

The Mechanism of the Silver(I) Catalyzed Reaction between Cerium(III) and Ammonium Persulphate

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The kinetics of the decomposition of ammonium persulphate and of the redox reaction with cerium(III), both of them catalyzed by silver(I), are investigated in an acid perchlorate-sulphate ionic medium. From the kinetic laws determined it is found that the two reactions have the same rate determining step. Furthermore, exactly two cerium(III) ions are oxidized for every persulphate ion decomposing in the silver catalyzed reaction, in contrast to what is the case with the corresponding uncatalyzed reaction.

On the basis of different facts a reaction mechanism is proposed, involving the formation of silver(II) and the radical ion $SO_4^{\cdot-}$ in the rate determining step.

It is found that silver(II) reacts more rapidly with ammonium ions than with water, while the reverse is valid for the reactivity of $SO_4^{\cdot-}$.

In a previous paper the decomposition of ammonium persulphate in aqueous solution and its redox reaction with cerium(III) in the absence of silver ions was investigated by the present authors¹. There it was found that at the acid concentrations used only a very small part of the decomposing persulphate was operating in the redox reaction. On the other hand, it is well known that in the presence of silver ions the persulphate ion is a much more effective oxidizing agent. Some workers²⁻⁴ have studied the silver ion catalyzed self-decomposition of ammonium persulphate, while in other investigations⁵⁻¹² also various reducing agents have been added. In the latter case it has often been postulated *a priori* that practically only the agents supplied were persulphate consuming, and it is remarkable that no one seems to have determined separately the kinetic laws of the self-decomposition and of the redox reactions under identical experimental conditions. From the different results reported it is only clear that in many cases the kinetic laws are of the same form and that the rate constants are of about the same order of magnitude. Thus it is easily understood that the discussions of reaction mechanisms have been very scanty or quite lacking.

It is the aim of the present investigation to study separately the silver ion catalyzed self-decomposition of ammonium persulphate and the redox reaction with cerium(III) in the same ionic medium and at the same temperature. Furthermore, the results arrived at in the previous investigation¹ with silver-free solutions will be taken into consideration in order to obtain a reliable basis for the discussion of the reaction mechanism.

EXPERIMENTAL

Chemicals. Silver perchlorate was prepared by precipitating silver oxide, washing carefully and dissolving in perchloric acid of analytical grade. The concentration of the stock solution was determined by titration according to Volhard.

Other chemicals and stock solutions used were prepared as before¹.

The redox reaction. Equal volumes of two solutions, one containing cerous perchlorate, ammonium persulphate, and perchloric acid and the other containing silver perchlorate, sodium sulphate, and sodium perchlorate, were tempered separately at 25.0 °C and then mixed as quickly as possible. At this temperature the redox reaction is very slow in the absence of silver ions, and thus a well defined starting-time for the reactions to be studied was obtained. Part of the reaction mixture was transferred to a light absorption cell, and at certain intervals the light extinction was determined at the wave length 400 m μ with a Beckman DU Spectrophotometer, modified to keep the cell temperature constant.

Since the decomposition of persulphate is slow at 25 °C even in the presence of silver ions (see below) it was necessary to have sodium sulphate present in advance, otherwise the cerium(IV) formed precipitated. Then, with a practically constant ionic medium it was possible to count on a constant value of the molar extinction of cerium(IV) in a measurement series. The molar extinction was calculated from the final extinction, corresponding to a complete oxidation of cerium(III), and thus the ceric concentrations at the different times were obtained.

The persulphate decomposition. The solutions were prepared and tempered as in the redox measurements above. Then equal volumes were mixed, samples were withdrawn and purified nitrogen was bubbled through them for ten minutes while still in the thermostat. Dilute sulphuric acid, an excess of ferrous sulphate and hot water were added rapidly, the time at the addition of the water being taken as the stop of the self-decomposition of persulphate in the sample. The analysis was completed as in the previous investigation¹.

In those cases where the solutions contained cerium, a correction for the ceric concentration had to be applied. This was easily performed, if the first sample in a run was withdrawn when all of the cerium was oxidized to cerium(IV) according to the measurements above.

