn. (5), if the over-all rate constant, k_0, for the decomposition of peroxodisulphate ion is introduced by the relationship $b(t) = b(0) \cdot \exp(-k_0 t)$

$$\frac{k_0}{b(0)-b(t)} \ln \frac{c}{c-z} = \beta - \gamma \frac{k_0 z}{b(0)-b(t)} \qquad (5)$$

More simply, eqn. (5) may be written

$$A = \beta - \gamma B \qquad (6)$$

where A and B are quantities which may be calculated for required values of t. In Fig. 3, the function A is plotted against B for each experiment; t being equal to 30, 100, and, usually, 200 min. The curve obtained — possibly a straight line — intercepts the B-axis at the value $\beta/\gamma = (5.0 \pm 0.3) \times 10^{-4}$ min^{-1}.

2. Velocity as a function of hydrogen-ion concentration

The rates of the decomposition of peroxodisulphate ion and of the formation of chromium(VI) were also studied using different values of the hydrogen-ion concentration.

In a separate series of experiments, the rate of evolution of oxygen gas was determined as a function of [H$^+$].

The additional electrolytes had the composition 0.70 M NaClO$_4$ + 0.15 M Na$_2$SO$_4$. All the runs had the same initial concentration of peroxodisulphate ion. The peroxodisulphate was in large excess. However, the initial concentration of chromium(III) was sufficiently high to make the oxidation rate independent of the parameter c.

In Figs. 4, 5, and 6, the concentration of chromium(VI), the concentration of peroxodisulphate, and the quantity of oxygen evolved, respectively, are
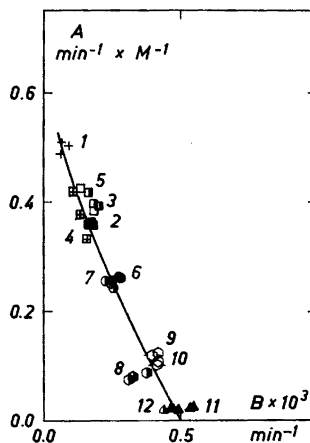

Fig. 3. Plot of A *versus* B [eqn. (6)]. The symbols used relate to the same concentrations as in Figs. 1 and 2.
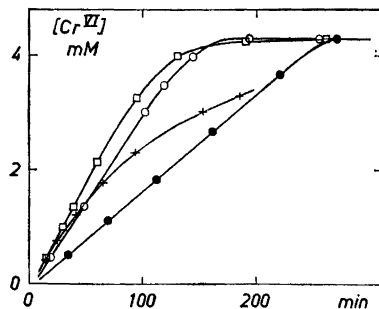
Fig. 4. Representative kinetic data for the reaction between Cr(III) and $S_2O_8^{2-}$ at different values of $[H^+]$ and with 0.70 M $NaClO_4$ + 0.15 M Na_2SO_4 as additional electrolytes.

The initial concentration of Cr(III) is 0.004 M; initial concentration of $S_2O_8^{2-}$, 0.10 M.

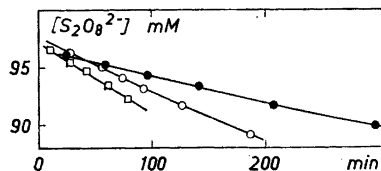| $[H^+]$, M:	0.002	0.039	0.067	0.417
Symbol:	●	○	□	+

Fig. 5. Decomposition of $S_2O_8^{2-}$. The symbols are defined in Fig. 4.

plotted *versus* the time of reaction for some representative runs. Each of the kinetic curves may be approximated to a straight line in its early part, the slope of which may easily be determined (except for the highest values of $[H^+]$).

The initial rates are plotted against the hydrogen-ion concentration in Figs. 7, 8, and 9. Clearly, *the peroxodisulphate decomposition* is described by eqn. (3) in the present measurements that range from a hydrogen ion concentration of 0.001 M to *ca.* 0.10 M. Knowing the concentration of peroxodisulphate ion (see Fig. 5), the following value of the first-order rate constant, k_1, for the uncatalyzed decomposition is obtained: $(2.3 \pm 0.2) \times 10^{-4}$ min^{-1}.
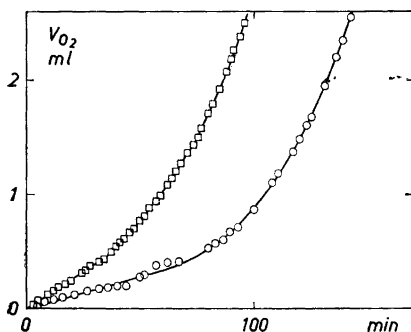

