On the Mechanism of the Thermal Decomposition of Peroxodisulfate Ion in Moderately Acidic Solutions

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The steady-state concentrations of hydrogenperoxomonosulfate ion, formed as an intermediate in the hydrogen ion-catalyzed path of the thermal decomposition of peroxodisulfate solutions of moderate acidities at 60 °C, were determined by reduction with oxovanadium(IV). The solutions initially contained cerium(III) sulfate complexes also. The rates of the consecutive steps in the chain decomposition reaction of HSO_5^- were calculated from those measurements. The chain reaction is induced by OH radicals from the initial step, $S_2O_8^{2-} + H_2O \rightarrow HSO_4^- + SO_4^- + OH$, in the uncatalyzed path of the peroxodisulfate decomposition. The major fraction of the OH radicals is consumed in the chain reaction, where the high rate constant, $\geqq 2\times10^9$ M^{-1} s^{-1}, estimated for the step OH + HSO_5^- at 20 °C might indicate that HSO_5^-, which is partly coordinated to Ce(III), reacts fast like free SO_5^{2-}. Thus, the peroxomonosulfate ligand competes effectively with the central cerium(III) ion for reaction with OH. This finding explains why the reaction OH + Ce(III) makes no detectable contribution to the oxidation of cerium(III), whereas SO_4^-, which reacts more slowly with HSO_5^-, is highly reactive in the reaction $SO_4^- +$ Ce(III) yielding cerium(IV). The results also explain why no $OH–SO_4^-$ interconversion equilibrium is attained at moderate acidities, and why there is no detectable formation of hydrogen peroxide according to the reaction OH + OH.

The peroxodisulfate ion is an important source of highly reactive species that are effective in oxidations of different metal ions and many types of organic molecules.[1,2] It has also been used frequently as an initiator of chain reactions in solution. Often, these oxidations are performed in moderately acidic solutions, and one fundmental question is the mechanism of the thermal decomposition of peroxodisulfate ion in such solutions. It has been shown[3] that the decomposition proceeds by two reaction paths, leading to the rate law shown in eqn. (1), the k_H path being the predominant one for solutions more acidic than pH ≈ 2.
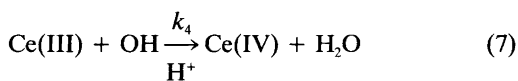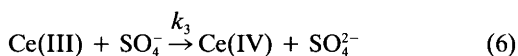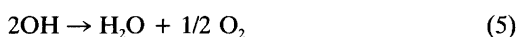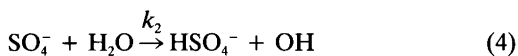
$$-\frac{d[S_2O_8^{2-}]}{dt} = (k_1 + k_H[H^+])\,[S_2O_8^{2-}] \qquad (1)$$

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

The unimolecular homolysis in eqn. (2) was

early[4,5] suggested as the initial rate-determining step in the k_1 path. Although, in fact, there is no clear evidence of the existence of this homolytic scission in the thermal decomposition, most authors have since that time kept to this mechanism. However, in an investigation in this laboratory,[6] it was found that the rate of oxidation of cerium(III) by peroxodisulfate is given by $k_1[S_2O_8^{2-}]$, when perchloric acid, sodium sulfate and sodium perchlorate form the additional electrolytes. The k_1 value obtained was close to that of eqn. (1) valid for alkaline solutions.[3] From this result, it was concluded that cerium(III) is oxidized by an intermediate generated in the k_1 path, and that only one such intermediate is formed from each peroxodisulfate ion decomposing in this path. As a consequence, the bimolecular reaction illustrated by eqn. (3) was suggested as the rate-determining initial step. As subsequent reactions in the k_1 path, the reactions (4) and (5) were accepted.[5] Reaction (5) only sug-

gests formation of oxygen from the OH radical in several consecutive steps. Furthermore, it was suggested that the radical ion SO_4^- is the intermediate that oxidizes cerium(III). Thus, in the presence of complex-forming sulfate ions, cerium(III) would effectively capture SO_4^-, reaction (4) being exchanged for reaction (6). On the other hand, in the acidic medium used, reaction (7) would be unimportant.

