

The Kinetics and Mechanism of the Reaction between Cerium(III) and Persulphate

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The kinetics of the thermal decomposition of persulphate in aqueous solutions and of the redox reaction between cerium(III) and persulphate are investigated in a perchlorate ionic medium and in a mixed perchlorate-sulphate medium. It is found that the oxidizing agent in the redox reaction is the intermediate radical ion SO_4^- , formed in a decomposition reaction of persulphate that is uncatalyzed by hydrogen ions. Evidence is also given that only one SO_4^- can be formed from every persulphate ion decomposing in this way.

The mechanism previously proposed for the persulphate decomposition is changed so as to be consistent with these results.

The fact observed that cerous sulphate complexes are oxidized more rapidly than the hydrated cerous ion is discussed in terms of an electron transfer mechanism.

The thermal decomposition of persulphate in aqueous solutions has been the subject of several investigations (*cf.* Kolthoff and Miller¹). The nature of some of the intermediate products formed in the decomposition has been convincingly established, but the mechanism proposed for the reaction has not been tested in more detail.

In preliminary measurements the present authors found that the oxidation of cerous salts by persulphate in the absence of catalyzing silver ions is noticeable only at such temperatures where the thermal decomposition of persulphate is significant. For this reason the present investigation was started with the aim of elucidating the mechanism of this redox reaction and in this way also of giving further information about the mechanism for the thermal decomposition of persulphate. Furthermore, a study of this oxidation of cerium(III) is the natural introduction to a close investigation of the corresponding reaction in the presence of silver ions.

EXPERIMENTAL

Chemicals. From calculated amounts of ammonium persulphate, Merck's p. a., solutions were prepared just before use.

Cerous perchlorate was obtained by heating cerous chloride with 70 % perchloric acid. The preparation obtained was free from chloride ions and was recrystallized from water.

A stock solution of ceric perchlorate was prepared by anodic oxidation at platinum of a cerous perchlorate solution, acidified with perchloric acid. After the oxidation the ceric concentration was about 75 % of the total cerium concentration.

Perchloric acid, sodium perchlorate, and sodium sulphate were of analytical grade.

The redox reaction. Two solutions, one containing cerous perchlorate and perchloric acid and the other containing ammonium persulphate, sodium sulphate (in certain experiments) and sodium perchlorate, were kept for thirty minutes in a paraffin-oil thermostat at 61° C. Then equal volumes were mixed, and after certain time intervals samples of 5 ml were withdrawn by pipette and added to an equal volume of ice-cooled water. After tempering in a thermostat at 20° C for thirty minutes the light extinction of the solution was determined at the wave length 400 $m\mu$ with a Hilger Uvispek Spectrophotometer or a Beckman Quartz Spectrophotometer (Model DU). The layer thickness was always 1 cm.

To determine the values of the molar extinction of cerium(IV) in the different samples of a measurement series it was necessary to perform a calibration series with the cerium(III) exchanged for the ceric-cerous mixture with 75 % cerium(IV) but otherwise with the same ionic composition. In a third measurement series of the same kind the cerium was initially present only as cerium(III) and in the same concentration as in the calibration series. The difference between the extinction values of the two last-mentioned series at a given time yields the extinction corresponding to the initial ceric concentration in the calibration series. Then the ceric concentrations in the different samples were obtained from their extinctions.

The persulphate decomposition. At the acid concentrations used the thermal decomposition of persulphate in aqueous solutions with the liberation of oxygen is rather rapid at 61° C, and for this reason a separate investigation of the kinetics of this decomposition was performed.

The solutions were prepared as in the measurements described above, and samples of 5 ml were withdrawn and added to the same volume of ice-cooled water in order to practically stop the reaction. From 5 ml of this mixture oxygen was removed by bubbling for ten minutes with purified nitrogen. Then 5 ml of dilute sulphuric acid, 5 ml of 0.1 *M* ferrous sulphate and about 50 ml of water of 70–80° C were added, causing a rapid reduction of the persulphate. An excess of ceric sulphate, strongly acidified with sulphuric acid, was added, and after cooling to room temperature the excess of ceric sulphate was titrated with ferrous sulphate, ferroin being used as indicator.

When the samples withdrawn contained cerium, the method described gave the sum of the persulphate and ceric concentrations. Then the ceric concentration, previously determined, was subtracted.

THE RATE LAWS FROM THE MEASUREMENTS

The following symbols for concentrations are used.

- a = the initial concentration of cerium(III).
- $b(t)$ = the concentration of persulphate at the time t .
- x = the concentration of cerium(IV).
- y = the concentration of an intermediate species, denoted A.