Fig. 6. Evolution of oxygen. The quantity V_{O_2} is the volume of oxygen collected at 26°C. The symbols are defined in Fig. 4.
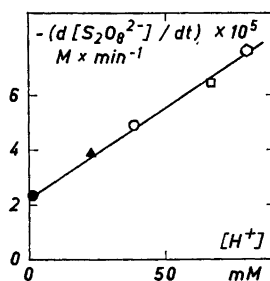

Fig. 7. Decomposition rate of peroxodisulphate ion as a function of $[H^+]$. The concentrations of Cr(III) and $S_2O_8^{2-}$ are given in Fig. 4. The different symbols only refer to different values of $[H^+]$.
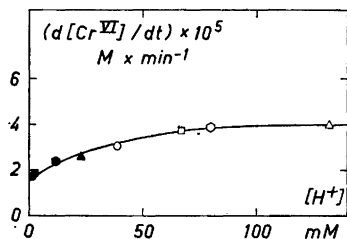
Fig. 8. Formation rate of chromium(VI) vs. [H+]. Concentrations of Cr(III) and $S_2O_8^{2-}$ are the same as in Fig. 4.
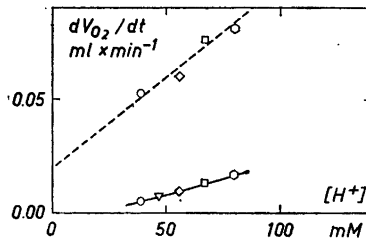
Fig. 9. Rate of evolution of oxygen as a function of [H+]. The solutions have the same composition as above (Figs. 4—8). The broken line refers to solutions after complete oxidation.

The rate of formation of chromium(VI) approaches a constant value for [H+] >0.10 M (Fig. 8). Extrapolation to [H+] = 0 (pH ≈3) gives the oxidation rate at an acidity, where the contribution from the hydrogen-ion catalyzed decomposition path is negligible. The following values were found.

$$pH <1: \quad \frac{dz}{dt} = 0.040 \pm 0.002 \text{ mM} \cdot \text{min}^{-1}$$

$$pH \approx 3: \quad \frac{dz}{dt} = 0.015 \pm 0.002 \text{ mM} \cdot \text{min}^{-1}$$

The volume of oxygen gas evolved was measured as a function of time both during the redox reaction and after a time when the oxidation of chromium(III) to chromium(VI) had gone to completion. The increase in the rate of formation of oxygen with increasing [H+] was found to be much lower during the oxidation of chromium(III) compared to when no reducing agent was present (Fig. 9).

DISCUSSION OF THE MECHANISM

The derivation of a rate law from a proposed mechanism. It appears that the experimental rate law is similar to that reported for the peroxodisulphate oxidation of cerium(III).[4] However, the mechanism must be different. The cerium(III) ions are oxidized only by the sulphate radical-ions formed in reaction (1). If the mechanism were the same in the present investigation, the rate of formation of chromium(VI) from chromium(III) ought to be one third that of the uncatalyzed decomposition of peroxodisulphate ion, irrespective of the pH of the solution — provided that the chromium(III) concentration is high enough for all the radicals formed to be captured.

The extrapolations to [H+] = 0 in Figs. 7 and 8 indicate that when practically no reaction occurs by the k_H path, the oxidation rate is two thirds of the rate of decomposition of peroxodisulphate ion.

At a hydrogen-ion concentration of 0.1 M, the rate of formation of chromium(VI) increases to twice the decomposition rate for the k_1 reaction path, within the limits of experimental error. The oxidation rate is then unaffected by a further fivefold increase of the hydrogen-ion concentration. This means

that, provided both the chromium(III) and the hydrogen-ion concentrations are sufficiently high, two chromium(III) ions are oxidized to chromium(VI) for every peroxodisulphate ion disappearing in the uncatalyzed decomposition.
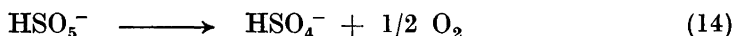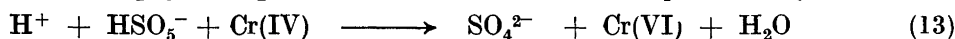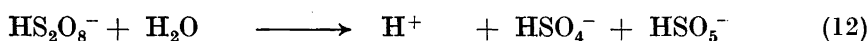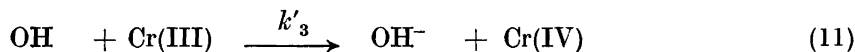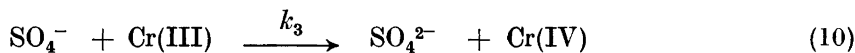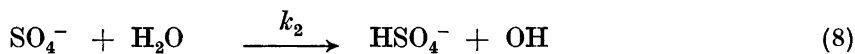
Thus it may be concluded that the radicals formed in the uncatalyzed decomposition of peroxodisulphate ion are effective in the rate-determining step of the oxidation. Probably, the chromium(III) ions are oxidized to chromium(IV) both by the sulphate radical-ion and the hydroxyl radical formed in reaction (1). Furthermore, the limited dependence upon $[H^+]$ in the concentration range where the k_H path contribution is appreciable proves that in the other two steps of the oxidation of Cr(III) to Cr(VI) some intermediate(s) from the k_H path must take part also.