$$S_2O_8^{2-} + H_2O \xrightarrow{k_1} HSO_4^- + SO_4^- + OH \qquad (3)$$

$$SO_4^- + H_2O \xrightarrow{k_2} HSO_4^- + OH \qquad (4)$$

$$2OH \rightarrow H_2O + 1/2\ O_2 \qquad (5)$$

$$Ce(III) + SO_4^- \xrightarrow{k_3} Ce(IV) + SO_4^{2-} \qquad (6)$$

$$Ce(III) + OH \xrightarrow[H^+]{k_4} Ce(IV) + H_2O \qquad (7)$$
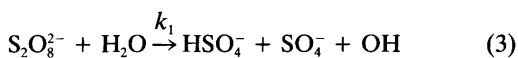
In order to further check these conclusions about the mechanism, another study[7] was carried out by measuring the rate of evolution of oxygen gas from peroxodisulfate solutions in the presence and absence of cerium(III) and at varying but moderate acidities: $[H^+] = 4\times10^{-3} - 4\times10^{-2}$ M. It was shown that the rate of oxygen production by the k_1 path in the presence of cerium (III) is one-half the rate in the absence of this species. This finding clearly indicates that reaction (2) cannot be the initial step, whereas reaction (3) is consistent with the result obtained. Nevertheless, as the reactions of the OH radical in the presence of cerium(III) were not elucidated in the mechanism suggested, some doubt or uncertainty has been expressed in later reviews.[8,9] For that reason, the present study was undertaken to elucidate to what extent the disappearance of OH can be explained by its participation in a chain reaction with the intermediate HSO_5^-, most probably formed[1] initially in the k_H path according to reaction (8). For this purpose, it is necessary to determine the steady-state concentration of this species in the overall process.

$$H^+ + S_2O_8^{2-} + H_2O \xrightarrow{k_H} HSO_5^- + HSO_4^- + H^+ \qquad (8)$$
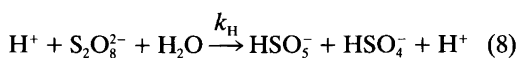
Experimental

Materials. Solutions of cerium(III), oxovanadium (IV) and dioxovanadium(V) perchlorates in dilute perchloric acid were prepared as in previous investigations.[6,10] Potassium peroxodisulfate, sodium sulfate, sodium perchlorate and perchloric acid were of analytical grade. Potassium hydrogenperoxomonosulfate was used in the form of Oxone (du Pont). Iodometric analysis of this substance showed that it contained 42 % $KHSO_5$. Stock solutions of the chemicals, except for the peroxo compounds, were prepared and analyzed by standard methods. The water was laboratory-distilled and then redistilled twice in an all-silica apparatus.

Measurements. Low concentrations of peroxomonosulfate cannot be determined iodometrically if peroxodisulfate at a much higher concentration is also present. However, in a previous investigation,[10] it was found that when peroxomonosulfate is added to an acidic solution of oxovanadium (IV) at 40 °C, an equivalent amount of vanadium (IV) is oxidized instantly. Furthermore, when peroxodisulfate is added to such an acidic solution, a little peroxomonosulfate appears at once and causes a quick oxidation of some vanadium (IV). On the other hand, there is no sign of a direct reaction between peroxodisulfate and vanadium(IV) at $[H^+] < 0.25$ M and at 40 °C. On the basis of these findings, the procedure described below was used for the determination of the steady-state concentration of peroxomonosulfate during oxidation of cerium(III) by peroxodisulfate ion.

