KINETICS AND MECHANISM OF OXIDATIONS BY PEROXYDISULFATE

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I. INTRODUCTION

The peroxydisulfate ion is one of the strongest oxidizing agents known in aqueous solution. The standard oxidation-reduction potential for the reaction

$$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^-$$

is estimated to be -2.01 volts (109). Reactions involving this ion, however, generally are slow at ordinary temperatures (118) and many peroxydisulfate oxidations have been studied kinetically.

The aim of this review is to summarize the results of these studies and to present the mechanisms advanced to account for the kinetic data. The material covered will include data published prior to 1961 but the review of the peroxydisulfate-iodide ion reaction is limited to selected articles.

The emphasis will be on kinetic studies, and preparative work involving peroxydisulfate as an oxidizing agent will not be mentioned except to supply credence to a kinetic pathway. Induced polymerizations using the peroxydisulfate ion will only be mentioned if they involve some aspect of general peroxydisulfate oxidation mechanisms.

Kinetic data, where not calculated in the original papers, are obtained from the Arrhenius equation

$$k = A \exp(-E/RT)$$

where k is the rate constant, A the frequency factor, E the energy of activation, and T the absolute temperature. The entropy of activation (ΔS) for the bimolecular reactions is calculated from the expression

$$A = (k'T/h) \exp(\Delta S/R)$$

where k' is the Boltzmann constant, h the Planck constant, and R the universal gas constant (46). The symbol μ will be used for the molar ionic strength.

The term "peroxydisulfate" is used by *Chemical Abstracts* although the International Union of Pure and Applied Chemistry (74) recently has recommended the name "peroxodisulfate." The trivial name "persulfate" is also in common use.

For many reducing agents, oxidation by peroxydisulfate does not proceed at a convenient rate at 25°, unless a catalyst is present, despite the fact that the standard free energy change is very favorable. The most thoroughly investigated catalyst is the silver(I) ion although reactions involving the copper(II) ion also have been studied. The rates of reactions catalyzed by these ions are, without exception, independent of the reductant concentration but depend on the first power of the peroxydisulfate and catalyst concentrations. Thus kinetic studies can be conveniently divided into two classes: (a) those involving the silver ion as a catalyst, (b) uncatalyzed investigations, although for some cases both types have been investigated.

The uncatalyzed oxidations can be further sub-

TABLE 1

Silver Ion Catalyzed Oxidations

No.	Reductant	μ, M	k_2 (25°), l. mole^{-1} min.$^{-1}$	A, l. mole^{-1} sec.$^{-1}$	E, kcal. mole^{-1}	ΔS, E.U.	References
1	Ammonium ion	0.5	0.267	2.08×10^9	15.9	−15.8	84, 119
2	Cerous ion	1.52	0.292	9.27×10^6	12.5	−22.1	34
3	Chromic ion	0.485	0.319	8.42×10^8	15.1	−18.8	165
4	Hydrazinium ion	0.58	0.326				36
5	Manganous ion	6.76	0.19				13
	(a) to MnO_4^{1-}	(2.24 M H_2SO_4)					
	(b) to Mn^{3+}	11.0	17.0 (22°)	8.38×10^5	11.7	−31.4	55
		(3.6 M H_2SO_4)					
	(c) to MnO_2	1.0	0.209	3.74×10^8	15.0	−20.2	57
6	Vanadyl ion	0.587	0.334				168
7	Acetone	0.225	0.55	3.63×10^9	15.8	−14.8	14
8	Water	0.015	1.29	6.2×10^{11}	17.9	−4.45	11
9	Formate ion	0.561	3.7	1.28×10^{11}	20.9	−8.17	61
10	Ammonia	0.297	8.89				82
11	Hydrogen peroxide	0.097	10.3 (13°)				116
12	Arsenious acid	0.04	23.9 (24°)	1.55×10^6	8.9	−31.1	60
13	Oxalate ion	0.45	26.4	1.3×10^9	12.9	−17.7	59

divided into: (i) reactions whose rates depend on the first power of the peroxydisulfate concentration and are independent of the reducing agent concentration, (ii) reactions whose rates depend on the first power of both the reductant and oxidant concentrations, (iii) reactions of an intermediate nature, involving fractional powers of the reactants, changes of order, or auto-catalytic characteristics.

II. THE SILVER ION CATALYZED REACTIONS

The observed rate law for the silver ion catalyzed oxidations of the reducing agents listed in Table 1 is

$$-d[S_2O_8^{2-}]/dt = k_2[S_2O_8^{2-}][Ag^+]$$

The velocity at any instant is proportional to the peroxydisulfate concentration and to the (constant) silver ion concentration. Thus the reactions are essentially bimolecular, although the data for any given concentration of catalyst conform to a unimolecular law. The value of the second order rate constant is thus independent of the silver ion concentration.

Because of the lack of dependence of the rate law on the reductant concentration, it has been suggested (36, 82, 165) that these reactions have a common rate-determining step

$$Ag^+ + S_2O_8^{2-} \rightarrow Ag^{3+} + 2SO_4^{2-} \qquad (1)$$

For reducing agents which are positive ions, the second order rate constants have values of the same magnitude and Fig. 1 shows a plot of log k_2 at 25° against the square root of the ionic strength for reductants 1 to 6 in Table 1. The data can be expressed in the linear form

$$\log k_2 = -0.193 - 0.38\ \mu^{1/2}$$

but there is a wide scattering of experimental points, indicating that the above rate-determining step may be oversimplified (130).

An examination of Table 1 shows that values of the rate constants for uncharged molecules and negatively charged ions are much larger than, but by no means as constant as, those for positively charged ions. The entropies of activation can also be divided into two groups, one with values of the order of −20 E.U., and the other ranging from −4 to −8 E.U. (H_2O and HCOOH).

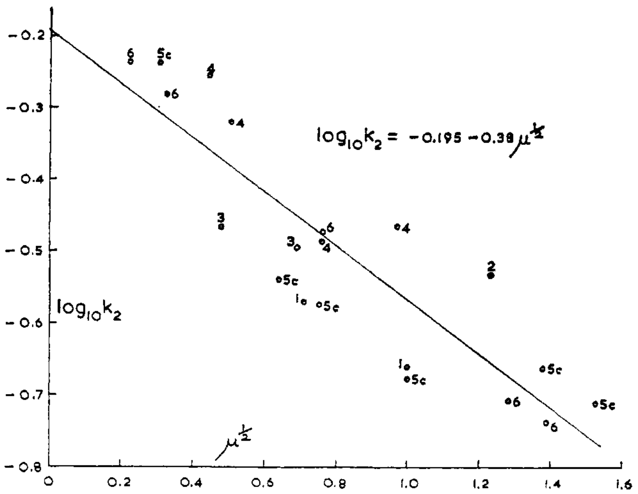

FIG. 1.—Log k_2 against the square root of the ionic strength, k_2 in l. mole^{-1} min.$^{-1}$ and μ in mole l.$^{-1}$. Numbers refer to the reactants in Table 1.

The entropy of activation (ΔS) of a bimolecular reaction is related to the frequency factor (A) by the equation (46)

$$A = k'T/h \exp(\Delta S/R) \qquad (2)$$

and if the radius of the activated complex in the transition state is taken to be 2Å. in water, then it can be shown that (47)

$$\Delta S = -10Z_AZ_B \text{ E.U.} \qquad (3)$$

where Z_A and Z_B are the charges on the reacting species.

If equation (1) were to be the rate-determining step, the entropy of activation should be approximately +20 E.U. from equation (3). This value is not observed and to avoid the discrepancy a mechanism has been postulated involving an equilibrium which is followed by a termolecular rate-determining step (57, 59, 60)

$$S_2O_8^{2-} \leftrightarrows 2SO_4^{\dot{-}} \quad \text{rapid} \tag{4a}$$

$$2SO_4^{\dot{-}} + Ag^+ \rightarrow 2SO_4^{2-} + Ag^{3+} \quad \text{slow} \tag{4b}$$

The rate of reaction will be given by

$$-d[S_2O_8^{2-}]/dt = k_{4b}[SO_4^{\dot{-}}]^2[Ag^+] \tag{4c}$$

and from the equilibrium (4a)

$$K = [SO_4^{\dot{-}}]^2/[S_2O_8^{2-}] \tag{4d}$$

where K is the equilibrium constant. Substitution of (4d) in (4c) gives

$$\begin{aligned} -d[S_2O_8^{2-}]/dt &= k_{4b}K[S_2O_8^{2-}][Ag^+] \\ &= k_{obs}[S_2O_8^{2-}][Ag^+] \end{aligned}$$

where $k_{obs} = k_{4b}K$; hence $k_{4b} = k_{obs}/K$.

Using an assumed value of $K = 10^{-8}$ and an experimental value of $k_{obs} = 0.452$ l. mole^{-1} min.$^{-1}$ (57), the frequency factor becomes 3.73×10^{16} l. mole^{-1} sec.$^{-1}$ and the entropy of activation +16.3 E.U., in agreement with equation (3).

An alternative initial step to explain the catalytic effect is (14, 30)

$$Ag^+ + S_2O_8^{2-} \rightarrow AgS_2O_8^{1-} \quad \text{(slow)} \tag{5}$$

followed by either

$$AgS_2O_8^{1-} \rightarrow Ag^{3+} + 2SO_4^{2-} \quad \text{(fast)}$$

or

$$AgS_2O_8^{1-} \rightarrow Ag^{2+} + SO_4^{2-} + SO_4^{\dot{-}} \quad \text{(fast)}$$

and the rapid oxidizing steps

$$Ag^{3+} + M^+ \rightarrow M^{2+} + Ag^{2+}$$

$$Ag^{2+} + M^{2+} \rightarrow M^{3+} + Ag^+$$

The formation of silver(II) compounds under conditions favorable for their stabilization (125) would be possible by the reaction

$$Ag^{3+} + Ag^+ \rightarrow 2Ag^{2+} \tag{6}$$

analogous to the equilibrium

$$Ag(III) + Ag(I) \rightleftarrows 2Ag(II) \tag{7}$$

postulated for the silver(I)–silver(II) exchange reaction (51). This mechanism does not explain the discrepancy between the observed and calculated values of the entropy of activation, but it does avoid the postulation of a termolecular rate determining step.

So far no mechanism has been proposed that can explain the constancy of the values for the second order rate constant, when positively charged reductants are used, and account for the increase and variation on changing to negatively charged ions or neutral molecules.