The mechanism of the acid-catalyzed decomposition of peroxodisulphate is not known in detail. Kolthoff and Miller [3] postulated the formation of SO_4 radicals as an intermediate product, but since the existence of this molecule has not been definitely established, we prefer to formulate the first step of the k_H path in terms of eqn. (12), suggested by Wilmarth and Haim.[2]

A plausible reaction mechanism at an acidity so high that the oxidation rate is independent of $[H^+]$ includes the oxidation of chromium(III) to chromium(IV) by SO_4^- and OH (eqns. (1), (8)—(11)) — with the limiting stoichiometry given by

$$S_2O_8^{2-} + 2\ Cr(III) \longrightarrow 2\ SO_4^{2-} + 2\ Cr(IV) \tag{7}$$
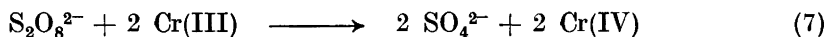
— followed by a relatively rapid oxidation of chromium(IV) to chromium(VI) by the intermediate formed in reaction (12). The reactions (13) and (14) must not be interpreted as single steps; they only indicate what species react and what products are formed.

$$SO_4^- + H_2O \xrightarrow{k_2} HSO_4^- + OH \tag{8}$$

$$OH \xrightarrow{k'_2} products \tag{9}$$

$$SO_4^- + Cr(III) \xrightarrow{k_3} SO_4^{2-} + Cr(IV) \tag{10}$$

$$OH + Cr(III) \xrightarrow{k'_3} OH^- + Cr(IV) \tag{11}$$

$$HS_2O_8^- + H_2O \longrightarrow H^+ + HSO_4^- + HSO_5^- \tag{12}$$

$$H^+ + HSO_5^- + Cr(IV) \longrightarrow SO_4^{2-} + Cr(VI) + H_2O \tag{13}$$

$$HSO_5^- \longrightarrow HSO_4^- + 1/2\ O_2 \tag{14}$$

If the concentrations of SO_4^- and OH are denoted x and y, respectively, the differential equations (15)—(17) are obtained.

$$\frac{dx}{dt} = k_1b(t) - k_2x - k_3x\ (c-z) \tag{15}$$

$$\frac{dy}{dt} = k_1b(t) + k_2x - k_2'y - k_3'y\ (c-z) \tag{16}$$

$$\frac{dz}{dt} = k_3x\ (c-z) + k_3'y\ (c-z) \tag{17}$$

Applying the steady-state approximation to the intermediate radicals SO_4^- and OH, we obtain the rate law

$$\frac{dz}{dt} = \frac{k_1\gamma \; (c-z)}{1+\gamma(c-z)} \; b(t) + \frac{k_1\gamma' \; (c-z)}{1+\gamma'(c-z)} \cdot \frac{2+\gamma \; (c-z)}{1+\gamma(c-z)} \; b(t) \tag{18}$$

where we have put $\gamma = k_3/k_2$ and $\gamma' = k_3'/k_2'$.

Comparison of the derived rate law with the observed kinetics. Presumably the sulphate radical-ion reacts more readily with chromium(III) than with water. Consequently the quotient $\dfrac{2+\gamma(c-z)}{1+\gamma(c-z)}$ is very nearly equal to 1 for not too low values of the chromium(III) concentration. From the approximate rate law

$$\frac{dz}{dt} = \frac{k_1\gamma \; (c-z)}{1+\gamma(c-z)} \; b(t) + \frac{k_1\gamma' \; (c-z)}{1+\gamma' \; (c-z)} \; b(t) \tag{19}$$

it is seen that the rate of formation of chromium(VI) approaches a limit, given by the equation

$$\lim_{(c-z)\to\infty} \frac{dz}{dt} = 2 \; k_1 b(t) \tag{20}$$

However, according to reaction (1), the product $k_1 b(t)$ is equal to the rate of uncatalyzed decomposition of peroxodisulphate ion. Hence, eqn. (20), derived from the postulated mechanism, is in agreement with the experimental observation that the oxidation rate for high enough values of [H$^+$] and c approaches twice the decomposition rate for the k_1 path.