The reaction vessel was a borosilicate glass bottle placed in a water thermostat at 60 °C. A fixed volume of a solution containing cerium(III) perchlorate, sodium sulfate, perchloric acid and sodium perchlorate was allowed to attain thermal equilibrium in the vessel. At time $t = 0$, a weighed amount of solid potassium peroxodisulfate was added. In some measurement series, peroxomonosulfate as solid Oxone was also added at the same time. After suitable time intervals, samples were withdrawn and mixed with equal volumes of a solution of oxovanadium(IV) perchlorate (10 mM) and perchloric acid (350 mM) at 20 °C. The mixed solutions were cooled to 25 °C and the concentration of vanadium(V)

formed was determined by absorbance measurements at 350 nm with a Zeiss PMQ-II instrument as described previously.[10] The concentration of vanadium(V) gives $[HSO_5^-]$ + 0.5 [Ce(IV)] during the oxidation of cerium(III); [Ce(IV)] was obtained from separate kinetic runs, at 400 nm. The constant absorbance after complete oxidation of cerium(III) yields the molar absorption coefficient for cerium(IV). In other separate measurements, it was confirmed that cerium(III) was not oxidized by Oxone. The hydrogen ion concentration in the reaction solution was measured as before.[7]

Results

Steady-state concentrations of peroxomonosulfate. If only peroxodisulfate was added at time $t = 0$, the value of $[HSO_5^-]$ was already fairly well reproducible after 5 min, corresponding to [Ce(IV)] $\approx 1.5 \times 10^{-4}$ M. As seen from Fig. 1, $[HSO_5^-]$ decreases as the oxidation of cerium(III) proceeds. Within the measurement range available, the plots of $[HSO_5^-]$ vs. [Ce(IV)] can be represented approximately by straight lines, the ordinate axis intercepts of which yield values for solutions free of cerium(IV). The results are: $[HSO_5^-] = (1.8 \pm 0.2) \times 10^{-4}$ and $(3.8 \pm 0.4) \times 10^{-4}$ M at $[H^+] = 2.0 \times 10^{-2}$ and 4.0×10^{-2} M, respectively, $[Ce(III)] = 1.0 \times 10^{-3}$ M and $[S_2O_8^{2-}] = 0.100$ M. The $[H^+]$ values correspond to the middle and the upper part, respectively, of the $[H^+]$ range used in the previous study.[7] In the lower part at $[H^+] \approx 4 \times 10^{-3}$ M, measurements of $[HSO_5^-]$ were not feasible.

When peroxomonosulfate as Oxone was also added at $t = 0$, its concentration at first decreased fairly rapidly, but the values were not reproducible. During this initial time, no formation of cerium(IV) was detectable. However, after about 5 min, cerium(IV) was formed at the same rate as in the absence of Oxone. At increasing [Ce(IV)], plots of $[HSO_5^-]$ vs. [Ce(IV)] (the dashed curves in Fig. 1) approach the straight lines determined in the absence of Oxone. This finding is a good indication that the values of $[HSO_5^-]$ determined are true steady-state concentrations.

The rate of formation of cerium(IV) is the same at the two different $[H^+]$ used (cf. Ref. 7). This indicates that at the low steady-state concentrations of peroxomonosulfate found, the rate of reduction of cerium(IV) in the reaction Ce(IV) +

HSO_5^- is negligible compared to the rate of its oxidation in the reaction Ce(III) + SO_4^-.

The chain reaction mechanism. From an investigation[11] of the photolytic decomposition of peroxodisulfate ion, it was concluded that hydrogenperoxomonosulfate ion is rapidly decomposed in a chain reaction induced by the radicals SO_4^- and OH. The earlier study[10] of the thermal reaction between vanadium(IV) and peroxodisulfate ion also gave a clear indication of the importance of these radicals, formed in reaction (3), for the decomposition of HSO_5^- in moderately acidic solutions. As this decomposition is not inhibited[7] by cerium(III), the chain reaction in the present case must be induced by the OH radical. Furthermore, as cerium(III) is not oxidized by any intermediate from the chain reaction, no step can involve formation of SO_4^-. Thus, reactions (3) and (8) are the initiation steps, and the propagation cycle is formulated in reactions (9) and (10), as has been suggested before.[12] As main termination step, reaction (11) is suggested.