The nature of the silver intermediate in these oxidations is not yet established. Much of the evidence points to a trivalent silver species (29, 35, 57, 166) although a one electron change in the oxidation state of the silver ion catalyst has been suggested (5, 11, 16, 43, 45, 116)

$$Ag^+ + S_2O_8^{2-} \rightarrow Ag^{2+} + SO_4^{2-} + SO_4^{\dot{-}} \tag{8}$$

This is in accordance with the observations of Higginson and Marshall (63) that one electron transfer is more likely in oxidation-reduction systems between a transition element ion and an ion derived from a nontransition element. Experimental evidence to support this hypothesis has been produced by a study of the reaction between peroxydisulfate and hydrogen peroxide catalyzed by both silver(I) ion and bis-dipyridyl silver(I) ion (116). The rate of reaction was found to be the same using both silver species and, since the latter is rapidly oxidized to bis-dipyridyl silver(II) ion by peroxydisulfate (125), a divalent rather than a trivalent intermediate was favored. However, these data could be interpreted to favor a trivalent silver species if the complex silver(II) ion, first formed, was further oxidized to an unstable silver(III) intermediate which was the active oxidizing species. Similarly, the fact that both cupric (2, 7, 17, 139) and cuprous (32) ions catalyze peroxydisulfate oxidations suggests that a copper(III) species is the reactive substance. The oxidation of the oxalatopentammine cobalt(III) ion by various oxidizing agents has been studied by Taube (160) and two products have been obtained, depending on the reagent used. With oxidants involving a one electron transfer the cobalt(III) is reduced to cobalt(II) but with two electron change oxidizing agents the pentammineaquocobalt(III) ion is the product. The peroxydisulfate—silver ion system brings about the reduction of the cobalt(III) complex, but, while this suggests that reaction (9) is operative, one electron oxidation *via* the equilibrium (7) is also possible.

III. THE FIRST ORDER UNCATALYZED PEROXYDISULFATE OXIDATIONS

A major problem arising from the first order uncatalyzed oxidations is to account for the increased rate of peroxydisulfate decomposition on addition of a reducing agent, when the rate law is independent of the concentration of this substance.

If the primary step is the decomposition of peroxydisulfate into sulfate free radicals

$$S_2O_8^{2-} \rightarrow 2SO_4^{\dot{-}} \quad \text{rate determining}$$

followed by a rapid attack of these on the reducing agent, then the rate of oxidation should be the same for all reducing agents in this class. This is not observed as shown in Table 2.

TABLE 2

Kinetic Data for the Uncatalyzed First Order Peroxydisulfate Oxidations

No.	Substrate	Rate constant × 10⁴ min.⁻¹	*T*, °C.	Energy of activation, kcal. mole⁻¹	Peroxydisulfate concentration, *M*	Reference
1	Water	0.33	40	28.39	0.0005	11
		1.60	50			
2	Hydrogen peroxide	0.175	30		0.01	162
3	Arsenious acid	5.08	30	20.78	0.08	58
		16.48	40			
4	Sodium thiosulfate	5.5	30	17.9	0.0125	66
		14.6	40			
5	Potassium formate	37.0	30	21.93	0.0133	154
		123.0	40			
6	Formic acid	52.7	30	8.19	0.01	157
		81.3	40			
7	2-Propanol	38.4	50	26.0		113
		137	60			

That sulfate free radicals are produced in the decomposition of peroxydisulfate is evident from the fact that in polymerization studies using peroxydisulfate labeled with sulfur-35 as an initiator, polymer fragments containing radioactive sulfate groups have been isolated (15, 104, 124, 147, 148).

The breakdown into free radicals probably is irreversible, as it seems likely that sulfate free radicals would exchange electrons with sulfate ions at a rate comparable with their recombination to peroxydisulfate. However, no exchange of sulfur-35 between sulfate and peroxydisulfate has been observed (38, 40, 112, 136, 161) under the conditions of the kinetic experiments, and consequently any proposed mechanism of decomposition involving an equilibrium between peroxydisulfate and sulfate or sulfate-ion radicals probably is incorrect. For example

$$S_2O_8^{2-} \rightleftarrows SO_4 + SO_4^{2-} \qquad (111,\ 112)$$

and

$$S_2O_8^{2-} \rightleftarrows 2SO_4^{\dot{-}} \qquad (57,\ 59,\ 60,\ 61)$$

Bartlett and Cotman (8) have suggested that radicals produced in the peroxydisulfate ion decomposition in aqueous solution cannot induce the peroxydisulfate decomposition. These authors base their statement on the fact that autocatalysis is not observed in the thermal decomposition and the reaction is first order in peroxydisulfate concentration. However, to explain the increased rate on addition of an oxidizable substrate, it is necessary to postulate that radicals produced from the reducing agent can induce peroxydisulfate decomposition, and this suggests that a similar radical mechanism operates in the absence of the reducing agent.

The first order dependence can be explained by a chain decomposition mechanism (8), analogous to that suggested for the uncatalyzed reaction between peroxydisulfate and oxalate (143).

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\dot{-}} \qquad \text{initial step} \qquad (1)$$

$$SO_4^{\dot{-}} + H_2O \xrightarrow{k_2} HSO_4^{1-} + OH^{\cdot} \qquad \text{slow, but faster than (1)} \qquad (2)$$

$$S_2O_8^{2-} + OH^{\cdot} \xrightarrow{k_3} HSO_4^{1-} + SO_4^{\dot{-}} + {}^1/{}_2O_2 \qquad \text{fast, but governed by (2)} \qquad (3)$$

$$SO_4^{\dot{-}} + OH^{\cdot} \xrightarrow{k_4} HSO_4^{1-} + {}^1/{}_2O_2 \qquad \text{chain termination} \qquad (4)$$

The primary step (1) is characteristic of all peroxydisulfate oxidations and may be initiated by impurities in the solution, dust, or light, as the aqueous decomposition of peroxydisulfate is known to be photosensitive (19, 115). In step (2) the sulfate free radicals react with water to produce hydroxyl free radicals. These in turn rapidly decompose the oxidizing ions present by steps (3) and (4).

Application of the steady state hypothesis to the radicals in the above scheme (see Appendix) leads to the rate law

$$-d[S_2O_8^{2-}]/dt = (k_1k_2k_3/k_4)^{1/2}[S_2O_8^{2-}]$$

This mechanism scheme is readily extended to include cases when an oxidizable substance is added in a finite concentration and the observed rate law is

$$-d[S_2O_8^{2-}]/dt = -d[X^{2-}]/dt = k_0[S_2O_8^{2-}]$$

where $[X^{2-}]$ is the concentration of the ion added, and k_0 is the observed velocity constant.

In such cases the rate constant is greater than that observed in the aqueous decomposition (Table 2) and the proposed mechanism is (143, 144, 150)

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\dot{-}} \qquad \text{initial step} \qquad (1)$$

$$SO_4^{\dot{-}} + H_2O \rightarrow HSO_4^{1-} + OH^{\cdot} \qquad (2a)$$

$$OH^{\cdot} + X^{2-} \rightarrow OH^{1-} + X^{\dot{-}} \qquad (2b)$$

$$X^{\dot{-}} + S_2O_8^{2-} \xrightarrow{k_3} SO_4^{2-} + SO_4^{\dot{-}} + X \qquad (3)$$

$$X^{\dot{-}} + SO_4^{\dot{-}} \xrightarrow{k_4} SO_4^{2-} + X \qquad (4)$$

Here the peroxydisulfate is decomposed by steps (1) and (3) leading to the rate expression (see Appendix)

$$\begin{aligned}-d[X^{2-}]/dt &= k_1[S_2O_8^{2-}] + k_3[X^{\dot{-}}][S_2O_8^{2-}]\\ &= (k_1 + k_3[X^{\dot{-}}])[S_2O_8^{2-}]\end{aligned}$$

where $[X^{\dot{-}}]$ is the concentration of the free radical produced from the reducing agent. By the steady state hypothesis the concentration of free radicals is constant. Thus $k_0 = k_1 + k_3[\mathrm{X}^{\dot{-}}]$, although the value of the constant free radical concentration may vary from reductant to reductant giving rise to the variation in rate constant in the different systems.

IV. AQUEOUS DECOMPOSITION OF PEROXYDISULFATE

The hydrolysis of the peroxydisulfate ion in neutral or alkaline solution is represented by the equation

$$\mathrm{S_2O_8}^{2-} + \mathrm{H_2O} \rightarrow 2\mathrm{HSO_4}^{1-} + {}^1\!/_2\mathrm{O_2}$$

in dilute acid by

$$\mathrm{S_2O_8}^{2-} + 2\mathrm{H_2O} \rightarrow 2\mathrm{HSO_4}^{1-} + \mathrm{H_2O_2}$$

and in concentrated acid by (49, 129, 131, 145)

$$\mathrm{S_2O_8}^{2-} + \mathrm{H_2O} \rightarrow \mathrm{H_2SO_5} + \mathrm{SO_4}^{2-}$$

The rate of decomposition at any pH is adequately expressed by the first order rate law (77, 78)

$$-\mathrm{d}[\mathrm{S_2O_8}^{2-}]/\mathrm{d}t = k_0[\mathrm{S_2O_8}^{2-}]$$

Table 3 lists the values published or calculated for k_0. For any temperature the observed rate constant increases with decreasing peroxydisulfate concentration and with decreasing pH.

More detailed investigations have found that in alkaline solution the rate is independent of the ionic strength, but in acid solution there is a negative salt effect (44, 103, 170). From this evidence the observed rate constant can be split into two parts, one acid catalyzed. Thus

$$k_0 = k_1 + k_2[\mathrm{H}^+] \quad \text{(see Table 4)}$$

Published values for the energy of activation are listed in Table 5. The values for k_1 and k_2 refer to the rate constants in Table 4. From the value of 28.39 kcal. mole^{-1} for the energy of activation associated with k_0, Bawn and Magerison (11) calculate the frequency factor to be 7.4×10^{13} sec.$^{-1}$.

Kolthoff and Miller (103) studied the kinetics of the decomposition in water enriched with oxygen-18 at varying pH, and found that in acid solution (0.5 M $\mathrm{HClO_4}$), all the oxygen produced came from the peroxydisulfate, but in alkaline solution (0.1 M NaOH), the oxygen came from the water. This observation led them to postulate different mechanisms for the hydrogen ion catalyzed and uncatalyzed decompositions.