THE DETERMINATION OF THE RATE LAWS

Symbols used in the equations below:

- a = the initial cerium(III) concentration,
- $b(t)$ = the persulphate concentration at the time t ,
- c = the silver(I) concentration,
- x = the cerium(IV) concentration,
- y = the concentration of the radical ion SO_4^- ,
- z = the silver(II) concentration.

Kinetics of the persulphate decomposition. In Fig. 1 $\ln b(t)$ has been plotted against t for different values of the parameters a , $b(0)$, and c and for the ionic medium 500 mM HClO_4 + 150 mM Na_2SO_4 + 50 mM NaClO_4 . The straight

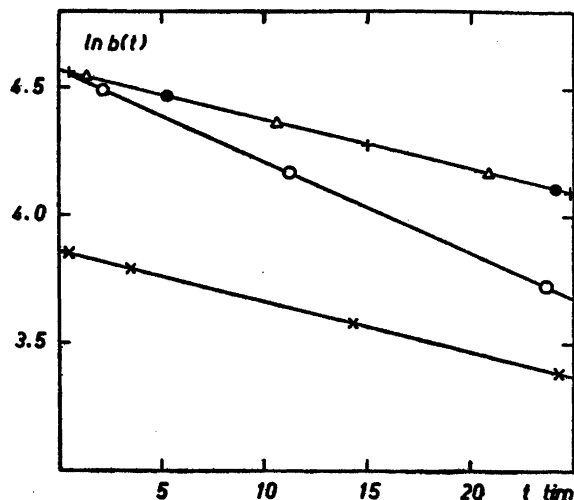


Fig. 1. $\ln b(t)$ as a function of t at different values of a , $b(0)$ (48.0 and 96.0 mM), and c . $a = 0$, $c = 1.20$ mM (+ and ×); $a = 1.74$ mM, $c = 1.20$ mM (Δ); $a = 8.69$ mM, $c = 1.20$ mM (\bullet); $a = 0$, $c = 2.40$ mM (\circ).

lines obtained indicate a first order reaction with respect to persulphate. The slope $-k_0'$ of the lines proves to be independent of a and $b(0)$ but almost proportional to c .

Since there is a competition between the silver ion catalyzed decomposition and the one existing in silver-free solutions we can expect the expression for k_0' to be of the form:

$$k_0' = k_0 + k_1' \cdot c \quad (1)$$

At the acid concentration used k_0 should be approximately equal to the rate constant of the hydrogen ion catalyzed decomposition¹. For $c = 1.20$ mM $k_0' = (3.20 \pm 0.05) \times 10^{-4} \text{ min}^{-1}$ while for $c = 2.40$ mM we get $k_0' = (5.90 \pm 0.05) \times 10^{-4} \text{ min}^{-1}$. From these values we can calculate $k_0 = (5 \pm 2) \times 10^{-5} \text{ min}^{-1}$ and $k_1' = 0.225 \pm 0.010 \text{ M}^{-1} \text{ min}^{-1}$. Thus k_0 is only a correction term in the present case. If its value is combined with $k_0 = 3.8 \times 10^{-3} \text{ min}^{-1}$, determined in the previous work¹ for the same ionic medium but at 61 °C, the activation energy 24 ± 2 kcal is obtained. Kolthoff and Miller¹³ give the value 26 kcal for the same reaction.

Kinetics of the redox reaction with cerium(III). In Fig. 2 the ceric concentration x has been plotted against t for different values of the parameters a , $b(0)$, and c and for the same ionic medium as above. It is evident that when the $(a-x)$ -values are not very low x is independent of a . Furthermore, since the variation in $b(t)$ is very slight for the short times used in the runs the curves in Fig. 2 consist of approximately straight lines. Thus it is easily found