$$OH + HSO_5^- \xrightarrow{k_5} H_2O + SO_5^- \tag{9}$$

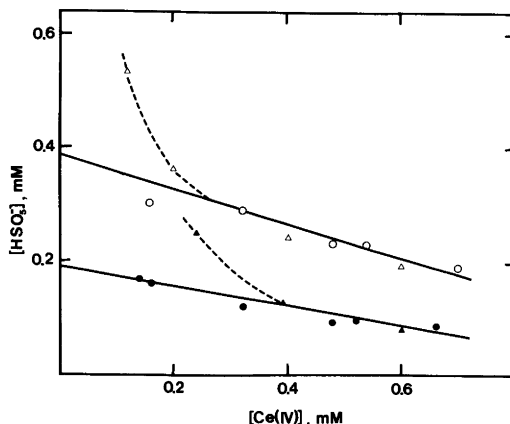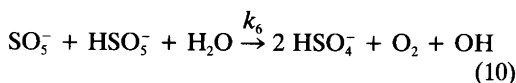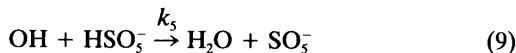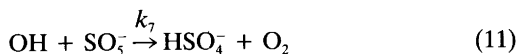$$SO_5^- + HSO_5^- + H_2O \xrightarrow{k_6} 2\,HSO_4^- + O_2 + OH \tag{10}$$

Fig. 1. The steady-state concentration of peroxomonosulfate during oxidation of cerium(III) by peroxodisulfate ion at 60 °C. Initial concentrations: 1.00 mM $Ce(ClO_4)_3$, 100 mM $K_2S_2O_8$, 0 (●, ○) or 5 mM (▲, △) $KHSO_5$ (as Oxone), 150 mM Na_2SO_4, 95 or 150 mM $HClO_4$ and 300 mM $NaClO_4$. $[H^+]$ = 20 mM (filled symbols) or 40 mM (open symbols).

$$OH + SO_5^- \xrightarrow{k_7} HSO_4^- + O_2 \qquad (11)$$

It is well known[1,11] that the autodecomposition of hydroxyl radicals with formation of molecular oxygen is quite susceptible to catalysis by trace "impurities", especially heavy metal ions present as low molecular weight colloids. At 60 °C and at the moderate acidities used, there is certainly considerable hydrolysis of the cerium(IV) formed in the reaction. Thus, various hydroxo species of cerium(IV) most probably function as effective catalysts. It can be assumed that the rate-determining step of the autodecomposition in the presence of such catalysts is first-order in OH. The first-order rate constant, k_8, should therefore include some unknown function of the cerium concentration.

In the following equations, r_j is the rate of a reaction with rate constant k_j. Application of the steady-state approximation to the intermediates OH, HSO_5^- and SO_5^-, involved in reactions (3), (4) and (7)–(11), then yields the relationships given by eqns. (12)–(14). Elimination of r_6 and r_7 from (12)–(14) results in eqn. (15); from suggested second-order expressions for r_4 and r_5, eqn. (16) is obtained. Thus, if $k_5/(k_4[Ce(III)] + k_8)$ can be calculated from the measured values of $[HSO_5^-]$, the rates r_5 and $r_4 + r_8$ can be obtained from eqns. (15) and (16).

$$r_4 + r_5 - r_6 + r_7 + r_8 = r_1 \qquad (12)$$

$$r_5 + r_6 = r_H \qquad (13)$$

$$r_5 - r_6 - r_7 = 0 \qquad (14)$$

$$r_4 + 4r_5 + r_8 = r_1 + 2r_H \qquad (15)$$

$$r_5/(r_4 + r_8) = k_5[HSO_5^-]/(k_4[Ce(III)] + k_8) \qquad (16)$$

Determination of rates. If second-order expressions for the rates r_4–r_7 are inserted in eqns. (13)–(15), elimination of the unknown steady-state concentrations of OH and SO_5^- yields the final eqn. (17). Here, the unknowns are $k_5/(k_4[Ce(III)]$