Mechanism of the Hydrogen Ion Independent Reaction (8, 103, 141).—

$$\mathrm{S_2O_8}^{2-} \rightarrow 2\mathrm{SO_4}^{\dot{-}} \tag{1}$$

$$\mathrm{SO_4}^{\dot{-}} + \mathrm{H_2O} \rightarrow \mathrm{HSO_4}^{1-} + \mathrm{OH}^{\cdot} \tag{2}$$

$$2\mathrm{OH}^{\cdot} \rightarrow \mathrm{H_2O} + {}^1\!/_2\mathrm{O_2} \tag{3}$$

Equations (1), (2), and (3) represent the simplest unimolecular decomposition of the peroxydisulfate ion in aqueous solution and are consistent with the kinetic data. Bartlett and Cotman (8) have pointed out, however, that a chain mechanism also can give rise to the observed kinetics

TABLE 3

Rate Constants for the Thermal Decomposition of Peroxydisulfate

T, °C.	$[\mathrm{S_2O_8}^{2-}]$, M	Initial conditions	k_0, (min.$^{-1}$)	Reference
25	0.05	0.05 M H$^+$	6.12×10^{-6}	48
25	0.048	0.5 M H$^+$	5×10^{-6}	45
40	0.0005	1:1 ethanol/water	3.3×10^{-5}	11
45	0.0005	1:1 ethanol/water	6.9×10^{-5}	11
50	0.01	0.1 M OH$^-$	6.0×10^{-5}	103
50	0.0005	1:1 ethanol/water	1.6×10^{-4}	11
50	0.10	0.1 M H$^+$	4.0×10^{-4}	103
50	0.01	0.1 M H$^+$	5.7×10^{-4}	103
50	0.10	0.2 M H$^+$	6.7×10^{-4}	103
50	0.10	0.3 M H$^+$	9.1×10^{-4}	103
50	0.10	0.4 M H$^+$	1.06×10^{-3}	103
50	0.10	0.5 M H$^+$	1.5×10^{-3}	103
50	0.10	1.0 M H$^+$	2.8×10^{-3}	103
50	0.10	1.5 M H$^+$	4.5×10^{-3}	103
50	0.10	2.0 M H$^+$	6.9×10^{-3}	103
55	0.0005	1:1 ethanol/water	3.0×10^{-4}	11
56			2.73×10^{-4}	110
60	0.01	0.01 M OH$^-$	3.0×10^{-4}	103
60	0.02	pH 8	2.93×10^{-4}	67
60	0.07	Neutral	4.13×10^{-4}	146
60	0.0655	Neutral	4.25×10^{-4}	146
60	0.0282	Neutral	4.82×10^{-4}	146
60	0.02	Neutral	5.2×10^{-4}	141
60	0.02	0.04 M H$^+$	1.09×10^{-3}	141
60	0.01	0.1 M H$^+$	1.9×10^{-3}	103
61	0.048	0.5 M H$^+$	3.8×10^{-3}	44
70		0.1 M OH$^-$	1.4×10^{-3}	169
70	0.01	0.01 M OH$^-$	1.4×10^{-3}	103
70		pH 9.8	1.5×10^{-3}	169
70	0.126	Neutral	1.6×10^{-3}	53
70	0.0552	Neutral	1.61×10^{-3}	146
70	0.0214	Neutral	1.80×10^{-3}	146
70		Neutral	1.80×10^{-3}	169
70	0.02	Neutral	1.85×10^{-3}	141
70	0.0141	Neutral	1.92×10^{-3}	146
70	0.01	Neutral	1.45×10^{-3}	102
70	0.00629	Neutral	2.01×10^{-3}	146
70		0.05 M H$^+$	3.4×10^{-3}	169
70	0.01	0.1 M H$^+$	6.4×10^{-3}	103
80	0.01	0.1 M OH$^-$	5.5×10^{-3}	103
80		pH 9.5	5.2×10^{-3}	169
80	0.092	pH 8	4.14×10^{-3}	9
80	0.02	pH 8	4.56×10^{-3}	67
80		pH 8	5.76×10^{-3}	8
80		Neutral	5.4×10^{-3}	169
80	0.126	Neutral	5.5×10^{-3}	53
80	0.0455	Neutral	5.14×10^{-3}	146
80	0.0188	Neutral	5.87×10^{-3}	146
80	0.00414	Neutral	6.58×10^{-3}	146
80		pH 1.7	1.03×10^{-2}	169
80	0.01	0.1 M H$^+$	2.10×10^{-2}	103
90	0.01	0.1 M OH$^-$	2.1×10^{-2}	103
90	0.130	Neutral	1.61×10^{-2}	53
90	0.01	0.1 M H$^+$	6.8×10^{-2}	103

TABLE 4

Rate Constants for the Hydrogen Ion Catalyzed Thermal Decomposition of Peroxydisulfate

k_1 (min.$^{-1}$)	k_2 (l. mole^{-1} min.$^{-1}$)	T, °C.	μ M	Reference
6.0×10^{-5}	5.1×10^{-3}	50	0.04	103
3.0×10^{-4}	1.6×10^{-2}	60	0.04	103
3.5×10^{-4}	1.0×10^{-2}	61	1.2	44
1.4×10^{-3}	5.0×10^{-2}	70	0.04	103
5.5×10^{-3}	1.6×10^{-1}	80	0.04	103
2.1×10^{-2}	4.7×10^{-1}	90	0.04	103

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-} \quad (1)$$

$$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^{1-} + OH^{\cdot} \quad (2)$$

$$OH^{\cdot} + S_2O_8^{2-} \rightarrow HSO_4^{1-} + SO_4^{\cdot-} + {}^1/_2O_2 \quad (4)$$

$$SO_4^{\cdot-} + OH^{\cdot} \rightarrow SO_4^{2-} + {}^1/_2O_2 \quad (5)$$

Thus equations (1), (2), (4), and (5) lead to first order kinetics (see Appendix) as step (5) accounts for the chain termination, rather than step (3).

TABLE 5

Energy of Activation (kcal. mole^{-1}) for the Thermal Decomposition of Peroxydisulfate

Alkaline solution (k_1)	Neutral solution (k_0)	Acid solution (k_2)	Reference
	29.1		146
	28.39		11
	28.37		141
33.3 (pH 13)		26.0 (pH 1)	103
32.1 (pH 8)			67
		24 ± 2 (pH 0.3)	45
32.5 (pH 9.5)	30.8	27.7 (pH 1.7)	169

Bartlett and Cotman (8) rejected the chain decomposition, though they considered it in some detail, on the grounds that the non-chain process was the simpler, but from consideration of more recent evidence (see p. 188) the reviewer believes that a chain mechanism is better suited to explain the results of peroxydisulfate oxidations generally.

An alternative mechanism for the hydrogen ion independent decomposition has been suggested by Fronaeus and Ostman (44) in which only one sulfate free radical is formed in the initial step

$$S_2O_8^{2-} + H_2O \rightarrow HSO_4^{1-} + SO_4^{\cdot-} + OH^{\cdot}$$

$$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^{1-} + OH^{\cdot}$$

$$2OH^{\cdot} \rightarrow H_2O + {}^1/_2O_2$$

Mechanism of the Acid Catalyzed Reaction (11, 103, 170).—

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^{1-}$$

$$HS_2O_8^{1-} \rightarrow SO_4 + HSO_4^{1-}$$

$$SO_4 \rightarrow SO_3 + {}^1/_2O_2$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

In strong acid

$$SO_4 + H_2O \rightarrow H_2SO_5$$

Rather fewer data have been published on this aspect of the decomposition and the evidence for the sulfur tetroxide molecule as an intermediate rests on the detailed study made by Kolthoff and Miller (103). Its formation explains the observation that the oxygen produced in the acid solution comes from the peroxydisulfate, but Bawn and Margerison (11) found that if SO_4 was present in the pH range 3–7, it did not show active radical characteristics, in that it did not attack the free radical capture agent, diphenyl picryl hydrazyl.

Saxena and Singhal (141) suggest the acid catalysis is caused by the reactions

$$SO_4^{\cdot-} + H^+ \rightarrow HSO_4^{\cdot}$$

$$HSO_4^{\cdot} + H_2O \rightarrow HSO_4^{1-} + OH^{\cdot} + H^+$$

and although they may take place, the oxygen production from the peroxydisulfate is not explained.

Measurements have been made to determine the amounts of peroxymonosulfuric acid and hydrogen peroxide produced when more concentrated (greater than 2 *M*) acid solutions are used (48, 103). These indicate that the peroxydisulfate first decomposes to give peroxymonosulfuric acid which hydrolyzes further to hydrogen peroxide.

The above results may be explained by the reactions

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^{1-} \quad (1)$$

$$HS_2O_8^{1-} + H_2O \rightarrow H_2SO_5 + HSO_4^{1-} \quad (2)$$

$$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4 \quad (3)$$

$$H_2O_2 \rightarrow H_2O + {}^1/_2O_2 \quad (4)$$

Step (1) is rate determining, producing the $HS_2O_8^{1-}$ ion which, because of the influence of the hydrogen ion, decomposes unsymmetrically by reaction with water, and involves the breaking of an O–S bond. In step (1) the reaction between two oppositely charged ions accounts for the negative salt effect. The peroxymonosulfuric acid formed by step (2) is further hydrolyzed to give hydrogen peroxide, which is thermally decomposed, producing oxygen originally from the peroxydisulfate. The difference in energy of activation from the catalyzed and uncatalyzed decompositions (see Table 3) may be due, in part, to the difference in the energy of the O–O and S–O bonds.

Investigations on the silver ion catalyzed decomposition of peroxydisulfate (11, 45, 48, 64) show that the rate can be expressed in the form

$$-d[S_2O_8^{2-}]/dt = k_0[S_2O_8^{2-}]$$

where

$$k_0 = k_1 + k_2[Ag^+]$$

and k_1 and k_2 are rate constants for the non-silver ion catalyzed and silver ion catalyzed decompositions, respectively.

Values for k_2 are shown in Table 6 and the energy of activation is found to be 17.9 kcal. mole^{-1}, with a frequency factor of 6.2×10^{11} l. mole^{-1} min.$^{-1}$ (11).

TABLE 6

Rate Constants for the Silver Ion Catalyzed Thermal Decomposition of Peroxydisulfate

T, °C.	k_2 (l. mole^{-1} min.$^{-1}$)	μ, M	Reference
18	0.20	0.15	64
25	1.29	0.015	11
25	0.210	0.30	48
25	0.225	1.288	45

V. SPECIFIC OXIDATIONS

A. THIOSULFATE ION

Kinetic studies (66, 91, 123, 150) of the reaction represented by the equation

$$S_2O_8^{2-} + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2SO_4^{2-}$$

have shown that the rate is first order in peroxydisulfate concentration and zero order in thiosulfate concentration over a wide range of reactant concentrations (71). This reaction also has been studied in conjunction with the polymerization of substituted vinyl compounds (22, 127) and the rate of reduction of the monomer concentration is independent of the thiosulfate concentration.

The reaction is extremely sensitive to traces of impurities in the water (91, 123) and the rate constant is markedly increased by catalytic amounts of cupric ions. Over a fifty-fold range in added cupric ions the reaction is first order in copper concentration and first order in peroxydisulfate concentration. Strangely enough the silver ion proves ineffective as a catalyst (91). The reaction is also accelerated by ferrous ion, iodide ion, hydrogen ion, and cane sugar (91) and by uranyl ion (71). Specific salts also have a pronounced effect (150), and the order of increase in the rate constant is $K^+ > NH_4^+ > Na^+ > Li^+$ for univalent cations (150).

A feature of this oxidation-reduction reaction that is unexpected from the stoichiometric equation is that the pH changes considerably during its course, demonstrating the presence of a side reaction. However, the nature of this side reaction has not been elucidated (150).

The energy of activation for the uncatalyzed reaction has been given as 15.5 kcal. mole^{-1} (128) and 17.9 kcal. mole^{-1} (66).

