Kinetics of the Silver(I)-catalyzed Decomposition of Peroxodisulphate in Aqueous Solution

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The kinetics of the silver(I)-catalyzed decomposition of the peroxodisulphate ion have been investigated in aqueous solution. Molecular oxygen is produced due to the decomposition of the peroxodisulphate ion in the presence of silver(I) ion. The rate of this decomposition and of the formation of oxygen is first order with respect to the concentrations of peroxodisulphate and silver(I) ions, and the rate of reaction obeys the expression $-d[S_2O_8^{2-}]/dt = 2\,d[O_2]/dt = k[Ag^+][S_2O_8^{2-}]$, where $k = 9.37 \times 10^{-3}$, 8.96×10^{-3}, 7.59×10^{-3}, 6.91×10^{-3}, and 6.92×10^{-3} dm^3 mol^{-1} s^{-1} at I = 0.03, 0.04, 0.06, 0.09, and 0.10 mol dm^{-3} at 25 °C, respectively; $k = 1.83 \times 10^7 \exp[-54\,200 \text{ J mol}^{-1}/RT]$ dm^3 mol^{-1} s^{-1} at five temperatures between 21 and 40 °C and at I = 0.10 mol dm^{-3}. The silver(I)-ion concentration remains constant throughout the reaction, which is composed of a silver(I)-catalyzed chain reaction. The rate of the silver(I)-catalyzed decomposition of peroxodisulphate is not influenced by the addition of cerium(III) ion, but greatly accelerated by acrylamide and/or copper(II) ion, and retarded by acrylonitrile. The formation of oxygen due to the reaction is completely retarded by the addition of cerium(III) ion. On the other hand, absorption of oxygen occurs in the case of the addition of acrylamide and acrylonitrile. Mechanisms are proposed to account for the results obtained.

PEROXODISULPHATE is a powerful two-electron oxidizing agent, and its reactions with organic and inorganic substrates have been extensively studied by many researchers, and reviewed by House,[1] Wilmarth and Haim,[2] Wilson,[3] and Buist.[4] Silver(I) ion is frequently used as a powerful catalyst for most peroxodisulphate reactions. Bawn and Margerison[5] have investigated the rate of reaction between peroxodisulphate and silver(I) ions in 50% (v/v) ethyl alcohol–water, by use of the free radical diphenylpicrylhydrazyl (dpph) as a radical scavenger and assuming that the rate-determining reaction is the production of the radicals $SO_4^{\cdot -}$, Ag^{2+}, and $OH^{\cdot}$ which are rapidly captured by the dpph. However, this reaction has not been investigated in purely aqueous solutions, and thus the aim of the present study was to propose a detailed mechanism for the reaction between peroxodisulphate and silver(I) ions in aqueous solution.

EXPERIMENTAL

Chemicals.—Reagent-grade potassium peroxodisulphate was recrystallized twice from redistilled water and dried at 25 °C in a vacuum desiccator. Silver(I) perchlorate was prepared by dissolving silver(I) oxide Ag_2O (guaranteed reagent, Wako Pure Chemical Co.) in perchloric acid solution. Sodium perchlorate used for adjusting the ionic strength was recrystallized twice from redistilled water. The redistilled water was prepared from anion–cation exchanged water by successive distillation from solutions with and without permanganate in a glass still. All other chemicals used were guaranteed reagents.

Procedure.—The reaction vessel was covered with black plastic adhesive tape to ensure darkness, and was placed in a thermostat bath. Aliquot samples were withdrawn at appropriate times and mixed with cation-exchange resin in order to remove the silver ions from the reacting solution. After filtration, the concentration of peroxodisulphate ion remaining was measured by polarography at 0.2 V *vs.* a saturated calomel electrode (s.c.e.) at 25 °C in a solution of 0.01 mol dm^{-3} perchloric acid, 0.1 mol dm^{-3} sodium perchlorate, and 0.01% gelatine, essentially as described previously.[6,7] Preliminary experiments showed that the reaction between peroxodisulphate and silver(I) ions was extremely retarded by the addition of the cation-exchange resin [see curve (5) in Figure 3]. Therefore, the loss of peroxodisulphate ion during the time required (*ca.* 10 min) for the filtration and for the measurement of the polarogram was, in practice, negligible. The concentration of molecular oxygen formed or absorbed due to reaction was measured by using a Warburg oxygen meter (Sasahara PAT No. 460958). The temperature of the reacting solution was maintained constant at 25.0 ± 0.05 °C by using two thermostat baths.