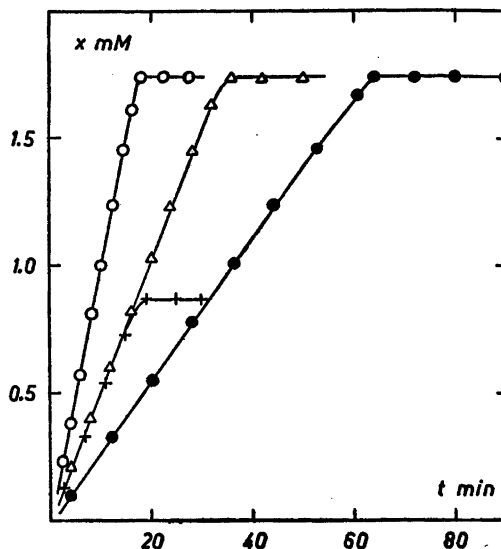


Fig. 2. x as a function of t at different values of a , $b(0)$, and c . $a = 0.870$ mM, $b(0) = 96.0$ mM, $c = 1.20$ mM (+); $a = 1.74$ mM, $b(0) = 96.0$ mM, $c = 1.20$ mM (Δ); $a = 1.74$ mM, $b(0) = 47.6$ mM, $c = 1.20$ mM (\bullet); $a = 1.74$ mM, $b(0) = 96.0$ mM, $c = 2.40$ mM (\circ).

from the slope of the first part of the curves that the reaction rate is proportional to the silver and persulphate concentrations.

$$\frac{dx}{dt} = k b(t) c \quad (2)$$

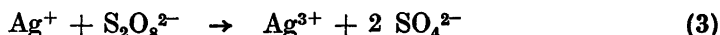
For the rate constant k the different runs give the average value 0.46 ± 0.01 $\text{M}^{-1}\text{min}^{-1}$. This means that within the limits of experimental random errors the relation $k = 2 k_1'$ has been found to be valid.

Since $dx/dt = 0$ for $x = a$, it is clear that eqn. (2) cannot be applicable for very small values of $a - x$, and it is very plausible that the first power of $a - x$ enters into the complete differential equation, as was the case with the corresponding equation for the uncatalyzed redox reaction¹.

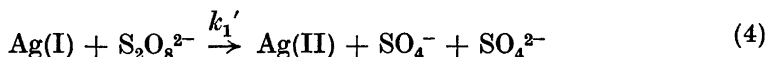
THE REACTION MECHANISM AND THE COMPLETE RATE LAW

Among the different partial reactions operating in the oxidation of cerium (III) we have the uncatalyzed persulphate decomposition, studied in the previous work¹. However, preliminary measurements showed that this reaction is quite negligible at 25°C. Thus the silver(I) catalyzed decomposition is the predominant starting reaction.

For this one Yost⁵ was the first to propose the mechanism



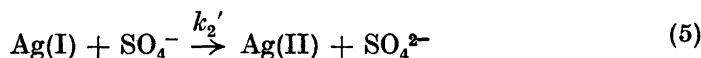
as the rate determining step. However, the experimental evidence for the formation of silver(III) is not very strong, and presumably the real reason for the formulation was the fact that the formation of the radical ion SO_4^- was not known at that time. Since the existence of silver(II) is certain we propose the following formulation of the first step



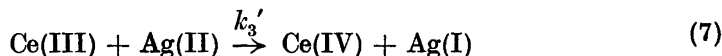
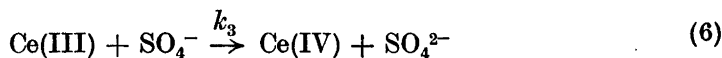
in analogy with the formulation for the uncatalyzed reaction¹. The formation of SO_4^- according to (4) is supported by the fact that on addition of silver(I) to persulphate this becomes more effective in initiating polymerizations (*cf.* Bacon¹⁴ and Morgan¹⁴).

In the previous work¹ the rate law obtained proved that in the absence of silver the amount of SO_4^- not consumed in the oxidation of cerium(III) disappeared in a reaction with the rate $k_2[\text{SO}_4^-]$, where k_2 is a constant. Thus it was concluded that SO_4^- reacted with water giving free oxygen (*cf.* Kolthoff and Miller¹³) and not with the ammonium ions, the concentration of which was not the same in the different runs.