Because of the independence of the rate on the thiosulfate concentration it seems probable that the uncatalyzed reaction proceeds through a free radical chain mechanism. This is also in agreement with the observed pH changes and initiation of vinyl polymerization by this reaction. The most complete mechanism proposed (150) is

$$\begin{array}{rcll}
S_2O_8^{2-} & \rightarrow & 2SO_4^{\cdot-} & k_1 \\
SO_4^{\cdot-} + H_2O & \rightarrow & HSO_4^{1-} + OH^{\cdot} & k_2 \\
OH^{\cdot} + S_2O_3^{2-} & \rightarrow & OH^{1-} + S_2O_3^{\cdot-} & \text{fast} \\
S_2O_3^{\cdot-} + S_2O_8^{2-} & \rightarrow & SO_4\cdot S_2O_3^{2-} + SO_4^{\cdot-} & k_3 \\
S_2O_3^{\cdot-} + SO_4^{\cdot-} & \rightarrow & SO_4\cdot S_2O_3^{2-} & k_4 \\
S_2O_3^{2-} + SO_4\cdot S_2O_3^{2-} & \rightarrow & S_4O_6^{2-} + SO_4^{2-} & \text{fast}
\end{array}$$

Making the usual steady state assumptions that the rate of change of the free radical concentration is zero, and that k_1 is slow, the rate law becomes (see Appendix)

$$-d[S_2O_8^{2-}]/dt = (k_1k_2k_3/k_4)^{1/2}[S_2O_8^{2-}]$$

which agrees with the experimentally obtained law. Other mechanisms that have been proposed (22, 123) either do not explain the observed pH changes or involve the thiosulfate concentration in the rate determining step.

B. OXALATE ION

The stoichiometric equation for the oxidation of oxalate ion by peroxydisulfate ion has the simple form

$$S_2O_8^{2-} + C_2O_4^{2-} \rightarrow 2SO_4^{2-} + 2CO_2$$

but the kinetics show all the characteristics of a complex chain reaction. Thus, Allen (2) found that the reaction has an induction period followed by auto-catalysis and then auto-inhibition and this was confirmed by later studies (140, 142, 143, 144, 153, 154).

All workers agree that the rate of oxidation is independent of the oxalate ion concentration and Saxena and Singhal (143) have shown that the rate is first order with respect to the peroxydisulfate ion concentration. Sodium oxalate (2), potassium oxalate (143, 155), and oxalic acid (140, 142, 143, 153, 155) have been used as a source of oxalate ion. Saxena and Singhal (143) found that the reaction was much faster using potassium oxalate instead of oxalic acid as the reducing agent, but the opposite effect was noted by Srivastava and Ghosh (155).

At ordinary temperatures and in the absence of metal ion catalysts the reaction has been found to be very slow (80) and the rate of oxidation has been measured at temperatures of 45° (140, 153, 155), 50° (32), 60° (140, 142, 143), and 69.7° (2), but, owing to the complex nature of the reaction, first order rate constants have not been calculated in many cases. Saxena and Singhal (140) have estimated the activation energy to be between 13.3 and 14.1 kcal. mole^{-1} but this is rather less than the approximate value of 22 kcal. mole^{-1} indicated by Srivastava and Ghosh (153).

The effect of oxygen on the rate has been measured (2, 32, 143) and, as expected for a free radical reaction involving reducing species, oxygen inhibition is exhibited. Passage of nitrogen or carbon dioxide through the reaction mixture causes a rate increase presumably due to the removal of dissolved oxygen (143).

Neutral salts have a retarding influence (140, 153, 155) but specific effects are greater than a negative salt effect caused by an increase in ionic strength. Hydrogen ions exert an accelerating influence (142).

The oxidation is extremely sensitive to traces of metal ions, especially cupric (2, 17) and argentous (16, 56, 59, 80, 83, 85). King (83, 85) found that values of the second order rate constants for the silver ion catalysis were about 4000 times greater than the values for the then known silver ion catalyzed peroxydisulfate oxidations, but he could not obtain reproducible results by following the rate of carbon dioxide evolution.

Allen (2) followed the reaction by measuring the peroxydisulfate ion concentration and obtained reproducible results and eliminated the induction period and autocatalytic nature observed by other investigators (16, 85, 153). A similar study has been made by Gupta and Ghosh (56, 59), their over-all results agreeing with those of Allen (2) in that the rate of peroxydisulfate ion decomposition can be expressed as

$$-d[S_2O_8^{2-}]/dt = k_2[S_2O_8^{2-}][Ag^+]$$

but there is less agreement in the values of the rate constant. The kinetic constants for the silver ion catalyzed oxidation are shown in Table 1. The effect of inert salts on the silver ion catalysis is similar to the non-catalyzed oxidation in that a general negative salt effect operates (16, 59) but there is a marked specific influence exerted by the various anions and cations.

Investigations on the catalytic effect of both cuprous (32) and cupric (2, 17, 153) copper give a rate law similar to the silver ion catalysis and a negative salt effect is observed when potassium sulfate is the added electrolyte (17). As with the uncatalyzed oxidation, the metal ion catalyzed reactions are accelerated by hydrogen ions (59).

The reduction of mercuric chloride to mercurous chloride using the peroxydisulfate–oxalate system as an inductor has also been studied kinetically (144). Preliminary investigations (143) showed that addition of mercuric chloride to the peroxydisulfate–oxalate reaction markedly increased the speed of oxalate oxidation. Measurements to determine the exponents in the rate law

$$d[Hg_2Cl_2]/dt = k[HgCl_2]^x[C_2O_4^{2-}]^y[S_2O_8^{2-}]^z$$

show (144) that $x = 0.5–1.0$, $y = 0$, $z = 1$. Induced reductions of this nature in oxalate systems have been cited as evidence for oxalate free radicals in the reactant solution (105).

The auto-catalytic nature of the uncatalyzed reaction probably is a result of a chain reaction (2) and this idea is supported by the kinetics of the induced mercuric chloride reduction (144). The most attractive mechanism that accounts for these features and does not conflict with other evidence from peroxydisulfate oxidations is (2, 143, 144)

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-} \quad \text{slow} \qquad (1)$$

$$SO_4^{\cdot-} + C_2O_4^{2-} \rightarrow SO_4^{2-} + CO_2^{\cdot-} + CO_2 \quad \text{fast} \qquad (2)$$

$$CO_2^{\cdot-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\cdot-} + CO_2 \quad \text{fast} \qquad (3)$$

$$\left.\begin{array}{l} CO_2^{\cdot-} + SO_4^{\cdot-} \rightarrow SO_4^{2-} + CO_2 \qquad (4) \\ CO_2^{\cdot-} + OH^{\cdot} \rightarrow CO_2 + OH^{1-} \qquad (5) \end{array}\right\} \text{chain termination}$$

The inhibition caused by oxygen and halide ions (153, 155) can be attributed to the reactions

$$CO_2^{\cdot-} + O_2 \rightarrow CO_2 + O_2^{1-} \qquad (6)$$

$$SO_4^{\cdot-} + Cl^{1-} \rightarrow SO_4^{2-} + Cl. \qquad (7)$$

In the reaction scheme the intermediate oxalate ion radical could be either $CO_2^{\cdot-}$ or $C_2O_4^{\cdot-}$, both of which have been proposed as "active oxalate" (105).

The mechanism for the silver ion catalyzed reaction is much more speculative but, as the value of the rate constant is much higher (59, 83, 85) than that of other silver ion catalyzed oxidations involving positively charged reductants, it is assumed that other active species, apart from higher-valent silver compounds, are present. Bhakuni and Srivastava (16) suggest OH^+ and $C_2O_4^{\cdot-}$ radicals as reactive intermediates but the reviewer prefers silver oxalate complexes as the reaction loses its chain decomposition characteristics in the presence of silver ions (59).

C. FORMATE ION

The peroxydisulfate–formate reaction has been studied by Indian chemists who have investigated both the silver catalyzed (61) and uncatalyzed (79, 154, 156, 157, 158) oxidations.

In the uncatalyzed reaction the stoichiometric equation is (79, 154)

$$S_2O_8^{2-} + HCOO^{1-} \rightarrow HSO_4^{1-} + SO_4^{2-} + CO_2$$

but, using identical methods of following the reaction, *viz.*, titration of suitable quantities of the reaction mixture with standard alkali, Kappanna (79) obtained markedly different results from those of an earlier study by Srivastava and Ghosh (154). The latter found that the rate of reaction was independent of the formate ion concentration but Kappanna concluded that the reaction was second order. The only difference in reagents and experimental conditions was that Srivastava and Ghosh used potassium formate solution at a temperature of 35°, whereas Kappanna used slightly differing concentrations of the sodium salt at 25°. However, these minor changes should not alter the order of the reaction. Kappanna gives no explanation for the differing molecularities and Srivastava and Ghosh do not mention his results in their later studies (156, 157, 158). In the absence of any further evidence, no conclusion can be reached about the order of this reaction, as the factors determining whether uncatalyzed peroxydisulfate oxidations will be first or second order are unknown. However, a first order reaction seems more likely by analogy with the similar peroxydisulfate–oxalate reaction.

Both authors studied the effect of inert salts on this reaction and are in agreement that the velocity decreases as the ionic strength increases. This would seem to invalidate the initial step as proposed by Kappanna

$$S_2O_8^{2-} + HCOO^{1-} \rightarrow X^{3-}$$

in which a positive salt effect would be expected. However, there are also large specific salt effects (156) and the application of the kinetic salt theory to elucidate the rate determining step may not be justifiable.

Both workers have made kinetic studies at different temperatures and the energy of activation can be calculated to be 21.93 (154) or 24.9 (79) kcal. mole^{-1}.

The mechanism for the reaction given by Srivastava and Ghosh (154) is

$$S_2O_8^{2-} + H_2O \rightarrow SO_4^{2-} + HSO_4^{1-} + OH^+ \quad \text{slow}$$
$$OH^+ + HCOO^{1-} \rightarrow H_2O + CO_2 \quad \text{fast}$$

Srivastava and Ghosh have made a further study of the oxidation using formic acid instead of potassium formate (156, 157) and following with extent of the reaction by measuring the electrical conductivity at different time intervals. The over-all molecular equation is

$$K_2S_2O_8 + HCOOH \rightarrow K_2SO_4 + H_2SO_4 + CO_2$$

but the rate was found to be independent of the formic acid concentration and the velocity of the reaction could be expressed as

$$-d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}]$$

where k is the unimolecular rate constant. Values for the rate constants are given in Table 7 for both formic acid and potassium formate as reducing agents, and also the values at varying temperatures.