RESULTS

With concentrations of 8.0×10^{-3} mol dm^{-3} potassium peroxodisulphate and 1.0×10^{-3} mol dm^{-3} silver(I) perchlorate, the peroxodisulphate ion concentration decreased according to a first-order rate law with respect to the concentration of peroxodisulphate ion [equation (1)]. This

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

rate law was satisfied over 90% completion of reaction. Some typical plots of log $[S_2O_8^{2-}]$ *vs.* t are given in Figure 1.

The rate constant $k_{obs.}$ in equation (1) was dependent on the initial concentration of the silver(I) ion even at much lower values than the peroxodisulphate concentration. Therefore, it is believed that the silver(I)-ion concentration is always constant due to rapid reformation *in situ*. Consequently, the full rate law is as in equation (2), where $[Ag^+]_i$

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

indicates the initial concentration of silver(I) ion. The rate of oxygen evolution due to the reaction was half the decomposition rate of the peroxodisulphate ion, according to equation (3). The rate constant k in equations (2) and (3)

$$d[O_2]_{formed}/dt = \tfrac{1}{2}k[Ag^+]_i[S_2O_8^{2-}] \qquad (3)$$

is shown in Table 1. For reaction times from zero to *ca.* 5 h, plots of $[O_2]_{formed}$ *vs.* t were, within the experimental error, linear (see Figure 2) and thus the rate constant k in equation (3) was evaluated from slopes of these plots.

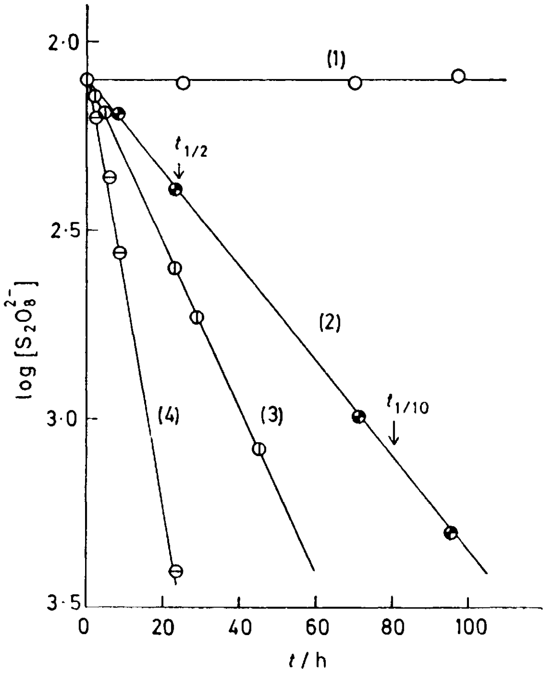

FIGURE 1 Examples of plots of log [$S_2O_8^{2-}$] *vs*. *t*. Conditions as in Table 3. Curves: (1), [$K_2S_2O_8$] = 8.0 × 10^{-3} mol dm^{-3}, [$HClO_4$] = 0.01 mol dm^{-3}; (2), (1) plus [$Ag(ClO_4)$] = 1.0 × 10^{-3} mol dm^{-3}; (3), (2) plus 1% acrylamide; (4), (3) plus [$Cu(SO_4)$] = 1.0 × 10^{-3} mol dm^{-3} in the absence of oxygen (bubbling N_2 through the reacting solution)

No hydrogen peroxide was detected in the reacting solution at any time as shown by the permanganate test.

Dependences of the Rate Constant on Temperature and Ionic Strength.—The rate constant k was determined at five temperatures between 21 and 40 °C, and is described by $k = 1.83 \times 10^7 \exp(-54\,200 \text{ J mol}^{-1}/RT)$ dm^3 mol^{-1} s^{-1} at an ionic strength $I = 0.1$ mol dm^{-3}. Values of the rate constant at different ionic strengths and temperatures are given in Table 2. Plots of log k *vs*. $I^{\frac{1}{2}}$ were linear with a slope of −1.1, the absolute value of which is smaller than that of 1.02 $Z_1Z_2 = -2.04$ predicted for this reaction.

