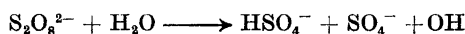# On the Mechanism of the Thermal Decomposition of Peroxodisulfate Ion

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The oxygen gas evolution from peroxodisulfate decomposing in an acidic sulfate-perchlorate medium has been investigated. In the presence of cerium(III) the rate of oxygen evolution in the uncatalyzed decomposition path was found to decrease by one half. It has also been confirmed that only one cerium(IV) ion is formed for each peroxodisulfate ion decomposing in the uncatalyzed path. These observations give strong support to the rate-determining initial step
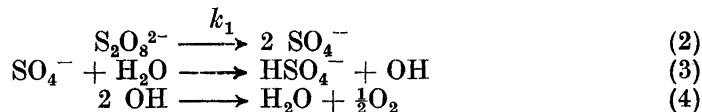$$S_2O_8^{2-} + H_2O \longrightarrow HSO_4^- + SO_4^- + OH$$

From the measurements some information about the later reactions of the decomposition scheme is also obtained.

The thermal decomposition of peroxodisulfate ion has been carefully studied by Kolthoff and Miller.[1] They showed that the decomposition occurs by two reaction paths, giving the rate law

$$-\frac{d[S_2O_8^{2-}]}{dt} = k[S_2O_8^{2-}] + k_H[H^+][S_2O_8^{2-}] \tag{1}$$

The k_H path is of importance only for $pH \leqq 2$.

For the k path Kolthoff and Miller accepted the following mechanism, previously proposed by Bartlett and Cotman [2]

$$S_2O_8^{2-} \xrightarrow{k_1} 2\ SO_4^- \tag{2}$$
$$SO_4^- + H_2O \longrightarrow HSO_4^- + OH \tag{3}$$
$$2\ OH \longrightarrow H_2O + \tfrac{1}{2}O_2 \tag{4}$$

Here reaction (2) is rate-determining, *i.e.* $k=k_1$, and reaction (4) is not a single step.

In an investigation of the oxidation of cerium(III) by peroxodisulfate the present authors [3] found the following rate law to be valid when perchloric acid and sodium perchlorate are the additional electrolytes.

$$\frac{d[Ce(IV)]}{dt} = \frac{k\alpha[Ce(III)]\cdot[S_2O_8{}^{2-}]}{1 + \alpha[Ce(III)]} \tag{5}$$
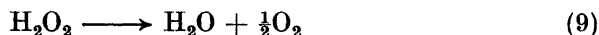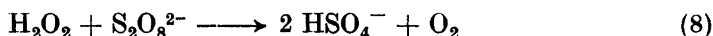
α is a constant and k has the same value as that found in eqn. (1) by Kolthoff and Miller in alkaline solutions. If sodium sulfate is part of the ionic medium, the α-value is so high that the maximum rate of oxidation $k[S_2O_8{}^{2-}]$ is obtained for cerium(III) concentrations higher than about 0.1 mM.

From these results we arrived at the conclusion that cerium(III) is oxidized by intermediates formed in the k path of the persulfate decomposition. However, if reaction (2) represented the correct rate-determining step of the decomposition, the maximum rate of oxidation of cerium(III) should have been $2k_1[S_2O_8{}^{2-}]$, $i.e.$ $2k[S_2O_8{}^{2-}]$. Thus our experimental results were not in agreement with the mechanism (2)—(4) and therefore we proposed the following rate-determining initial step

$$S_2O_8{}^{2-} + H_2O \longrightarrow HSO_4{}^- + SO_4{}^- + OH \tag{6}$$
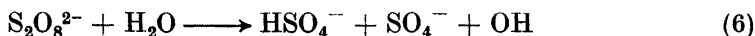
and assumed that only the sulfate radical ion can oxidize cerium(III).