TABLE 7

Kinetic Data for the Peroxydisulfate–Formate Oxidation

HCOOH (157, 158); $E = 8.19$ kcal. mole^{-1}

μ, M	0.03	0.06	0.09	0.12
k, min.$^{-1}$	0.00814	0.00739	0.00515	0.00475
T, °C.		30	35	40
k, min.$^{-1}$		0.00527	0.00748	0.00814

HCOOK (154, 156); $E = 21.93$ kcal. mole^{-1}

μ, M		0.54	0.69	0.84
k, min.$^{-1}$		0.00645	0.00615	0.00586
T, °C.	30	35	40	45
k, min.$^{-1}$	0.00373	0.00709	0.01234	0.02132

The oxidation of both formic acid and potassium formate is catalyzed by cupric and argentous ions and measurements made by Srivastava and Ghosh (157) show that the effect of the silver ion is the greatest. Gupta and Nigam (61), using formic acid, showed that the rate is proportional to the silver and peroxydisulfate ion concentrations and independent of the reductant concentration. Kinetic data are shown in Table 1.

It seems difficult to explain the large difference in the energy of activation for the uncatalyzed oxidation of formic acid when the values for the uncatalyzed oxidation of potassium formate and the silver ion catalyzed oxidation of formic acid are so similar and the experimental method may be at fault.

D. CERIUM(III) ION

The oxidation of cerous to ceric ion by peroxydisulfate has been investigated by Fronaeus and Ostman (44) who found that the rate of formation of ceric ion was dependent on the first power of the peroxydisulfate concentration but was of no simple order with respect to the cerous ion, as the dependence on the cerous ion concentration decreased with increasing cerous ion.

The rate law obtained was given in the form

$$\frac{d[Ce^{4+}]}{dt} = \frac{k[Ce^{3+}][S_2O_8^{2-}]}{1 + \alpha[Ce^{3+}]}$$

and evidence is put forward that suggests cerous sulfate complexes take part in the rate determining step. The proposed mechanism is

$$S_2O_8^{2-} + H_2O \rightarrow HSO_4^{1-} + SO_4^{\dot{-}} + OH^{\cdot}$$
$$SO_4^{\dot{-}} + H_2O \rightarrow HSO_4^{1-} + OH^{\cdot}$$
$$Ce(SO_4)_j^{3-2j} + SO_4^{\dot{-}} \rightarrow Ce(SO_4)_j^{4-2j} + SO_4^{2-}$$
$$j = 0, 1, \ldots$$
$$2OH^{\cdot} \rightarrow H_2O + {}^1/_2O_2$$

The silver ion catalyzed reaction also has been studied (34, 45) and the reaction rate expressed by the equation

$$d[Ce^{4+}]/dt = k_2[Ag^+][S_2O_8^{2-}]$$

However, the values of the rate constant k_2 differ by a factor of two in the two investigations. Cone (34) used 1 M sulfuric acid to prevent cerous ion hydrolysis, while Fronaeus and Ostman (45) used 0.5 M perchloric acid and the different acid concentrations may cause the difference in the rate constant.

E. MANGANESE(II) ION

In the presence of silver ion the oxidation of manganous ion takes place at a measurable rate at 25° according to the equation (10, 36, 57)

$$S_2O_8^{2-} + Mn^{2+} + 2H_2O \xrightarrow{Ag^+} 2SO_4^{2-} + MnO_2 + 4H^+ \quad (1)$$

At higher temperatures and in strong acid, the oxidation can proceed to the permanganate stage (13, 159)

$$5S_2O_8^{2-} + 2Mn^{2+} + 8H_2O \xrightarrow{Ag^+} 2MnO_4^{1-} + 10SO_4^{2-} + 16H^+ \quad (2)$$

At intermediate acid concentrations manganese(III) is formed (55)

$$S_2O_8^{2-} + 2Mn^{2+} \xrightarrow{Ag^+} 2Mn^{3+} + 2SO_4^{2-} \quad (3)$$

The optimum acid concentration for the formation of manganese(III) is 3.6 M H_2SO_4 (55) but under these conditions the oxidation is complicated by the formation of hydrogen peroxide from the acid catalyzed decomposition of peroxydisulfate (103).

Kinetic studies have been made on reactions (1), (2), and (3) and in all cases the rate of oxidation is independent of the manganous ion concentration and first order with respect to peroxydisulfate and silver ion concentration (13, 36, 55, 57). Kinetic constants for the reactions are listed in Table 1.

The following mechanism has been proposed (57)

$$S_2O_8^{2-} \rightleftarrows 2SO_4^{\dot{-}}$$

$$2SO_4^{\dot{-}} + Ag^+ \rightarrow Ag^{3+} + 2SO_4^{2-}$$

$$Ag^{3+} + 2Mn^{2+} \rightarrow Ag^+ + 2Mn^{3+}$$

$$2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$$

F. AMMONIA AND AMMONIUM ION

The thermal decomposition of ammonium peroxydisulfate in acid solution (44) is similar to that of potassium peroxydisulfate and no oxidation of the ammonium ion is observed, but in the presence of silver ions the ammonium ion is oxidized to nitrogenous substances, the nature and amount depending on the pH. In alkaline solutions nitrogen gas is formed and in acid solutions the nitrate ion (86). Stoichiometric equations are

$$2NH_3 + 3S_2O_8^{2-} \xrightarrow{Ag^+} N_2 + 6SO_4^{2-} + 6H^+$$

$$NH_4^+ + 4S_2O_8^{2-} + 3H_2O \xrightarrow{Ag^+} NO_3^{1-} + 8SO_4^{2-} + 10H^+$$

In these silver ion catalyzed oxidations the rate was found to be independent of the ammonia or ammonium ion concentration and first order in silver and peroxydisulfate ion concentration.

Early investigations (29, 82, 84, 119, 167) were based on the assumption that only one of the nitrogen species was produced in the reaction and it is not surprising that there is little agreement between workers as to the value of the rate constant for the oxidation. Fronaeus (43) has made a careful study of the reaction under a variety of conditions by measuring the e.m.f. of the system with a platinum electrode. Using a divalent silver ion as an intermediate (see p. 187) Fronaeus postulates the reactions

$$Ag(I) + S_2O_8^{2-} \rightarrow Ag(II) + SO_4^{\dot{-}} + SO_4^{2-} \quad (1)$$

$$Ag(I) + SO_4^{\dot{-}} \leftrightarrows Ag(II) + SO_4^{2-} \quad (2)$$

$$8Ag(II) + NH_4^+ + 3H_2O \rightarrow 8Ag(I) + 10H^+ + NO_3^{1-} \quad (3)$$

and in low ammonium ion concentrations

$$SO_4^{\dot{-}} + H_2O \rightarrow HSO_4^{1-} + OH^{\cdot} \quad (4)$$

$$Ag(II) + H_2O \rightarrow Ag(I) + H^+ + OH^{\cdot} \quad (5)$$

$$2OH^{\cdot} \rightarrow H_2O + {}^1/{}_2O_2 \quad (6)$$

where equations (3), (5), and (6) are not simple steps.

Electromotive force measurements give the sum of the rate steps (3), (4), and (5) as

$$\text{Rate} = \text{Constant}[Ag(II)][NH_4^+]^{0.4}/[Ag(I)]^{0.8}[H^+]^{1.1}$$

which agrees with an expression derived from the concentrations used and the proposed reaction steps.

Chaltykyan and Beilerian (30) have found that peroxydisulfate does not oxidize ammonia in the presence of cuprous ion; instead the cuprous ion is immediately oxidized to cupric ion.

G. ARSENIOUS ACID

Both the silver ion catalyzed (60) and uncatalyzed (54, 58) oxidations of arsenious acid have been investigated and the equation proposed for the reaction is

$$S_2O_8^{2-} + H_2O + H_3AsO_3 \rightarrow H_3AsO_4 + 2H^+ + 2SO_4^{2-}$$

In the absence of silver ions the rate is given by the expression

$$-d[S_2O_8^{2-}]/dt = k_1[S_2O_8^{2-}]$$

and in the presence of silver ions by the expression

$$-d[S_2O_8^{2-}]/dt = k_2[S_2O_8^{2-}][Ag^+]$$

In both cases values for the rate constants were markedly different using different samples of arsenious acid and consistent results could only be obtained when using a particular sample. This was attributed to impurities in the solutions and to the different arsenious ions that could be present.

Values for the rate constants are given in Table 8 and the other kinetic constants are listed in Tables 1 and 2.

TABLE 8

Kinetic Data for the Peroxydisulfate–Arsenious Acid Oxidation

T, °C.	k_1 (min.$^{-1}$) × 10^4	k_2 (l. mole^{-1} min.$^{-1}$)	Reference
24		23.96	60
29		30.54	60
30	5.08		58
35	8.80		58
39		50.00	60
40	16.48		58
45	25.48		58
45	19.89		54

Both reactions are inhibited by alkali metal and halide ions and in the silver catalyzed oxidation increasing hydrogen ion concentration causes the value of the second order rate constant to rise to a maximum at 0.05 M sulfuric acid and then fall again (60).

H. HYDROGEN PEROXIDE

Hydrogen peroxide and peroxydisulfate react together to form oxygen according to the equation (42, 162)

$$S_2O_8^{2-} + H_2O_2 \rightarrow O_2 + 2HSO_4^{1-}$$

The kinetics were first studied by Friend (42), who found the rate to be independent of the hydrogen peroxide concentration and first order with respect to peroxydisulfate concentration. A study over a wider range of reactant concentrations has been made by Tsao and Wilmarth (162), who give the empirical rate law for the reaction at 30° as

$$\frac{-d[S_2O_8^{2-}]}{dt} = [S_2O_8^{2-}]\left\{\frac{9.5 \times 10^6}{[H_2O_2]} + \frac{7.6 \times 10^7[S_2O_8^{2-}]}{[H_2O_2]} + 2.9 \times 10^{10}[S_2O_8^{2-}] + 7.9 \times 10^8\right\}^{-1/2}$$

With varying hydrogen peroxide and peroxydisulfate ion concentrations this rate expression approaches the limiting forms

(i) 0.001–0.005 M H_2O_2 and 0.001–0.025 M $K_2S_2O_8$

$$-d[S_2O_8^{2-}]/dt = k_{(i)}[S_2O_8^{2-}][H_2O_2]^{1/2}$$

(ii) 0.025 M H_2O_2 and 0.002–0.01 M $K_2S_2O_8$

$$-d[S_2O_8^{2-}]/dt = k_{(ii)}[S_2O_8^{2-}]$$

(iii) 1.0 M H_2O_2 and 0.1–0.25 M $K_2S_2O_8$

$$-d[S_2O_8^{2-}]/dt = k_{(iii)}[S_2O_8^{2-}]^{1/2}$$

The over-all mechanism ascribed to the reaction is (162)

$$\begin{aligned} S_2O_8^{2-} &\rightarrow 2SO_4^{\cdot -} \\ SO_4^{\cdot -} + H_2O &\rightarrow H^+ + SO_4^{2-} + OH^{\cdot} \\ OH^{\cdot} + H_2O_2 &\rightarrow H_2O + HO_2 \\ HO_2 + S_2O_8^{2-} &\rightarrow O_2 + HSO_4^{1-} + SO_4^{\cdot -} \\ HO_2 + H_2O_2 &\rightarrow O_2 + H_2O + OH^{\cdot} \end{aligned}$$

but the step

$$SO_4^{\cdot -} + H_2O_2 \rightarrow HO_2 + HSO_4^{1-}$$

which is assumed to operate in similar peroxydisulfate oxidations (p. 192) is omitted (52) for kinetic reasons (162).