TABLE 1

Rate constants obtained at various concentrations of peroxodisulphate and silver(I) ion *

$10^3[AgClO_4]_i$ / mol dm^{-3}	$10^3[K_2S_2O_8]_i$ / mol dm^{-3}	10^3k/dm^3 mol^{-1} s^{-1}	
		I_a	I_b
0.50	8.0	7.32	7.80
1.0	8.0	7.71	7.52
1.5	8.0	6.81	7.39
2.0	8.0	6.67	6.94
5.0	1.0	7.23	7.22
5.0	2.0	6.78	7.54
5.0	4.0	6.90	6.55
5.0	5.0	7.71	5.47
5.0	5.8	7.30	5.87
5.0	7.7	6.02	7.23
4.0	8.0	6.81	
5.0	8.0	5.64	
6.0	8.0	6.65	
8.0	8.0	6.63	
10	8.0	7.25	
	means	6.90	6.94

* [$HClO_4$] = 0.014 mol dm^{-3}, I = 0.1 mol dm^{-3} ($Na[ClO_4]$), 25 °C, in the dark. I_a = Rate constant evaluated from the plot of ln [$S_2O_8^{2-}$] *vs*. *t* according to equation (2); I_b = rate constant evaluated from the plot of $[O_2]_{formed}$ *vs*. *t*. according to equation (3).

TABLE 2

Effects of temperature, ionic strength, and acidity *

θ_c / °C	I / mol dm^{-3}	[$HClO_4$] / mol dm^{-3}	10^3k / dm^3 mol^{-1} s^{-1}
21	0.10	0.001	4.98
25	0.10	0.001	6.90
30	0.10	0.001	8.96
35	0.10	0.001	13.9
40	0.10	0.001	17.9
25	0.03	0.001	9.37
25	0.04	0.001	8.96
25	0.06	0.001	7.59
25	0.09	0.001	6.91
25	0.10	0.004	6.92
25	0.10	0.005	7.14
25	0.10	0.009	6.81
25	0.10	0.014	7.33
25	0.10	0.054	7.33
25	0.10	0.070	7.21

* [$Ag(ClO_4)$] = 5.0 × 10^{-3} mol dm^{-3}, [$K_2S_2O_8$] = 8.0 × 10^{-3} mol dm^{-3}, in the dark; rate constant evaluated from the plot of ln [$S_2O_8^{2-}$] *vs*. *t*.

Effect of Acidity.—The results in Table 2 show that the rate of reaction is not appreciably affected by the acidity over the range 0.001—0.07 mol dm^{-3} in perchloric acid. The rate of decomposition of peroxodisulphate in the absence of silver(I) ion was negligible compared with that in the presence of silver(I) ion (see Figure 1). It is known that the thermal decomposition of peroxodisulphate ion occurs according to the rate law [8] $-d[S_2O_8^{2-}]/dt = (k_1 + k_2[H^+])$-