In the presence of silver(I), on the other hand, measurements showed that also in cerium-free solutions practically no oxygen was evolved, even if the persulphate decomposition was considerable. Thus we must conclude that silver(I) reacts more readily than water with SO_4^- according to



Furthermore, we have the two simultaneous reactions



where (6) is the reaction studied in the previous investigation¹.

Finally, since no oxygen is evolved the amount of silver(II) not consumed in reaction (7) evidently must attack the ammonium ions. According to Marshall² ammonium persulphate decomposes in the presence of silver salts with the formation of nitrate ions. Thus we have the stoichiometric formula



Of course the reaction (8) involves several steps, and we can presume, that the reaction is first order with respect to silver(II). Then the reaction rate is equal to $\varphi \cdot z$, where φ may be a function of different concentrations.

If the mechanism (4)–(8) is correct the following system of differential equations should be applicable.

$$\frac{dx}{dt} = (a - x) (k_3 y + k_3' z) \quad (9)$$

$$\frac{dy}{dt} = k_1' b(t) c - \{k_2' c + k_3 (a - x)\} y \quad (10)$$

$$\frac{dz}{dt} = c \{k_1' b(t) + k_2' y\} - \{\varphi + k_3' (a - x)\} z \quad (11)$$

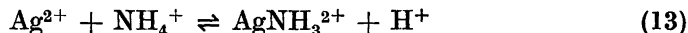
Referring to the deductions of the previous paper¹ and remembering that $b(t) = b(0)e^{-k_0 t}$ we can establish that if the condition $k_2' \gg k_1'$ (that is $k_2' c \gg k_1' c \approx k_0'$) is fulfilled the steady-state approximation is valid for SO_4^- at all cerous concentrations. Thus we can put $dy/dt = 0$ in eqn. (10) and get an expression for y . When this expression is introduced into eqn. (11) it is found that an equation of a similar type as eqn. (10) is obtained, and the necessary and sufficient condition for the applicability of the steady-state approximation also to silver(II) at all cerous concentrations is that $\varphi \gg k_1' c$.

Applying the steady-state approximations we can easily eliminate the variables y and z , and for dx/dt we get the following complete expression:

$$\frac{dx}{dt} = \frac{k_1' (a - x) b(t) c}{\varphi + k_3' (a - x)} \left\{ 2 k_3' + \frac{k_3 \varphi}{k_2' c + k_3 (a - x)} \right\} \quad (12)$$

If φ is a quantity negligible in comparison with $k_3' (a - x)$ this equation becomes identical with the simple eqn. (2) with $k = 2 k_1'$, which is experimentally verified for not very low cerous concentrations. Thus the mechanism proposed with the reaction (4) as the rate determining step and with the different rate constants fulfilling the conditions stated seems plausible.

According to this mechanism silver(II) reacts more rapidly with ammonium ions than with water, while, as mentioned in the foregoing, the reverse is valid for the reactivity of the radical ion SO_4^- . This state of things could be due to a tendency of silver(II) to form ammine complexes. Then in our acid solutions the equilibrium



would exist, followed by a rapid decomposition of the ammine complex in a first order reaction involving an electron transfer from the ligand to the central ion. In this case the function φ can be expected to be of the form $\varphi = \text{constant} \cdot [\text{NH}_4^+]$, since $[\text{H}^+]$ is constant.

The measurements of the persulphate decomposition show clearly that c did not vary with time, even if the decrease in $b(t)$ was considerable. This means that z was either very small in comparison with c or a constant fraction of the total silver concentrations. Now, applying the steady-state approximations to the cerium-free solutions and using the expression for φ we get $z/c = \text{constant} \cdot b(t) / [\text{NH}_4^+]$. But from the reactions (4), (5) and (8) it is evident that $b(t) / [\text{NH}_4^+]$ decreases with time, and thus z must be $\ll c$ throughout the runs.

After the completion of the present investigation a paper by Bawn and Margerison¹⁶ about the rate of persulphate decomposition has appeared. For the silver catalyzed reaction they have also proposed (4) as the rate determining step. For the uncatalyzed reaction, however, they have accepted the previous mechanism of Bartlett and Cotman¹⁷, which has turned out to be inconsistent with experimental facts¹.

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