The catalytic effects of silver(I) ion (116, 151, 152), silver(II) ion (116), and copper(II) ion (139) have been investigated. The silver(II) ion has similar catalytic properties to that of the silver(I) ion (116).

I. ALCOHOLS

The knowledge of steps in the mechanism for the oxidation of organic compounds by peroxydisulfate has been advanced considerably by the study of the peroxydisulfate–alcohol reaction (6, 7, 8, 102, 113, 114, 117, 122, 164).

It has been found that addition of alcohols (methanol, ethanol, and 2-propanol) to peroxydisulfate in water increases its rate of decomposition but that the addition of allyl acetate has little effect. Addition of allyl acetate to the alcohol–peroxydisulfate reaction, however, eliminates the acceleration due to the alcohol and the rate of decomposition of peroxydisulfate is almost the same as that in the presence of allyl acetate alone (102, 164).

An extensive study of the peroxydisulfate oxidation of 2-propanol (7, 113, 117, 122, 164) shows the rate of decomposition of peroxydisulfate to be related to the initial peroxydisulfate concentration by the equation

$$-d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}] \qquad (1)$$

$$= k_p[S_2O_8^{2-}]\frac{[S_2O_8^{2-}]_0}{a + [S_2O_8^{2-}]_0} \qquad (2)$$

therefore

$$k = k_p \frac{[S_2O_8^{2-}]_0}{a + [S_2O_8^{2-}]_0} \qquad (3)$$

when the alcohol concentration is kept constant, and to the initial alcohol concentration by the equation

$$k = k_s \frac{[ROH]_0}{b + [ROH]_0} \qquad (4)$$

when the peroxydisulfate concentration is constant. The subscript zero refers to initial concentrations and a and b are empirical constants.

Equation (2) means that any single kinetic experiment obeys an integrated first-order law, which shows that the rate of disappearance of peroxydisulfate is first order with respect to time. With respect to concentration (106), however, the reaction is second order at low values of peroxydisulfate and first order at high values, and somewhere between these two extremes for intermediate peroxydisulfate concentrations. In a similar fashion, equation (4) implies the rate is first order with respect to alcohol concentration at low alcohol concentrations and independent of the alcohol concentration at high values.

Equations (2) and (4) can be combined to give

$$k = k_{\max}\frac{[ROH]_0[S_2O_8^{2-}]_0}{(b + [ROH]_0)(a + [S_2O_8^{2-}]_0)}$$

The values of $k_{\max}$, b, and a are 1.18, 0.0070, and 0.0015, respectively (117).

These results were further developed in a comprehensive study of the oxidation by Ball, Crutchfield, and Edwards (7).

The reaction is extremely sensitive to traces of dissolved oxygen and dissolved copper impurities. In the presence of oxygen two different paths operate, one involving oxygen inhibition. When all the oxygen is removed the second path operates. The energy of activation for the oxygen inhibited path is between 25 and 27 kcal. mole^{-1} and the rate is independent of the oxygen and alcohol concentration. This is the part of the oxidation studied by Levitt and Malinowski (113), who found an energy of activation of 26 kcal. mole^{-1}. In the absence of oxygen the decomposition is first order in peroxydisulfate and one-half order in 2-propanol (7) with an activation energy of 21 kcal. mole^{-1}.

No completely satisfactory mechanism has been proposed to explain all of the above results, but from the results of the allyl acetate experiments (102) these steps are most likely (8, 164)

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot -} \qquad (1)$$

$$SO_4^{\cdot -} + R_2CHOH \rightarrow R_2\dot{C}OH + HSO_4^{1-} \qquad (1a)$$

or

$$SO_4^{\cdot -} + H_2O \rightarrow OH^{\cdot} + HSO_4^{1-} \qquad (1b)$$

and

$$OH^{\cdot} + R_2CHOH \rightarrow R_2COH + H_2O \qquad (1c)$$

then

$$R_2\dot{C}OH + S_2O_8^{2-} \rightarrow R_2C{=}O + HSO_4^{1-} + SO_4^{\cdot -} \qquad (2)$$

$$R_2\dot{C}OH + SO_4^{\cdot -} \rightarrow R_2C{=}O + HSO_4^{1-} \qquad (3a)$$

Equations (1) and (1b) are those involved in the thermal decomposition in aqueous solution (see pp. 189, 190). The increased rate of decomposition caused by the addition of alcohol must be due to either equation (2) where the peroxydisulfate is attacked by a free radical not present in the water decomposition, or by the reaction

$$R_2CHOH + S_2O_8^{2-} \rightarrow R_2\dot{C}OH + HSO_4^{1-} + SO_4^{\cdot -} \quad (4)$$

That the peroxydisulfate does not directly attack the alcohol, as in equation (4), is inferred from the addition of allyl acetate to the peroxydisulfate–alcohol reaction. If direct attack took place the rate of the peroxydisulfate decomposition would still be increased even in the presence of the free radical capture agent (allyl acetate); however, this is contrary to experimental results (102).

Equation (3a) is a chain termination step and there are others that could also be involved, *e.g.*

$$2R_2\dot{C}OH \rightarrow R_2CHOH + R_2C{=}O \quad (3b)$$

Analysis of the kinetic scheme of equations 1–1b–1c–2–3a leads to the rate law (164)

$$\text{Velocity} = (2k_1k_{1b}k_2/k_{3a})^{1/2}[S_2O_8^{2-}]$$

This scheme also accounts for the decrease in the rate constant at low peroxydisulfate or alcohol concentrations (113, 117) as the chain terminating steps then become important.

An alternative mechanism involving an equilibrium between peroxydisulfate and 2-propanol (117)

$$R_2CHOH + S_2O_8^{2-} \rightleftarrows R_2CHO\overset{+}{O}HSO_3^{-} + SO_4^{2-}$$

has been shown to be incorrect (164) for when the reaction is performed in the presence of sulfate labeled with sulfur-35 there is no loss of specific activity in the sulfate. Also a direct reaction between peroxydisulfate and alcohol has been ruled out previously by the allyl acetate experiments.

Sequence 1–1a–2–3a predicts the rate law (7)

$$\text{Velocity} = (k_1k_{1a}k_2/k_{3a})^{1/2}[S_2O_8^{2-}][R_2CHOH]^{1/2}$$

which agrees with the observed rate law in the absence of oxygen. The oxygen inhibition is attributed to the removal of the reducing radical $R_2\dot{C}OH$ by the dissolved gas.

The oxidation of methanol by peroxydisulfate (8, 102) does not conform to the previous rate law, the expression being

$$-d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}]^{3/2}[CH_3OH]^{1/2}$$

Equations 4–1a–2–3b in that sequence (where R = H) have been suggested as the mechanism for the decomposition (8) and the rate of disappearance from this should be (8, 102)

$$-d[S_2O_8^{2-}]/dt = k_4[S_2O_8^{2-}][CH_3OH] + k_2(k_4/k_{3b})^{1/2}[S_2O_8^{2-}]^{3/2}[CH_3OH]^{1/2}$$

Neglecting the first term provides a rate equation that agrees with experiment but the validity of this step cannot be fully justified and it has been shown that the reaction in equation (4) does not take place (102).

The sequence of equations 1–1a–2–3b leading to the rate law

$$-d[S_2O_8^{2-}]/dt = k_1[S_2O_8^{2-}] + k_2(k_1/k_{3b})^{1/2}[S_2O_8^{2-}]^{3/2}$$

also has been proposed (8, 102) for the methanol oxidation. In this, the first term is negligible compared to the second when the methanol concentration is large, but the sequence does not account for the dependence on the square root of the methanol concentration.

A possible explanation for these results is that the products of the reaction (formaldehyde and formate ion) may be affecting the kinetics, as both these compounds will react with peroxydisulfate (81, 102, 154). Experimentally it is found that as the methanol concentration decreases, the amount of formaldehyde formed, based on peroxydisulfate decomposed, also decreases (8). If the peroxydisulfate were also reacting with the products, it could account for the high power of the peroxydisulfate concentration involved in the rate law.

The rate of oxidation was increased markedly by the addition of cupric ions but reached a maximum value as the cupric ion concentration was increased (7). This phenomenon also was observed in the metal ion catalysis of the peroxydisulfate–iodide reaction and it is suggested (49) that the role of the cupric ion is to assist the electron transfer to the reducing agent. The direct oxidation

$$S_2O_8^{2-} + Cu^{2+} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + Cu^{3+}$$

is excluded on kinetic grounds as the sulfate free radicals can only be produced from steps (1) and (2), (7).

J. ORGANIC SULFUR COMPOUNDS

Kinetic studies on the oxidation of thioacids (62, 107, 108), sulfoxides (39, 67), mercaptans (39, 111, 112), and thiophenes (37) in neutral or alkaline solution show that a limiting rate is attained above a certain concentration of sulfur compound but the reaction is always first order in peroxydisulfate.

An empirical rate law

$$-d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}]$$

where $k = a[S]/(b + [S])$, has been suggested (111), where [S] is the concentration of organic sulfur compound and a and b are empirical constants.

The energy of activation of the rate determining step for most of the above compounds lies between 24 and 26 kcal. mole^{-1} (39, 67).

The effect of varying the structure of the compound oxidized has received considerable attention (39, 67, 107, 108) and it appears that an electron withdrawing group adjacent to the sulfur atom decreases the rate of oxidation. Levitt (111, 112) has suggested a mechanism for the oxidation of mercaptans, thought to be operative in all organic peroxydisulfate oxidations, which is based on the reversible decomposition of the peroxydisulfate ion into sulfur tetroxide and a sulfate ion

$$S_2O_8^{2-} \rightleftarrows SO_4 + SO_4^{2-}$$

However, this step is now considered unlikely (7, 38), as no exchange of sulfur-35 between peroxydisulfate and sulfate ions has been observed (38).

VI. SECOND ORDER OXIDATIONS

A. IODIDE ION

The reaction between peroxydisulfate and iodide ion has been reviewed briefly by Morgan (126) and some of the work prior to 1953 summarized. A more detailed account of the work prior to 1954 is given by Meretoja (120). This reaction also has been studied to a much greater extent than other peroxydisulfate oxidations and not all aspects will be covered here. The following section will deal with the work prior to 1961 with some mention of early publications to make a consistent account. Emphasis will be on the mechanism and methods for determining the rate rather than on the theories that this reaction often is used to illustrate.