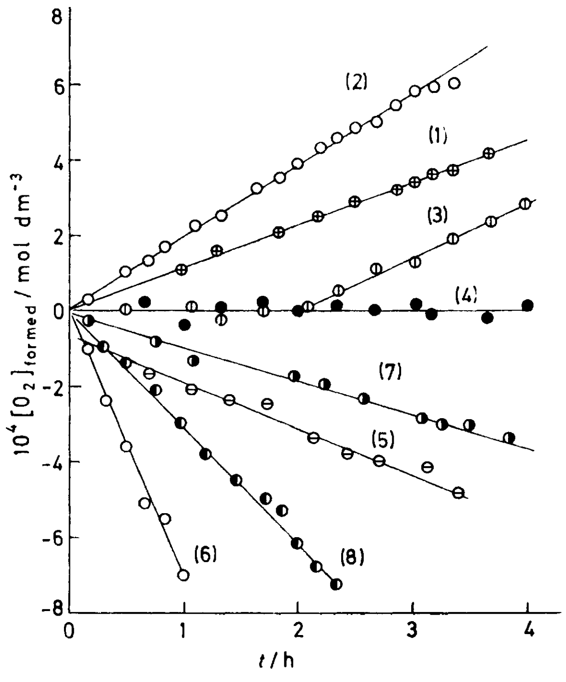

FIGURE 2 Examples of plots of $[O_2]_{formed}$ *vs*. *t*. Conditions as in Table 3. Curves: (1), [$K_2S_2O_8$] = 8.0 × 10^{-3} mol dm^{-3}, [$Ag(ClO_4)$] = 1.0 × 10^{-3} mol dm^{-3}, and [$HClO_4$] = 0.01 mol dm^{-3}; (2), (1) plus [$Cu(SO_4)$] = 2 × 10^{-3} mol dm^{-3}; (3), (1) plus [Ce^{III}] = 1 × 10^{-3} mol dm^{-3} as the sulphate salt; (4), (1) plus [Ce^{III}] = 1.5 × 10^{-3} mol dm^{-3}; (5), (1) plus 0.5% acrylamide; (6), as (5) but [$Ag(ClO_4)$] = 4 × 10^{-3} mol dm^{-3}; (7), (1) plus 1% acrylonitrile and [$Ag(ClO_4)$] = 1.0 × 10^{-3} mol dm^{-3}; (8), as (7) but [$Ag(ClO_4)$] = 4 × 10^{-3} mol dm^{-3}

$[S_2O_8^{2-}]$. In the case of the line (1) in Figure 1, 5×10^{-5} mol dm^{-3} peroxodisulphate ion requires 100 h for complete decomposition and thus the value of $(k_1 + k_2[H^+])$ is evaluated as 2×10^{-8} s^{-1} in 0.01 mol dm^{-3} perchloric acid at 25 °C.

Influence of Acrylamide, Acrylonitrile, Cerium(III), *and Copper*(II).—The rate of the silver(I)-ion catalysed decomposition of peroxodisulphate was greatly accelerated by the addition of acrylamide and/or copper(II) ion, but not influenced by the addition of cerium(III) ion, and retarded by the addition of acrylonitrile. The rate of the reaction obeyed equation (2) irrespective of the presence of acrylamide, cerium(III), and copper(II), but did not obey this equation in the presence of acrylonitrile. The presence of both acrylamide and copper(II) ion accelerated the reaction particularly, and the rate in the absence of oxygen was much larger than that in the presence of oxygen (see Table 3).

When acrylonitrile was added to a reacting solution of peroxodisulphate ion with silver(I) ion a white sediment of polyacrylonitrile was found and the reaction ceased. This behaviour is illustrated in Figure 3. At the time of complete retardation, no silver(I) ion was detected in the solution upon addition of HCl solution. All the silver(I) ions are thought to be coprecipitated with the polyacrylonitrile sediment.

TABLE 3

Influence of cerium(III) ion, acrylamide, and/or copper(II) ion on the rate of reaction [a]

Substances added	10^3k/dm^3 mol^{-1} s^{-1}
1×10^{-3} mol dm^{-3} Ce^{III}	7.29
2×10^{-3} mol dm^{-3} Ce^{III}	7.59
3×10^{-3} mol dm^{-3} Ce^{III}	7.71
5×10^{-4} mol dm^{-3} Cu^{II}	8.80, 8.75 [b]
8×10^{-4} mol dm^{-3} Cu^{II}	9.18
1×10^{-3} mol dm^{-3} Cu^{II}	10.2, 8.75 [b]
1.5×10^{-3} mol dm^{-3} Cu^{II}	9.83 [b]
2×10^{-3} mol dm^{-3} Cu^{II}	12.6 [b]
1% Acrylamide (aa)	13.5 (N_2), 14.2 (Air), 14.9 (O_2)
1% aa–1×10^{-5} mol dm^{-3} Cu^{II}	15.0 (N_2)
1% aa–5×10^{-5} mol dm^{-3} Cu^{II}	17.0 (N_2)
1% aa–1×10^{-4} mol dm^{-3} Cu^{II}	27.8 (N_2), 15.8 (Air), 16.1 (O_2)
1% aa–1×10^{-3} mol dm^{-3} Cu^{II}	37.3 (N_2), 15.7 (Air), 16.2 (O_2)

[a] $[Ag(ClO_4)] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[K_2S_2O_8] = 8.0 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 0.01$ mol dm^{-3}, $I = 0.1$ mol dm^{-3}, 25 °C, in the dark. The gases indicated in parentheses were bubbled through the reacting solution to give a saturated solution of each gas. Rate constant evaluated from the plot of ln $[S_2O_8^{2-}]$ *vs*. t. [b] As in *a*, except the rate constant was evaluated from the plot of $[O_2]_{formed}$ *vs*. t.