$+ k_8)$ and k_5k_6/k_7. At 60 °C, the most probable values[3,6] of the rate constants in eqn. (1) are $k_1 = 5.0 \times 10^{-6}$ s^{-1} and $k_H = 1.6 \times 10^{-4}$ M^{-1} s^{-1}. Then, when the experimental steady-state concentrations of HSO_5^- are inserted into eqn. (17), two relationships are obtained, from which the unknown parameters can be determined as $k_5/(k_4 [Ce(III)] + k_8) = (7 \pm 2) \times 10^3$ M^{-1}; $k_5k_6/k_7 = 4 \pm 1$ M^{-1} s^{-1}.

$$k_5 [HSO_5^-]/(k_4 [Ce(III)] + k_8 + 4 k_5 [HSO_5^-]) + 2 k_5k_6 [HSO_5^-]^2 r_1/\{k_7(r_1 + 2 r_H)^2\} - (k_4 [Ce(III)] + k_8) k_6 [HSO_5^-] r_H/ \{k_7 (r_1 + 2 r_H)^2\} = r_H/(r_1 + 2 r_H) \qquad (17)$$

From these quantities, relative values of the steady-state rates $r_4 + r_8$ and r_5–r_7 have been calculated (Table 1) according to eqns. (13)–(16) for the $[H^+]$ used in the present measurements. In the previous investigation,[7] the maximum rate $r_1 + r_4 (= r_3 + r_4)$ of oxidation of cerium(III) was found to be $(5.2 \pm 0.3) \times 10^{-6} [S_2O_8^{2-}]$ M s^{-1}, at the same time that the rate r_1 of the k_1 path was $(4.8 \pm 0.3) \times 10^{-6} [S_2O_8^{2-}]$ M s^{-1}. These rates give $r_4/r_1 \leqq 0.20$. Thus, at the acidities used, the relative rate r_8/r_1 of the catalyzed autodecomposition of the hydroxyl radical does not seem to be negligible. Finally, the lower limits $k_8/(k_4 [Ce(III)]) \geqq 0.8$, obtained at $[H^+] = 2.0 \times 10^{-2}$ M, and $k_5/(k_4 [Ce(III)] + k_8) \geqq 5 \times 10^3$ M^{-1} yield the estimate $k_5/k_4 \geqq 9$.

Discussion

In the chain mechanism, reaction (11) was presumed to be the predominating termination step. In this reaction, HSO_6^- is probably formed as an intermediate that can be expected to break down rapidly to give products. In an isotope study[13] of the nonradical reaction $HSO_5^- + SO_5^{2-}$, evidence was given of the existence of HSO_6^- as an intermediate. Reaction (11) would then take place via an addition, and there are many examples[14]

Table 1. Relative rates of the different steps in the thermal decomposition of peroxodisulfate ion in the presence of cerium(III).

$10^2 [H^+]$/M	r_H/r_1	$(r_4+r_8)/r_1$	r_5/r_1	r_6/r_1	r_7/r_1
4.0	1.28	0.28	0.82	0.46	0.36
2.0	0.64	0.36	0.48	0.16	0.32

showing that the OH radical is especially reactive in such reactions. Possible termination steps besides reaction (11) are the reactions OH + OH and $SO_5^- + SO_5^-$. Thus, in eqns. (12), (14) and (15), the rates of these reactions have been neglected. The OH + OH reaction has the rate constant[15] 10^{10} M^{-1} s^{-1} at room temperature, whereas k_4 in reaction (7) has a value[16] of about 2×10^8 M^{-1} s^{-1}. Accordingly, as it is certain that [Ce(III)] $\gg$ 10^2 [OH] in the measurement solutions, the rate r(OH + OH) should be quite negligible as compared to r_4 in eqns. (12) and (15).