If we postulate the oxidation of chromium(IV) to chromium(V) as rate-determining (*cf.* Tong and King [10]), the derived rate law will not be in accordance with the experimental kinetic behaviour.

Another alternative, though chemically less plausible, is that the OH radical reacts much faster than SO_4^-, so that the first term on the right-hand side of eqn. (18) is only a correction term. If this is true, the product $\gamma(c-z)$ is very likely much less than 1 in the concentration range of chromium(III) covered. So the rate law reduces to the following expression

$$\frac{dz}{dt} = \frac{2 \; k_1\gamma'(c-z)}{1+\gamma' \; (c-z)} \; b(t) \tag{21}$$

which has the same limiting value as is indicated by eqn. (20).

If eqn. (21) were the correct rate expression, the plot in Fig. 3 should be a straight line having an intercept on the B-axis of $2k_1$. This agrees with observed data — within the experimental error. However, the first-mentioned alternative represented by eqns. (18)—(20) is not inconsistent with the experimental material. The few higher points in Fig. 3 might well be part of a steeper line corresponding to the first term in the rate equation (18). In fact, a slight deviation from a straight line is justified by the assumption of the mechanism leading to eqn. (18).

Evidently, the mechanism proposed by Bartlett and Cotman,[7] involving reaction (2) as the rate-determining step can explain our experimental data equally well. It would lead to a rate law of the same type as eqn. (21). But,

since this mechanism is not consistent with other experimental results,[4,8] it is not taken up here.

pH Dependence. When practically all the peroxodisulphate disappears by the uncatalyzed decomposition path, reaction (13) cannot occur. The sulphate radical-ion and the hydroxyl radical are then responsible for the whole oxidation of Cr(III) to Cr(VI). This should reduce the limiting oxidation rate to one third of the value found at high acidities, *i.e.* to two thirds of the rate of the uncatalyzed decomposition of the peroxodisulphate ion. This is in accord with our experimental findings (see Figs. 7 and 8).

If eqn. (13) represented a rapid two-electron transfer, or two fast steps, the rate of formation of chromium(VI) ought to increase linearly with increasing $[H^+]$-values, until the final rate was reached at the hydrogen-ion concentration where the rate of disappearance of peroxodisulphate ion had trebled. From Fig. 8 it is clear that this is not found. At the same time no oxygen ought to be evolved below this $[H^+]$-value. However, the evolution of oxygen gas is in fact appreciable at much lower values of $[H^+]$ (see Fig. 9). Evidently, the decomposition of HSO_5^-, stoichiometrically indicated by eqn. (14), is a reaction competing with the oxidation of the chromium(IV) species in acid solutions. The proposed intermediate HSO_5^- probably oxidizes one of the two remaining unstable oxidation states of the chromium effectively and the other one rather ineffectively. This can explain the approximately maximum increase of the oxidation rate and the very low rate of formation of oxygen gas at low values of the hydrogen-ion concentration.

Complex formation. In most of the experiments accounted for in Section 1, the peroxodisulphate was not in great excess, and it may partly appear as complexes with chromium(III). It can be expected that when a cationic complex is formed between chromium(III) and the peroxodisulphate ion, the decomposition by the hydrogen-ion catalyzed path will become much slower. This suggestion is consistent with the marked decrease in the values of the over-all first-order rate constant observed at high values of the ratio $c \cdot b(0)^{-1}$ (*cf.* Table 1).

REFERENCES

1. Yost, D. M. *J. Am. Chem. Soc.* **48** (1926) 152.
2. Wilmarth, W. K. and Haim, A. *Mechanisms of Oxidation by Peroxydisulfate Ion.* In Edwards, J. O. (Ed.), *Peroxide Reaction Mechanisms*, Wiley-Interscience, New York 1962, p. 175.
3. Kolthoff, I. M. and Miller, I. K. *J. Am. Chem. Soc.* **73** (1951) 3055.
4. Fronæus, S. and Östman, C. O. *Acta Chem. Scand.* **9** (1955) 902.
5. House, D. A. *Chem. Rev.* **62** (1962) 185.
6. Yablonsky, H. A. *The Thermal Decomposition of Peroxydisulfate in Aqueous Solution,* (Diss.), Stevens Institute of Technology, Hoboken, N. J. 1964.
7. Bartlett, P. D. and Cotman, J. D. *J. Am. Chem. Soc.* **71** (1949) 1419.
8. Fronæus, S. *To be published in Acta Chem. Scand.*
9. Walden, G. H., Jr., Hammett, L. P. and Clapman, R. P. *J. Am. Chem. Soc.* **55** (1933) 2649.
10. Tong, J. Y. and King, E. L. *J. Am. Chem. Soc.* **82** (1960) 3805.

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