TABLE 4

Influence of cerium(III), copper(II), acrylamide, and acrylonitrile on the rate of evolution and absorption of oxygen [a]

Substances added	10^8v_i/mol dm^{-3} s^{-1}
None	2.8, 5.6,[b] ±0.0 [c]
1×10^{-3} mol dm^{-3} Ce^{III}	±0.0
5×10^{-4} mol dm^{-3} Cu^{II}	3.5
1×10^{-3} mol dm^{-3} Cu^{II}	3.5
1.5×10^{-3} mol dm^{-3} Cu^{II}	3.9
2×10^{-3} mol dm^{-3} Cu^{II}	5.0
1% Acrylonitrile (an)	−2.4,[b] −3.5,[d] ±0.0 [c]
2% an	−6.5,[b] −8.3 [d]
0.5% Acrylamide (aa)	−3.5, −9.8,[b] −19,[d] ±0.0 [c]
1% aa	−8.0
1% aa–1×10^{-3} mol dm^{-3} Cu^{II}	−7.8
1% aa–1.5×10^{-3} mol dm^{-3} Cu^{II}	−8.0
1% aa–2×10^{-3} mol dm^{-3} Cu^{II}	−8.2

[a] Conditions as in Table 3; initial rate (v_i) evaluated from the plot of $[O_2]_{formed}$ *vs*. t; + and − indicate the evolution and absorption of oxygen, respectively. [b] As *a* except $[Ag(ClO_4)] = 2 \times 10^{-3}$ mol dm^{-3}. [c] As *a* except in the absence of silver(I) ion. [d] As *a* except $[Ag(ClO_4)] = 4 \times 10^{-3}$ mol dm^{-3}.

The rate of oxygen evolution was accelerated by the addition of copper(II) ion to the reacting solution, whereas the absorption of oxygen occurred upon addition of acrylonitrile (an), acrylamide (aa), and a copper(II)–aa mixture. The rate of absorption of oxygen was much smaller in the presence of an than in aa (see Table 4). In case of cerium(III) addition, neither evolution nor absorption of oxygen occurred for some periods of the reaction, but evolution of oxygen started after a certain time which increased with increasing concentration of cerium(III) added, indicating that the cerium(III) was oxidized to the cerium(IV) ion during this time. This behaviour is illustrated in Figure 2.

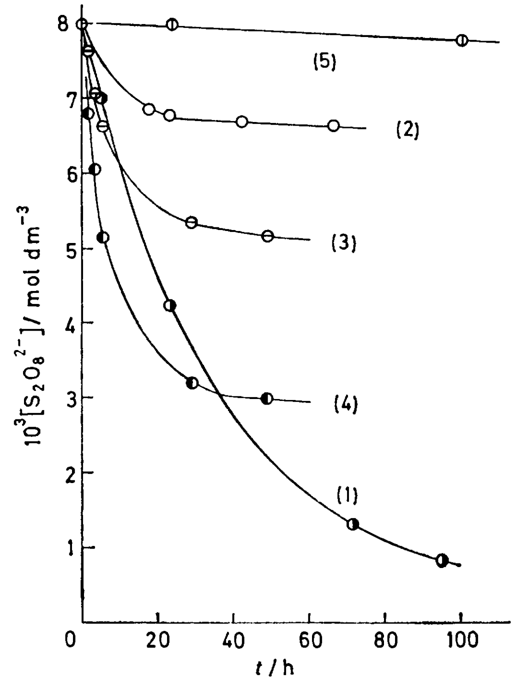

FIGURE 3 Effect of acrylonitrile and cation-exchange resin. Conditions as in Table 3. Curves: (1), $[K_2S_2O_8] = 8.0 \times 10^{-3}$ mol dm^{-3}, $[Ag(ClO_4)] = 1.0 \times 10^{-3}$ mol dm^{-3}, and $[HClO_4] = 0.01$ mol dm^{-3}; (2), (1) plus 1% acrylonitrile (an); (3), as (2) but $[Ag(ClO_4)] = 2 \times 10^{-3}$ mol dm^{-3}; (4), as (2) but $[Ag(ClO_4)] = 5 \times 10^{-3}$ mol dm^{-3} and 2% an; (5), (1) plus 3.5 g dm^{-3} of cation-exchange resin, but $[Ag(ClO_4)] = 0.01$ mol dm^{-3} and $[HClO_4] = 0.05$ mol dm^{-3}