A simple estimate of the rate constant $k(SO_5^- + SO_5^-)$ would be obtained if it is assumed that $k(SO_5^- + SO_5^-)/k_6 \approx k_7/k_5$. However, this would not take into account the presumed particularly high reactivity of OH in the addition reaction (11). For this reason, it seems plausible to presuppose that $k(SO_5^- + SO_5^-)$ is at least ten times smaller than $k_6 k_7/k_5$. Then, from the second-order rate expressions for r_1, the relationship $r(SO_5^- + SO_5^-) \lesssim 0.1\ r_6 r_7/r_5$ is obtained, and the values in Table 1 yield $r(SO_5^- + SO_5^-) \lesssim 0.01\ r_1$ and $0.02\ r_1$ at $[H^+] = 2.0 \times 10^{-2}$ and 4.0×10^{-2} M, respectively. Thus, these rates should also be negligible in eqns. (14) and (15). Furthermore, for $k_5 > 10^9$ M^{-1} s^{-1} (see below) and a reasonable value of k_7, it can be inferred from the relationship $k_5 k_6/k_7 = 4$ that k_6 is several orders of magnitude smaller than k_5. This means that SO_5^- exhibits a low reactivity in comparison with the OH radical.

If it is assumed that the ratio k_5/k_4 is approximately independent of the temperature, the estimate $k_5/k_4 \gtrsim 9$, valid at 60 °C, can be combined with values of rate constants determined in photolytic and radiolytic studies at room temperature. From the value of k_4 given above and the ratio k_5/k_4, the estimate $k_5 \gtrsim 2 \times 10^9$ M^{-1} s^{-1} is obtained. This value is much higher than one determined radiolytically[12] for the reaction OH + HSO_5^- at pH = 7, namely 1.7×10^7 M^{-1} s^{-1}. On the other hand, it is consistent with the value 2.1×10^9 M^{-1} s^{-1}, obtained at pH = 11 and ascribed[12] to the reaction OH + SO_5^{2-}.

Since peroxoanions exhibit a high nucleophilic power,[17] it might be expected that at the steady-state concentrations obtained, HSO_5^- is in part coordinated to cerium(III) and cerium(IV). To check this presumption, the ligand number $\bar{n}$ in the system Ce^{3+}/HSO_5^- at low ligand concentrations was determined by a spectrophotometric method[18] at 296 nm, 20 °C and at unit ionic

strength, with 2.0×10^{-2} M perchloric acid and sodium perchlorate as supporting electrolytes. These measurements gave the stability constant $\beta_1 = (2.1 \pm 0.2) \times 10^3$ M^{-1}. The system Ce^{3+}/SO_4^{2-} is known to have a weak complex formation with $CeSO_4^+$ as the predominant complex with a stability constant[19] of 15.5 M^{-1} for the same conditions as for the system above. In the system $Ce^{3+}/HSO_5^-/SO_4^{2-}$, the mixed ligand complex Ce$(HSO_5)(SO_4)$ can be formed in addition to the simple complexes. If its concentration is neglected, a lower limit for $\bar{n} = (C_{HSO_5^-} - [HSO_5^-])/C_{Ce(III)}$ is given by the expression 2.1×10^3 $[HSO_5^-]/(1 + 15.5\ [SO_4^{2-}] + 2.1 \times 10^3\ [HSO_5^-])$. Here, $[HSO_5^-]$ means the free ligand concentration.