In spite of our experimental findings later authors have in general kept to the homolytic scission of the peroxodisulfate ion. On the basis of investigations by Tsao and Wilmarth [4] on the photolytic decomposition of peroxodisulfate ion, Wilmarth and Haim [5] have proposed the following reactions in addition to steps (2) and (3).

$$2 \; OH \longrightarrow H_2O_2 \tag{7}$$

$$H_2O_2 + S_2O_8{}^{2-} \longrightarrow 2 \; HSO_4{}^- + O_2 \tag{8}$$

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2 \tag{9}$$

Furthermore, they consider the reverse of reaction (3) to be of importance and leading to an $OH-SO_4{}^-$ equilibrium.

Of the two competing reactions (8) and (9), the first one should predominate [5] in weakly acidic solutions giving $k=2k_1$. In basic solutions the hydrogen peroxide should decompose rapidly according to reaction (9) and in this case the same relation, $k=k_1$, is obtained as with reaction (4).

Since we found that the rate of oxidation of cerium(III) in acidic solutions was the same as the rate of peroxodisulfate decomposition in alkaline solutions it is clear that this extended mechanism is also inconsistent with our previous observations. However, our conclusions were based partly on the investigation of Kolthoff and Miller. For that reason we have considered it desirable to further investigate the mechanisms of the uncatalyzed path of the thermal peroxodisulfate decomposition and the oxidation of cerium(III), but this time by studying the rate of oxygen gas evolution from the reaction solutions.

THEORETICAL

In acidic solutions in which $[H^+] \lesssim 0.5$ M, oxygen gas is liberated by decomposition of peroxodisulfate according to the overall reaction

$$S_2O_8^{2-} + H_2O \longrightarrow 2\ HSO_4^- + \tfrac{1}{2}O_2 \qquad (10)$$
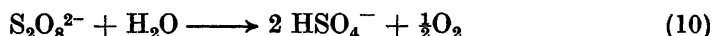
If V' denotes the volume of the oxygen gas evolved per litre of solution at the time t, then eqn. (1) yields the following rate expression in the absence of cerium(III).

$$dV'/dt = f(k + k_H[H^+])[S_2O_8^{2-}] \qquad (11)$$

where f is a constant, depending on the temperature and pressure of the oxygen gas.

If cerium(III) is oxidized only by intermediates formed in the k path of the peroxodisulfate decomposition and if these intermediates are effectively captured, then in the presence of cerium(III) no oxygen gas should come from the k path if reaction (2) is the rate-determining initial step. Thus, for the total rate of oxygen gas evolution in this case we should get:

$$dV''/dt = fk_H[H^+][S_2O_8^{2-}] \qquad (12\ a)$$

On the other hand, if reaction (6) is the rate determining step and only sulfate radical ions can oxidize cerium(III), then the oxygen gas coming from the k path will decrease to one half and the following equation should be valid.

$$\frac{dV''}{dt} = f\left(\frac{k}{2} + k_{H^\cdot}[H^+]\right)[S_2O_8^{2-}] \qquad (12\ b)$$

Thus, there is a possibility to test the different mechanisms on the basis of measurements of the oxygen gas evolution.

For the rate of formation of cerium(IV) we have the relationship

$$\frac{d(V' - V'')}{dt} = g\ \frac{d[Ce(IV)]}{dt} \qquad (13)$$

where the value of the constant g depends upon whether the disappearance of the hydroxyl radicals can be formulated according to reaction (4) or according to reactions (7) and (8). As will be shown below some information about the later reactions of the decomposition scheme can be obtained from corresponding values of $[Ce(IV)]$ and $V' - V''$.

EXPERIMENTAL

Chemicals. Cerium(III) perchlorate was obtained as in the previous investigation.[3] Sodium perchlorate was prepared from *p.a.* perchloric acid and *p.a.* sodium carbonate and recrystallized twice. Potassium peroxodisulfate, sodium sulfate, and perchloric acid were all of analytical grade. Stock solutions of these chemicals, with the exception of potassium peroxodisulfate, were prepared and analyzed using standard methods. The water used was distilled twice in an all-silica apparatus.

The kinetic runs. The apparatus consisted of an 100 ml Erlenmeyer Pyrex flask equipped with a ground-glass joint. The flask was placed in a water thermostat at 65°C

and was connected to a thermostatted (25°C) gas buret by means of a narrow PVC tube. The gas buret had a leveling tube so that the pressure in the closed system could be kept equal to the atmospheric pressure (about 760 torr).