DISCUSSION

From the results obtained, the kinetic character of the silver(I)-catalyzed decomposition of peroxodisulphate ion in aqueous solution is summarized as follows: (1) the rate of reaction is first order with respect to the concentrations of both the peroxodisulphate and silver(I) ions; (2) the silver(I)-ion concentration remains constant up to completion of reaction; (3) the rate of oxygen formation due to reaction is half that of the decomposition of peroxodisulphate ion; (4) the rate of decomposition of peroxodisulphate ion is greatly affected by the addition of the radical scavengers acrylamide, acrylonitrile, and copper(II) ion, but not affected by the addition of cerium(III) ion; and (5) the rate of formation of oxygen is greatly affected by the addition of the radical scavengers and ceases altogether on addition of cerium(III) ion. These results suggest the mechanism in equations (4)—(10). All reactions (5)—(10) are assumed

$$Ag^+ + S_2O_8^{2-} \xrightarrow{k} Ag^{II} + SO_4^{\cdot -} + SO_4^{2-} \tag{4}$$

$$H_2O + SO_4^{\cdot -} \rightleftharpoons OH^{\cdot} + HSO_4^- \tag{5}$$

$$Ag^+ + OH^{\cdot} \longrightarrow Ag^{II} + OH^- \tag{6}$$

$$Ag^+ + SO_4^{\cdot -} \longrightarrow Ag^{II} + SO_4^{2-} \tag{7}$$

$$2Ag^{II} \rightleftharpoons Ag^+ + Ag^{III} \tag{8}$$

$$H_2O + Ag^{III} \rightleftharpoons AgO^+ + 2H^+ \tag{9}$$

$$AgO^+ \longrightarrow Ag^+ + \tfrac{1}{2}O_2 \tag{10}$$

to be much faster than (4). The rate equations (2) and (3) are well explained by the above mechanism. The disproportionation of Ag^{II} has been investigated by several researchers [9-15] and reactions (8)—(10) were proposed by Kirwin *et al.*[15]

The fact that the rate of the reaction between peroxodisulphate and silver(I) ions is accelerated by the addition of copper(II) ion may suggest the alternative reactions (11)—(12). The formation of $HO_2^{\cdot}$ could result

$$2OH^{\cdot} \longrightarrow H_2O_2 \tag{11}$$

$$H_2O_2 + Ag^{II} \longrightarrow Ag^+ + HO_2^{\cdot} + H^+ \tag{12}$$

$$HO_2^{\cdot} + Ag^{II} \longrightarrow Ag^+ + O_2 + H^+ \tag{13}$$

in the reduction of copper(II) to copper(I), thus leading to the acceleration of the decomposition of peroxodisulphate due to its fast reduction by copper(I) ion, *i.e.* as in equations (14) and (15). The rate constant for

$$Cu^{II} + HO_2^{\cdot} \rightleftharpoons Cu^+ + O_2 + H^+ \tag{14}$$

$$S_2O_8^{2-} + Cu^+ \longrightarrow Cu^{II} + SO_4^{\cdot -} + SO_4^{2-} \tag{15}$$

reaction (15) has been reported as $1.4 \times 10^3\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at 25 °C,[16] being 2×10^5 times larger than that for reaction (4). Collinson *et al.*[17] reported that the polyacrylamide radicals are capable of reducing some metal ions such as copper(II). Therefore, the acceleration effect of acrylamide on the silver(I)-catalysed decomposition of peroxodisulphate should be due to the reduction of the peroxodisulphate ion by the polyacrylamide radicals, as in equations (16)—(18) where $R^{\cdot}$

$$nCH_2{=}CHCONH_2 + OH^{\cdot} \text{ and/or } SO_4^{\cdot -} \longrightarrow R^{\cdot} + OH^- \text{ and/or } SO_4^{2-} \tag{16}$$

$$S_2O_8^{2-} + R^{\cdot} \longrightarrow R^+ + SO_4^{\cdot -} + SO_4^{2-} \tag{17}$$

$$2R^{\cdot} \longrightarrow R{-}R \tag{18}$$

indicates the polyacrylamide radical. The absorption of molecular oxygen during the reaction is thought to be due to reactions (19) and (20).