The $[H^+]$ values for the solutions used in the kinetic measurements yield $K_a\ (HSO_4^-) = 2.8 \times 10^{-2}$ M and $K_a\ (HS_2O_8^-) = 1.4 \times 10^{-1}$ M at 60 °C and at unit ionic strength. Then, for these solutions $[SO_4^{2-}] = 9 \times 10^{-2}$ and 6×10^{-2} M are obtained at $[H^+] = 2 \times 10^{-2}$ and 4×10^{-2} M, respectively. Finally, at the steady-state concentrations of HSO_5^- measured, $\bar{n}$ can be calculated by combining the two expressions above. The results are $\bar{n} = 0.090$ and 0.20. As these values are lower limits, it is found that in both cases, at least half the peroxomonosulfate is present as cerium(III) complexes at 20 °C. The complex formation should greatly weaken the bond to the proton so that the ligand can be expected to react fast with OH, like the free SO_5^{2-}, probably by electron transfer. Thus, the path OH + Ce(III) · HSO_5^- should be predominant in reaction (9), the peroxomonosulfate ligand competing effectively with the central cerium(III) ion for reaction with OH. The decrease in the steady-state concentration of HSO_5^- as the formation of cerium(IV) proceeds (Fig. 1) can then be explained by a moderate increase in the rate of reaction (9), when cerium (III) is exchanged for cerium(IV) as central ion.

However, it should be emphasized that the estimate above of k_5 at room temperature must be looked upon as a very uncertain one for the following reasons. The value of k_5/k_4 at room temperature might very well be up to three times lower than at 60 °C. Furthermore, the value of k_4 used has been obtained from the ratio[16] k(OH + Ce(III))/k(OH + Tl$^+$) = 2.4×10^{-2}, valid for 0.4 M sulfuric acid as medium, and a radiolytically determined value[20] of k(OH + Tl$^+$), reported as 1×10^{10} M^{-1} s^{-1} without any limits of error. An in-

spection of the method of calculating the last-mentioned constant shows that a two or three times smaller value is also compatible with the measurements. The constant also pertains to 10^{-3} M Tl_2SO_4 in the absence of any additional electrolyte. In conclusion, the estimated value of k_5 might be too high by one order of magnitude. According to another radiolysis study[21] k_5 has the value 2.9×10^8 M^{-1} s^{-1}. Consequently, it is not certain that the complex formation with cerium (III) has a substantial influence on the rate of reaction (9). From Table 1, it is evident that the major fraction, $(r_5 - r_6 + r_7)/r_1$, of the OH radicals formed in reaction (3) is used up in the chain reaction, and only a fairly low relative rate, r_8/r_1, of the presupposed catalyzed decomposition of OH is required to make any contribution, r_4/r_1 from reaction (7), to the formation of cerium(IV) undetectably small ($\leqq 0.20$).

For the radical ion SO_4^-, the conditions are quite different. It reacts much faster[6] with cerium (III) sulfate complexes than with the hydrated Ce^{3+} ion. The reason for this is most probably a high rate of the self-exchange reaction SO_4^- + SO_4^{2-}, by which SO_4^- rapidly enters the inner sphere coordination shell. The ratio k_3/k_2 of the rate constants in reactions (6) and (4) was determined previously[6] and found to be $\geqq 7 \times 10^4$ M^{-1} at 60 °C. This ratio, combined with the rate constant $k_3 = 1.4 \times 10^8$ M^{-1} s^{-1} of reaction (6), determined in a photolytic study[22] at room temperature and with 1.0 M sulfuric acid as ionic medium, yields $k_2 \leqq 2 \times 10^3$ s^{-1}. The value is in accordance with an earlier estimate[23] of $k_2 = 10^3 - 10^4$ s^{-1}. Furthermore, from some radiolysis experiments[12] with peroxodisulfate, it has been found that the rate constant of the reaction SO_4^- + HSO_5^- is $< 10^5$ M^{-1} s^{-1}. Thus, it is evident that sulfate complexes of cerium(III) can compete favourably with both water and peroxomonosulfate for reaction with the sulfate radical ion.