100 ml of a solution containing sodium sulfate, perchloric acid, and sodium perchlorate was allowed to reach thermal equilibrium in the reaction vessel and at the same time the solution was saturated with oxygen gas. A weighed amount of potassium peroxodisulfate was added and stirring was achieved using a Teflon-covered magnet. The system was then closed and when the evolution of oxygen became stable its rate was followed with the gas buret. Afterwards a second run was performed using a solution of the same composition to which cerium(III) perchlorate had been added.

The determination of $[H^+]$. The hydrogen ion concentration in the reaction solutions at 65°C was measured by means of a Radiometer "combined electrode" GK 202. The glass electrode was calibrated with perchloric acid solutions containing sodium perchlorate so that the ionic strength was the same as in the reaction solutions.

MEASUREMENTS

The rate of evolution of oxygen gas was measured on solutions of the following initial concentrations

$$\begin{cases} a \text{ mM } \text{Ce(ClO}_4)_3 \\ 100 \text{ mM } \text{K}_2\text{S}_2\text{O}_8 \\ C_H \text{ mM } \text{HClO}_4 \\ 150 \text{ mM } \text{Na}_2\text{SO}_4 \\ 700 \text{ mM } \text{NaClO}_4 \end{cases}$$

Here a had the value 0 or 1.73 and C_H was varied from 20.0 to 160 corresponding to a variation in $[H^+]$ from 3.8 to 44.5 mM. At these acidities the solutions containing cerium were at the beginning of the runs somewhat turbid owing to hydrolysis of cerium(III)

In Figs. 1 and 2 some of the runs are represented. The slope dV''/at is constant as long as cerium(III) is present (see Fig. 2). The slope then changes abruptly and acquires the same value as dV'/dt for a cerium-free solution of the same $[H^+]$-value (see Fig. 1). Thus, according to eqn. (13) the rate of formation of cerium(IV) is independent of $[Ce(III)]$ which means that in the ionic medium used, the oxidizing radicals are effectively captured. This is in accordance with our previous observations.

In Fig. 3 dV'/dt and dV''/dt have been plotted *versus* $[H]^+$. As expected both functions can be represented by straight lines and by extrapolation to $[H^+]=0$ it is found that the intercept of dV''/dt on the ordinate axis is *one half* of the intercept of dV'/dt. This is in agreement with eqn. (12 b) and the suggested initial reaction (6) but is inconsistent with eqn. (12 a) and reaction (2) as initial step.

Furthermore, the difference $(dV'/dt)-(dV''/dt)$ turns out to be independent of the value of $[H^+]$. From eqn. (13) we consequently arrive at the conclusion that there is no net oxidation of cerium(III) by intermediates formed in the k_H path of the peroxodisulfate decomposition. Nor can these cause a net reduction of cerium(IV) formed by intermediates in the k path.

Wilmarth and Haim [5] have suggested the possibility that impurities in analytical grade perchloric acid can change the stoichiometry of the
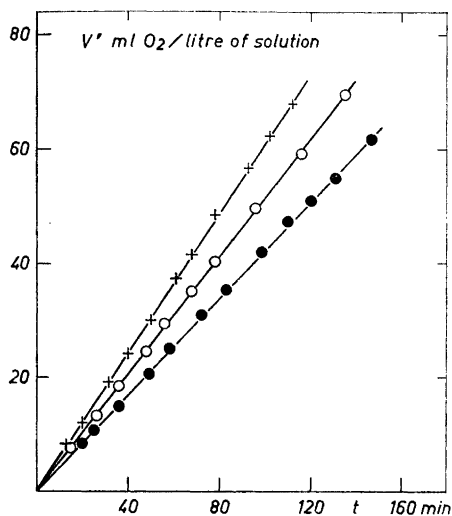
Fig. 1. The volume V' as a function of time t for the following initial concentrations: $[Ce(III)] = 0$; $[H^+] = 3.8$ mM (●); $[H^+] = 7.0$ mM (O); $[H^+] = 16.0$ mM (+).
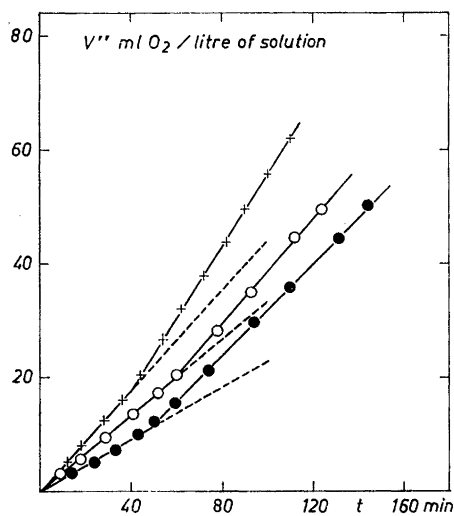
Fig. 2. The volume V'' as a function of time t for the following initial concentrations: $[Ce(III)] = 1.73$ mM; $[H^+] = 3.8$ mM (●); $[H^+] = 7.0$ mM (O); $[H^+] = 16.0$ mM (+).