The stoichiometric equation for the reaction is

$$S_2O_8^{2-} + 2I^{1-} \rightarrow I_2 + 2SO_4^{2-} \qquad (1)$$

but the oxidation usually has been considered to be bimolecular (120) as the velocity constants as calculated from the experimental results (88, 100, 120, 134, 149) by means of the equation

$$-d[S_2O_8^{2-}]/dt = k_2[S_2O_8^{2-}][I^{1-}] \qquad (2)$$

or one of its integrated forms (120), show less variation than if equations for unimolecular or termolecular reactions are used.

The slow oxidation of iodide ion by peroxydisulfate was first observed by Marshall (118) and the first kinetic study was by Price (134), who followed the extent of the reaction by taking samples at known time intervals and determining the amount of iodine produced by titration with thiosulfate. The values of the rate constant so obtained decreased as the reaction proceeded, the decrease being attributed to the formation of the tri-iodide ion according to equation (3).

$$I^{1-} + I_2 \rightleftarrows I_3^{1-} \qquad (3)$$

The effect of this equilibrium on the reaction has been studied (88, 89, 95, 98) and it was found that the tri-iodide ion reacts with the peroxydisulfate but at about half the rate of the iodide ion (88). By saturating the reactant solutions with iodine, King and Jette (88) were able to simplify the theoretical treatment for the system, as under these conditions the ratio of iodide to tri-iodide ion remains constant. With iodine saturated solutions the rate constants were some 25% less, and using the known value for the equilibrium constant in equation (3), values of k_2 and k_2' in the rate expression

$$-d[S_2O_8^{2-}]/dt = k_2[S_2O_8^{2-}][I^{1-}] + k_2'[S_2O_8^{2-}][I_3^{1-}] \qquad (4)$$

were found to be 0.126 and 0.0642 l. mole^{-1} min.$^{-1}$, respectively, using 0.01 N reagents at 25°. In many studies of this reaction the detailed effect of the tri-iodide ion on the rate has been ignored and values of the rate constant in equation (2) obtained by plotting the observed values against time and extrapolating to zero time (3, 88, 90, 120).

Using the latter method the rate constant can be expressed in the form (120) $k_2 = 1.34 \times 10^8 \exp(-12{,}700/RT)$ l. mole^{-1} sec.$^{-1}$ in the 20–40° temperature range.

Other methods of following the production of iodine have been used in order to avoid the tri-iodide formation. King and Jette (89) added an immiscible inert organic solvent to the reaction mixture to remove the iodine produced in the aqueous layer. The values of k_2 obtained were generally more constant than when the iodine was allowed to accumulate but the average value varied with the solvent added. The reaction also has been performed in the presence of hydroxyl ion (89) which removes the iodine according to the equations

$$S_2O_8^{2-} + 2I^{1-} \rightarrow I_2 + 2SO_4^{2-}$$

$$3I_2 + 6OH^{1-} \rightarrow 5I^{1-} + IO_3^{1-} + 3H_2O$$

and over-all

$$3S_2O_8^{2-} + I^{1-} + 6OH^{1-} \rightarrow 6SO_4^{2-} + IO_3^{1-} + 3H_2O$$

This method gave constant values of the rate constant and they were in agreement with those obtained when no hydroxyl ions were present. An accurate method has been developed involving the successive addition of small quantities of sodium thiosulfate solution to the reaction mixture (66, 71, 72, 87). The thiosulfate reacts very rapidly with the iodine liberated (4) from the peroxydisulfate oxidation and the solution remains free from iodine until all the thiosulfate has been used up. The time of reappearance of iodine has been determined by means of a photo-cell (87) or by using a polarized electrode (71). Equations representing the reactions in the solution are

$$S_2O_8^{2-} + 2I^{1-} \rightarrow I_2 + SO_4^{2-} \qquad \text{slow}$$

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^{1-} + S_4O_6^{2-} \qquad \text{fast}$$

Thus the iodide ion concentration remains constant and the kinetics become pseudo-first order according to the equations

$$-d[S_2O_8^{2-}]/dt = k_1[S_2O_8^{2-}]$$

where

$$k_1 = k_2[I^{1-}]$$

However, this method suffers from the disadvantage that unless only the initial rate of the reaction is followed, the ionic strength of the solution increases with addition of thiosulfate. Also the possibility of oxidation of thiosulfate by peroxydisulfate cannot be excluded. Despite these objections this method gives very accurate rate constants (73), especially in dilute solution. The method has been adapted to more concentrated solutions by mixing solutions of peroxydisulfate, iodide, and thiosulfate and titrating the undecomposed thiosulfate with standard iodine (66, 91). The simultaneous reactions involved in this system are

$$S_2O_8^{2-} + 2I^{1-} \rightarrow I_2 + 2SO_4^{2-}$$
$$2S_2O_3^{2-} + I_2 \rightarrow 2I^{1-} + S_4O_6^{2-}$$
$$2S_2O_3^{2-} + S_2O_8^{2-} \rightarrow S_4O_6^{2-} + 2SO_4^{2-}$$

In this case no tri-iodide is formed, the ionic strength remains constant, and the fact that the peroxydisulfate oxidizes the thiosulfate is an essential part of the kinetic analysis. The rate equation for the peroxydisulfate–iodide reaction is

$$-d[S_2O_8^{2-}]/dt = k_2[S_2O_8^{2-}][I^{1-}]$$

and for the peroxydisulfate–thiosulfate reaction

$$-d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}] \text{ (see p. 190)}$$

Thus, if the two methods of peroxydisulfate decomposition are additive, the rate equation for the mixed reaction is

$$-d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][I^{1-}]$$

but, owing to the rapid nature of the thiosulfate–iodine reaction to produce iodide ions, the iodide ion concentration remains constant and the rate equation becomes

$$\begin{aligned} -d[S_2O_8^{2-}]/dt &= (k + k_1)[S_2O_8^{2-}] \\ &= k_0[S_2O_8^{2-}] \end{aligned}$$

where k_0 is observed rate constant, and $k_1 = k_2[I^{1-}]$. Hence $k_2 = (k_0 - k)/[I^{1-}]$. Thus the calculation of the bimolecular peroxydisulfate-iodide rate constant involves a knowledge of the first order peroxydisulfate-thiosulfate rate constant at the ionic strength in question, and assumes that the latter is the same in the presence of iodide ions, this latter assumption being rather doubtful in view of the large specific effect of ions on the peroxydisulfate–thiosulfate reaction (91).

To account for the observed kinetics, it has been suggested that the reaction takes place in two steps (21, 100)

$$S_2O_8^{2-} + I^{1-} \rightarrow I\,S_2O_8^{3-} \quad \text{slow} \quad (1)$$
$$IS_2O_8^{3-} + I^{1-} \rightarrow I_2 + 2SO_4^{2-} \quad \text{fast} \quad (2)$$

An alternative decomposition of the activated complex $IS_2O_8^{3-}$ has been proposed by Soper and Williams (149)

$$IS_2O_8^{3-} \rightarrow I^{\cdot} + S_2O_8^{2-} \quad (2a)$$
$$S_2O_8^{2-} + I^{1-} \rightarrow 2SO_4^{2-} + I^{\cdot} \quad \text{fast} \quad (2b)$$
$$I^{\cdot} + I^{\cdot} \rightarrow I_2 \quad \text{fast} \quad (3)$$

However, it is possible to account for the observed kinetics by a third mechanism (49) based directly on the Eyring theory of absolute reaction rates (50).

$$\left.\begin{aligned} S_2O_8^{2-} + I^{1-} &\rightleftarrows IS_2O_8^{3-} \\ IS_2O_8^{3-} &\rightarrow I^{+} + 2SO_4^{2-} \end{aligned}\right\} \begin{aligned} &\text{rate} \quad (1a) \\ &\text{determining} \quad (1b) \end{aligned}$$
$$I^{+} + I^{1-} \rightarrow I_2 \quad \text{fast} \quad (3a)$$

That monopositive iodine will be formed is not unlikely as peroxydisulfate can slowly oxidize a solution of potassium iodide in concentrated hydrochloric acid to iodine monochloride. Also, in the presence of potassium iodide and pyridine, peroxydisulfate will form orange crystals of bis-(pyridyl)-iodine(I) peroxydisulfate. Higginson and Marshall's generalization (63) that oxidation–reduction reactions between ions derived from ions from two non-transition elements, whether metallic or non-metallic, usually occur in two electron steps, also favors equations 1a–1b as the primary reactions.

In his original study of the peroxydisulfate reaction, Price (134) found that the rate was increased by traces of cupric and ferrous ions. Since that time this catalytic effect has been investigated extensively (1, 18, 49). It has been suggested that to accelerate the oxidation the catalyst must be capable of reversible oxidation–reduction (1), the catalytic system with the greatest negative oxidation–reduction potential generally giving the greatest acceleration (49). The action of metal ion and aromatic molecule catalysts is to facilitate the electron transfer to the iodide ion, the proposed mechanism being (49)

$$S_2O_8^{2-} + M^{n+} \rightarrow S_2O_8M^{n-2} \quad (1)$$
$$S_2O_8M^{n-2} + I^{-} \rightarrow I^{+} + 2SO_4^{2-} + M^{n+} \quad (2)$$
$$I^{+} + I^{-} \rightarrow I_2 \quad (3)$$

This mechanism is in accordance with the magnetic data obtained from the ferrous–iodide–peroxydisulfate ion system (18), where a relatively stable diamagnetic intermediate was detected, thus indicating that the previous view (100) that the reaction proceeds through the formation of ferric ion is incorrect.

The oxidation of iodide by peroxydisulfate is a reaction between ions of like charge type and many investigators (87, 92, 93, 94, 96, 97, 149) have used it to test the predictions of the Brønsted theory of kinetic salt effects (21) and the Debye–Hückel limiting law. The results of these experiments have been summarized, and the data extended by Meretoja (120). Later work, however, indicates that the salt effect depends more on the concentration and nature of the cation than on the ionic strength, as the rate increases differently using different salts (23, 24, 25, 26, 68, 69, 70, 71, 72, 73, 137).

Theories on reaction rates in iso-dielectric and iso-composition systems also have been tested using the peroxydisulfate–iodide reaction (3, 27, 28, 99, 120, 121), the dielectric constant of the system being varied by

TABLE 9

Kinetic Data for the Oxidation of the Divalent Iron Group Ions by Peroxydisulfate

Values of k_2 are at zero ionic strength at 25° with units of l. mole^{-1} min.$^{-1}$; $E°$ is the standard electrode potential in volts; dipy is for α,α'-dipyridyl; 4,4'-Me$_2$dipy is for 4,4'-dimethyldipyridyl; *o*-phen is for orthophenanthroline; 5Me-phen is for 5-methylphenanthroline

No.	Ion	k_2	*A* (l. mole^{-1} sec.$^{-1}$)	*E* (kcal. mole.$^{-1}$)	E^0, volts	Reference
1	Fe^{2+}	(129, 70)	1.0×10^{11}	12.1	−0.771	41, 135
2	$Os(dipy)_3^{2+}$	49.0	2.8×10^{8}	9.4	−0.87	75
3	$Fe(4,4'\text{-}Me_2dipy)_3^{2+}$	6.68	3.2×10^{8}	10.6	−0.94	76
4	$Fe(dipy)_3^{2+}$	0.55	5.7×10^{8}	12.4	−1.12	76
5	$Fe(o\text{-}phen)_3^{2+}$	0.30	1.5×10^{9}	13.3	−1.14	76
6	$Fe(5Me\text{-}phen)_3^{2+}$	0.11	1.6×10^{8}	12.6	−1.15 *ca.*	76
7	$Ru(dipy)_3^{2+}$	0.009	5.0×10^{8}	14.6	−1.37	76

addition of ethanol (3), methanol (120, 121) or dioxane, (27, 28).