Conclusions

After the publication of the previous study[7] another investigation was reported[24] in which the production of acid (HSO_4^-) in the decomposition of peroxodisulfate at pH = 8.0 was followed in the absence or presence of styrene as radical scavenger. When these results are interpreted correctly (see Ref. 9), it is found that one $S_2O_8^{2-}$ yields one HSO_4^- in the initial step. This is pos-

sible only if $S_2O_8^{2-}$ reacts with one H_2O. From these results, together with those from the previous study, it is evident that the left-hand side of reaction (3) is confirmed as well as the formation of HSO_4^- and SO_4^-. The only possibility, then, for the other intermediate formed is that it is identical to the OH radical. Thus, the mechanism of the k_1 path is quite clear. Experiments of a third type have also been reported,[25] the results of which were taken as evidence in favour of reaction (2) as rate-determining initial step. However, serious objections can be raised to these experiments and to the conclusions drawn. Since these objections have been presented in detail in a review paper,[9] they are not repeated here.

The entropy of activation for the k_1 path is 47 J mol^{-1} K^{-1} (cf. Ref. 9). Such a positive value is usually regarded as indicative of unimolecular homolysis, whereas a bimolecular radical formation step would have a negative entropy of activation. However, the sign of ΔS^+ cannot be conclusively interpreted in this simple manner for reactions in solution when one of the reactants is a solvent molecule. In fact, it is very plausible that at least one H_2O is bound by a hydrogen bond to the peroxo group in $S_2O_8^{2-}$ (aq.) in the ground state. Then, for the activated complex, the decomposition would involve fission of the peroxide bond coupled with an electron transfer from the water oxygen to the peroxide oxygen taking part in the hydrogen bond. This means that reaction (3) would be only formally bimolecular, but in reality unimolecular, and the left member of reaction (3) could also be denoted $S_2O_8^{2-} \cdot H_2O$.

The present experiments explain why hydroxyl radicals formed in decomposing peroxodisulfate solutions of moderate acidities, containing cerium(III) sulfate complexes, give no detectable contribution to the oxidation of cerium(III), whereas sulfate radical ions formed simultaneously are highly reactive with the complexes, yielding cerium(IV). Thus, these results are complementary to the previous ones. They also explain some other earlier observations. The rate law obtained[6] for the oxidation of cerium(III) with peroxodisulfate in an acidic perchlorate medium proves that, in addition to reaction (6), reaction (4) is also of some importance. On the other hand, even in the presence of hydrogensulfate ions in the medium there is no indication of the reverse of reaction (4), reported[26] to have the rate constant $k(OH + HSO_4^-) = 8 \times 10^5$ M^{-1} s^{-1}.

As this value is much lower than that of k_5 estimated above, it is evident that HSO_4^- cannot compete effectively with HSO_5^- for reaction with OH, and thus no $OH–SO_4^-$ interconversion equilibrium is attained.

It is well known that the rate of decomposition of peroxodisulfate in the k_1 path exhibits a maximum at pH ≈ 7 (see Ref. 9). This has been accounted for by the plausible proposal[1] that in weakly acidic solutions, OH radicals yield hydrogen peroxide that would give rise to the reaction:

$$H_2O_2 + S_2O_8^{2-} \rightarrow 2HSO_4^- + O_2 \qquad (18)$$
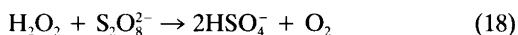
This could double the rate of peroxodisulfate decomposition compared with that valid for alkaline solutions. On the other hand, it has been shown[7] that reaction (18) is of no importance at pH $\approx 1.4–2.4$. This fact cannot be explained by a decrease in the rate of formation of OH radicals, since the maximum rate of reaction (6), approximately equal to k_1 $[S_2O_8^{2-}]$, was found[7] to be independent of $[H^+]$ within the range mentioned. However, from the sequence $r(OH + OH) \ll r_4 < (r_5 - r_6 + r_7)$ arrived at above, it can be concluded that the formation of hydrogen peroxide in the present medium is prohibited by the consumption of OH radicals in the chain reaction. This conclusion is also valid in the absence of cerium(III).

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