oxidation of cerium. However, in the present measurements an eight-fold variation in the total concentration of this acid had no noticeable influence.

The rate constants of the peroxodisulfate decomposition. In cerium-free solutions the stoichiometry of the oxygen gas evolution is given by reaction (10).

Applying the gas law we then get the following expression for the calculation of k and k_H.

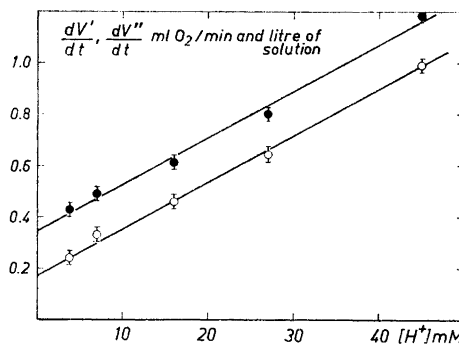$$2 \, \frac{dV'}{dt} \, \frac{p}{RT} = k[S_2O_8^{2-}] + k_H[H^+][S_2O_8^{2-}] \tag{14}$$

Fig. 3. The rates dV'/dt (●) and dV''/dt (O) of the oxygen gas evolution as functions of $[H^+]$. The circles represent mean values from several kinetic runs.

From Fig. 3 a value of 0.35 ± 0.02 ml/min and litre of solution is obtained for dV'/dt at $[H^+]=0$. With $p\approx1$ atm, $T=298°K$, and $[S_2O_8^{2-}]=100$ mM the calculations give $k=(2.9\pm0.2)\times10^{-4}$ min^{-1}. Furthermore, from the slope of the straight lines in Fig. 3 we calculate $k_H=(1.5\pm0.1)\times10^{-2}$ M^{-1} min^{-1}. Approximately the same value for k_H is obtained from the measurements of Kolthoff and Miller.[1]

The rate of the oxidation of cerium(III). Using low initial cerium concentrations and in the range of acidity used, we can regard $[S_2O_4^{2-}]$ as approximately constant during the reaction. Under these conditions the kinetic law (eqn. (5) with $\alpha=\infty$) can be expressed by the simple equation

$$[Ce(IV)]-[Ce(IV)]_0 = k[S_2O_4^{2-}]t \qquad (16)$$

The abrupt change in the slope of the V''-curves denotes the time t' for complete oxidation of cerium(III). Since the zero time in the runs is somewhat arbitrarily chosen the value of $[Ce(IV)]_0$ is not known. This means that in different runs t' can vary even if the total cerium concentration is kept constant. However, if we use the maximum value obtained for t' we can put $[Ce(IV)]_0\approx0$. For $[S_2O_8^{2-}]=100$ mM and $[Ce(IV)]=1.73$ mM we found $t'_{max}=55\pm5$ min and then eqn. (16) yields $k=(3.1\pm0.2)\times10^{-4}$ min^{-1}.