$$R^{\cdot} + O_2 \rightleftharpoons RO_2^{\cdot} \tag{19}$$

$$Ag^+ + RO_2^{\cdot} \longrightarrow RO_2^- + Ag^{II} \tag{20}$$

When both acrylamide and copper(II) ion were added to the reacting solution the decomposition rate of peroxodisulphate was accelerated more in the absence of oxygen than in its presence. In this case, copper(II) ion will be reduced to copper(I) ion by the polyacrylamide radicals and the copper(I) will reduce the peroxodisulphate ion according to reaction (15).

$$Cu^{II} + R^{\cdot} \longrightarrow R^+ + Cu^+ \tag{21}$$

The rate constant for reaction (21) has been reported as $1.2 \times 10^3\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at 25 °C,[17] very close to that for reaction (15). Therefore, a chain reaction composed of reactions (15) and (21) is the cause of the acceleration of the decomposition of peroxodisulphate in the presence of both acrylamide and copper(II) ion. In the presence of oxygen, the copper(I) ion is oxidized by the $RO_2^{\cdot}$ radicals, competing with reaction (15), and thus oxygen terminates the chain reaction composed of reactions (15) and (21).

$$RO_2^{\cdot} + Cu^+ \longrightarrow RO_2^- + Cu^{II} \tag{22}$$

The rate of the silver(I)-catalyzed decomposition of peroxodisulphate was not influenced by the addition of cerium(III) ion, whereas, the oxygen evolution due to the reaction stopped for a certain period and then started some time later at the same velocity as in the absence of cerium(III). This is interpreted in terms of reactions (23) and (24).

$$Ce^{III} + Ag^{II}, OH^{\cdot}, \text{and/or } SO_4^{\cdot -} \longrightarrow Ce^{IV} + Ag^+, OH^-, \text{and/or } SO_4^{2-} \tag{23}$$

$$Ce^{IV} + Ag^+ \rightleftharpoons Ce^{III} + Ag^{II} \tag{24}$$

The rate constant for the forward reaction of (24) is estimated as *ca.* $3 \times 10^{-6}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at 25 °C and 0.01 mol dm^{-3} H^+ from the data reported by Higginson *et al.*[18] Reaction (23) will be extremely fast. Therefore, any one of Ag^{II}, $OH^{\cdot}$, and $SO_4^{\cdot -}$ will be exhausted by reaction (23) before occurrence of reactions (8)—(13). Bawn and Margerison[5] reported the rate constant for reaction (4) to be $2.15 \times 10^{-2}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at 25 °C in 50% (v/v) ethyl alcohol and at $I = 0.015$ mol dm^{-3}. The rate constant under the same conditions but in an aqueous medium is $1.1 \times 10^{-2}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$. Thus, the value of Bawn and Margerison[5] is twice that obtained in the present study. The difference is thought to be attributable to the permittivity which is 49.5 and 73.1 for the 50% (v/v) ethanol and for the aqueous solution at 40 °C, respectively.[19]

From reviews,[1,2] the rate constants of the silver(I)-catalyzed oxidation of NH_4^+, Cr^{3+}, VO^{2+}, N_2H_4, Mn^{2+}, and Ce^{3+} by peroxodisulphate ion are 3.5×10^{-3}—$9 \times 10^{-3}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at 25 °C. These values are in agreement with those in Tables 1 and 2, but somewhat smaller than those of Bawn and Margerison.[5] With the majority of the inorganic and organic substrates, the oxidation by peroxodisulphate ion is catalyzed by silver(I) ion and the rate of the silver(I)-catalyzed oxidation is close to the rate of the reaction between peroxodisulphate ion and silver(I) ion, indicating a common rate-determining step involving the reaction of peroxodisulphate ion with silver(I) ion, *i.e.* reaction (4). The catalysis by the silver(I) ion indicates that water as the solvent itself acts as the reducing substrate for the decomposition reaction of peroxodisulphate ion.

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