B. DIVALENT IRON GROUP IONS

Kinetics of the oxidations of ferrous ion (41, 101, 138), ferrous dipyridyl (41, 76) and phenanthroline complex ions (76), ferrocyanide ion (65), tris-(dipyridyl)-osmium(II) ion (75, 76), and tris-(dipyridyl)-ruthenium-(II) ion (76) have been studied and the results for the dipositive ions are summarized in Table 9. The rates of the reaction follow second order kinetics, but for three of the ferrous complexes, the oxidations were followed under conditions where pseudo first order kinetics applied (76).

For the dipositive ions the stoichiometric equation is

$$2M^{2+} + S_2O_8^{2-} \rightarrow 2M^{3+} + 2SO_4^{2-} \quad (1)$$

where M^{2+} and M^{3+} represent the divalent ion and its oxidation product. The rate determining step is assumed to be (41, 75, 101)

$$M^{2+} + S_2O_8^{2-} \rightarrow M^{3+} + SO_4^{2-} + SO_4^{-} \quad \text{slow} \quad (2)$$

followed by (41, 101)

$$M^{2+} + SO_4^{-} \rightarrow M^{3+} + SO_4^{2-} \quad \text{fast} \quad (3)$$

The standard free energy change corresponding to equation (1) is given by

$$\Delta G = -2F[E^0(S_2O_8^{2-}) - E^0(M^{2+})]$$

where $E^0(S_2O_8^{2-})$ is the standard oxidation–reduction potential for the SO_4^{2-}–$S_2O_8^{2-}$ couple and $E^0(M^{2+})$ that of the M^{2+}–M^{3+} couple.

Figure 2 shows a plot of log k_2 against $E^0(M^{2+})$ and the straight line obtained can be expressed by the relation log $k_2 = 6.94E^0(M^{2+}) + 7.46$.

Thus the rates can be related directly to the standard free energy change + (76).

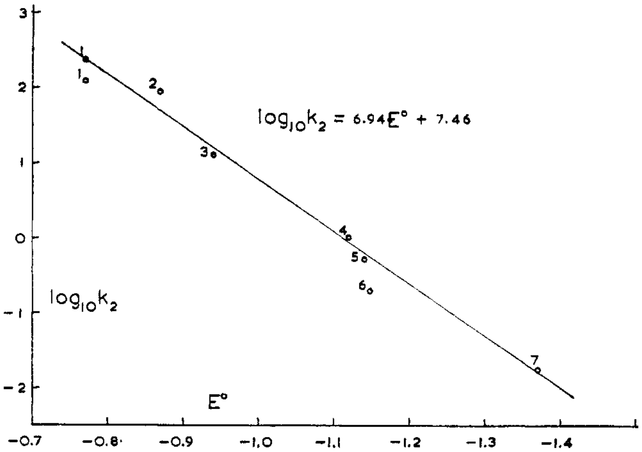

FIG. 2.—Log k_2 against $E^0(M^{2+})$ for the divalent iron group, k_2 in l. mole^{-1} sec.$^{-1}$ and E^0 in volts. Numbers refer to the ions in Table 9.

The ferrocyanide oxidation (65) cannot be included with the above, as the negative charge on the ion induces different coulombic interactions. In neutral solutions the second order constants are not constant with change in time or initial concentration of the reactants. However, in 0.5 *M* potassium sulfate solutions these irregularities disappear and the variations in neutral solution are attributed to the presence of the strong electrostatic field. From mean values in neutral solution the bimolecular rate constant for the reaction

$$2Fe(CN)_6^{4-} + S_2O_8^{2-} \rightarrow 2Fe(CN)_6^{3-} + 2SO_4^{2-}$$

can be represented by the equation

$$k_2 = 3.2 \times 10^9 \exp(-11{,}900/RT) \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

VII. MISCELLANEOUS

Organic Nitrogen Compounds.—Only a few kinetic investigations have been made in this field. The reaction with amines (12, 31, 33) is dependent on pH, being much faster in alkaline media.

With hydrazobenzene (163) the rate determining step is first order in both reactants but the value for the rate constant depends on the initial reactant concentration. The over-all reaction has an energy of activation of 16 kcal. mole^{-1} (163).

Aldehydes and Ketones.—In the silver ion catalyzed oxidation of acetone with peroxydisulfate (14) the kinetics obey the usual law for this type (see Table 1) and it has been shown that acetic acid and carbon dioxide are the reaction products, according to the equation

$$CH_3COCH_3 + 4K_2S_2O_8 + 3H_2O \xrightarrow{Ag^+} CH_3COOH + CO_2 + 8KHSO_4$$

The salt effect on this reaction is negative. The uncatalyzed oxidation of formaldehyde and acetaldehyde also has been studied (81).

Copper Compounds.—The oxidation of cuprous chloride to the cupric state according to the over-all equation

$$2CuCl + K_2S_2O_8 \rightarrow K_2SO_4 + CuSO_4 + CuCl_2$$

has been studied (30) and an ion-radical mechanism proposed with the main reactions being

$$Cu^+ + S_2O_8^{2-} \rightarrow CuS_2O_8^{1-}$$

$$CuS_2O_8^{1-} \rightarrow Cu^{2+} + SO_4^{2-} + SO_4^{-\cdot}$$

$$SO_4^{-\cdot} + Cu^+ \rightarrow Cu^{2+} + SO_4^{2-}$$

as second order kinetics are observed. Addition of chloride ions decreases the rate but addition of ammonia gives a much faster reaction (30).

The rate of the dissolution of metallic copper in aqueous peroxydisulfate solutions has been found to be dependent on the first power of the peroxydisulfate concentration at concentrations less than 0.5 *M*, with a tendency to zero order at higher concentrations (20). At peroxydisulfate ion concentrations greater than 0.25 *M*, the activation energy is constant at 10.3 kcal. mole^{-1}.

Americium(III) Ion.—The oxidation of americium(III) to americium(VI) may be accomplished with peroxydisulfate (132) but it is essential that the acid concentration be kept low. The rate of reaction is given by the expression (133).

$$-d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}] + k'[S_2O_8^{2-}][H^+]$$

but if acidities higher than 0.5 *M* are used, the amount of americium(VI) decreases as the hydrogen peroxide formed from the acid-catalyzed thermal decomposition of peroxydisulfate (p. 190) acts as a reducing agent for americium(VI).

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VIII. APPENDIX

Steady State Analysis of the Mechanism for the First Order Uncatalyzed Peroxydisulfate Oxidations

Let R be a radical and P the product from an oxidizable substrate, S. The proposed steps for the general case are

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{-\cdot} \tag{1}$$

$$SO_4^{-\cdot} + H_2O \xrightarrow{k_2} OH^\cdot + SO_4^{1-} \tag{2}$$

$$OH^\cdot + S \xrightarrow{k_3} OH^{1-} + R \tag{3}$$

$$R + S_2O_8^{2-} \xrightarrow{k_4} P + SO_4^{2-} + SO_4^{-\cdot} \tag{4}$$

$$R + SO_4^{-\cdot} \xrightarrow{k_5} P + SO_4^{2-} \tag{5}$$

Several differential equations can be set up from this scheme

$$-d[S_2O_8^{2-}]/dt = k_1[S_2O_8^{2-}] + k_4[R][S_2O_8^{2-}] \tag{6}$$

$$-d[S]/dt = k_3[OH^\cdot][S] \tag{7}$$

$$d[SO_4^{-\cdot}]/dt = 2k_1[S_2O_8^{2-}] - k_2[SO_4^{-\cdot}] + k_4[R][S_2O_8^{2-}] - k_5[R][SO_4^{-\cdot}] \tag{8}$$

$$d[R]/dt = k_3[OH^\cdot][S] - k_4[R][S_2O_8^{2-}] - k_5[R][SO_4^{-\cdot}] \tag{9}$$

$$d[OH^\cdot]/dt = k_2[SO_4^{-\cdot}] - k_3[OH^\cdot][S] \tag{10}$$

By the steady state hypothesis, $[SO_4^{-\cdot}]$, [R], and $[OH^\cdot]$ are constant, therefore

$$d[SO_4^{-\cdot}]/dt = d[R]/dt = d[OH^\cdot]/dt = 0 \tag{11}$$

Thus, from (10) and (11)

$$k_2[SO_4^{-\cdot}] = k_3[OH^\cdot][S] \tag{12}$$

Substitution of (12) in (7) gives

$$-d[S]/dt = k_2[SO_4^{-\cdot}] \tag{13}$$

and substitution of (12) in (9) gives

$$d[R]/dt = k_2[SO_4^{-\cdot}] - k_4[R][S_2O_8^{2-}] - k_5[R][SO_4^{-\cdot}] = 0 \tag{14}$$

Adding equations (8) and (14)

$$k_1[S_2O_8^{2-}] = k_5[R][SO_4^{-\cdot}] \tag{15}$$

and subtracting equations (8) and (14)

$$k_2[SO_4^{-\cdot}] = k_1[S_2O_8^{2-}] + k_4[R][S_2O_8^{2-}] \tag{16}$$

Thus, from equations (6), (13), and (16)

$$-d[S_2O_8^{2-}]/dt = -d[S]/dt$$

Now, from equation (15)

$$[SO_4^{-\cdot}] = k_1[S_2O_8^{2-}]/k_5[R] \tag{17}$$

and substitution of (17) in (16) gives

$$k_1 + k_4[R] = k_1k_2/k_5[R] \tag{18}$$

Therefore

$$k_4[R]^2 + k_1[R] - k_1k_2/k_5 = 0 \tag{19}$$

Solving this quadratic gives

$$[R] = [-k_1 \pm (k_1^2 + 4k_1k_2k_4/k_5)^{1/2}]/2k_4 \tag{20}$$

and substitution for [R] in (6) gives

$$\text{Rate} = {}^1/_2[k_1 \pm (k_1^2 + 4k_1k_2k_4/k_5)^{1/2}][S_2O_8^{2-}] \tag{21}$$

which simplifies to

$$\text{Rate} = (k_1k_2k_4/k_5)^{1/2}[S_2O_8^{2-}] \tag{22}$$

if k_1 is small.

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