Hence, we can conclude that in the acidic medium used the rate of oxidation of cerium(III) is equal to the rate of the uncatalyzed decomposition of peroxodisulfate.

The value obtained for k at 65°C is not higher than that found in our previous study at 61°C. The reason for that is probably the higher concentration of sodium perchlorate in the present investigation, since we found earlier [3] that the rate of oxidation decreased when the concentration of sodium perchlorate was increased.

The later steps of the decomposition mechanism. The different proposed paths leading from hydroxyl radicals to oxygen gas can be tested fairly directly without making use of the conclusions about the initial step.

Since it has been proved above that cerium(III) is oxidized only by intermediates formed in the uncatalyzed peroxodisulfate decomposition it is evident from reaction (3) that for the oxidation of one mole of cerium the amount of hydroxyl radicals formed decreases by one mole. Thus, the final value of the difference between V' and V'', measured at a common time after complete oxidation of cerium(III), should correspond to 0.25 mole of oxygen per mole of cerium(IV) formed, if hydroxyl radicals are consumed according to the overall reaction (4). On the other hand, if reactions (7) and (8) predominate, the final value of $V'-V''$ should correspond to 0.5 mole of oxygen per mole of cerium(IV) formed.

From the curves corresponding to $[H^+]=3.8$ and 7.0 mM in Figs. 1 and 2 we get the mean value $V'-V''=11\pm1$ ml oxygen per litre of solution for $[Ce(IV)]=1.73$ mM. The value obtained corresponds to a decrease in the amount of oxygen evolved of 0.26 ± 0.03 mole for one mole of cerium(IV) formed. The result is in good agreement with reaction (4) but obviously reaction (8) cannot be of great importance in the present medium. Further-

more, no conclusive evidence for the formation of hydrogen peroxide as an intermediate is available and thus there is no reason to split up reaction (4) into the partial reactions (7) and (9).

DISCUSSION

The measurements on the oxygen gas evolution clearly prove that in the initial step of the uncatalyzed path of the thermal decomposition of peroxodisulfate in aqueous solution two different kinds of intermediates are formed and that only one kind can oxidize cerium(III). Thus reaction (2) cannot be the rate-determining step in aqueous solutions. On the other hand reaction (6) as rate-determining step is in complete agreement with the experimental results if the sulfate radical ion is the effective oxidizing agent in the redox reaction with cerium(III).

As far as the present authors know the only quantitative investigation giving some evidence in favor of reaction (2) as rate-determining step is a study by Kolthoff et al.[6] on the rate of capture of sulfate radical ions by styrene. However, it was pointed out that the determination was rather uncertain.

From a recent study on peroxodisulfate oxidation of carboxylates Eberson et al.[7] concluded that sulfate radical ions give coupling products whereas hydroxyl radicals do not. The yield of coupling products, based on reaction (2) never exceeded 50 %. Since it has been shown [8] that sulfate radical ions react very fast with acetic acid and formic acid the yield seems remarkably low, and more probable values are obtained if the yield is calculated on the basis of reaction (6).

The present measurements have also confirmed our previous observation that only one cerium(IV) ion can be formed for each peroxodisulfate ion decomposing in the k path. This finding implies that sulfate radical ions are produced practically exclusively in reaction (6). Thus in the medium used the rate of decomposition of hydroxyl radicals according to reaction (4) must be much higher (at least ten times) than the rate of the reverse of reaction (3).

Finally, it can be mentioned that Wilmarth and Haim [5] in a commentary to our previous investigation referred to a study by Sworski [9] on the reduction of cerium(IV) by formic acid induced by cobalt-60 γ-radiation. To interpret the data obtained, using a sulfuric acid medium, this author assumes that hydroxyl radicals oxidize cerium(III) and formic acid but sulfate radical ions (or HSO_4) only oxidize cerium(III). Evidently some of these assumptions are neither compatible with our present results nor with results from the recent studies [7,8] cited above. However, it is by no means clear that the explanation given by Sworski is the only possible one. Furthermore, it may be questioned if strongly energized radicals formed by γ-radiation can be treated as equals to radicals formed in thermal decomposition of peroxodisulfate.

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