Kinetics of the persulphate decomposition. The rate of decomposition of persulphate was studied for different values of $b(0)$, a and the hydrogen ion concentration. In Fig. 1 $\ln b(t)$ is plotted against t . Straight lines are obtained, indicating a first order reaction in every measurement series. For the ionic medium 500 *mM* HClO_4 + 500 *mM* NaClO_4 , the rate constant $k_0 = (5.0 \pm 0.1) \times 10^{-3} \text{ min}^{-1}$ is obtained. When the ionic medium has the composition 500 *mM* HClO_4 + 150 *mM* Na_2SO_4 + 50 *mM* NaClO_4 , we get $k_0 = (3.8 \pm 0.1) \times 10^{-3}$

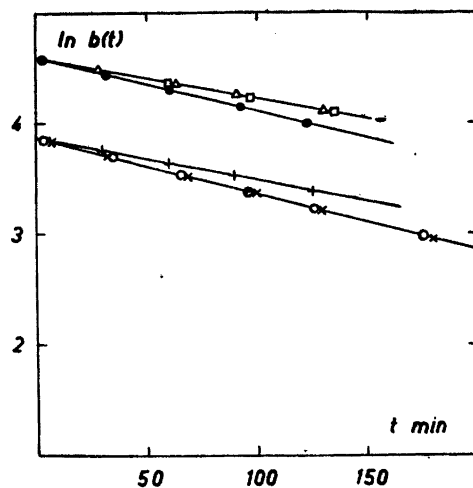


Fig. 1. $\ln b(t)$ as a function of t at different values of $b(0)$ (48.2 and 98.6 mM), a , and $[H^+]$. $a = 0$, $[H^+] = 500$ mM (\bullet and \circ); $a = 1.74$ mM, $[H^+] = 500$ mM (\times); $a = 0$, $[H^+] = 378$ mM (Δ and $+$); $a = 1.74$ mM, $[H^+] = 378$ mM (\square).

min^{-1} . In the last-mentioned case the hydrogen ion concentration, determined by measurements with the quinhydrone electrode, had the value 378 mM.

Since HS_2O_8^- is a strong acid (cf. Kolthoff and Miller¹) a rather small addition of persulphate to the ionic medium cannot change the $[H^+]$ -values appreciably. Thus, within the limits of the experimental random errors the k_0 -values obtained are proportional to the $[H^+]$ -values and independent of the small amounts of cerium in the solutions.

Kolthoff and Miller¹ have found that in alkaline and neutral solutions the decomposition is slow with the value $3.0 \times 10^{-4} \text{ min}^{-1}$ for the rate constant at 60° C (corresponding to $3.5 \times 10^{-4} \text{ min}^{-1}$ at 61° C, calculated from the activation energy given¹), independent of the values of pH and the ionic strength. Thus persulphate decomposes by two competing reactions, one uncatalyzed and the other catalyzed by hydrogen ions, and then in our measurements the correct expression for k_0 is:

$$k_0 = 3.5 \times 10^{-4} + 1.00 \times 10^{-2} [H^+] \text{ min}^{-1} \quad (1)$$

Kinetics of the redox reaction. In Fig. 2 the concentration x of cerium(IV) has been plotted against t with a and $b(0)$ as parameters and with perchloric acid and sodium perchlorate in constant concentrations as additional electrolytes. From the dependence of dx/dt at $t = 0$ upon a and $b(0)$ it is easily found that the formation of cerium(IV) is a first order reaction with respect to persulphate but of no simple order with respect to cerium(III), since the dependence on a decreases with increasing a -values. Thus it is natural to try to represent the rate expression by a differential equation of the form:

$$\frac{dx}{dt} = \frac{k(a-x)b(t)}{1+a(a-x)} \quad (2)$$

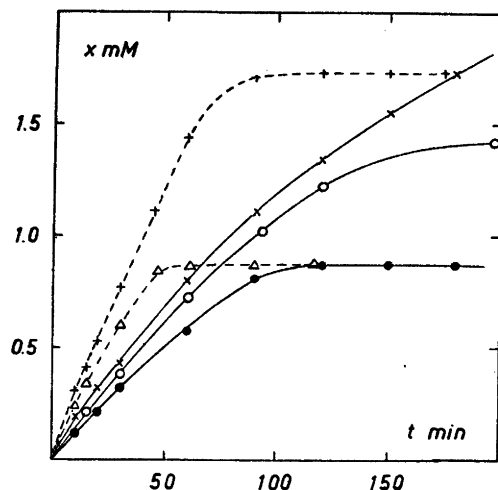


Fig. 2. The relation between x and t at different values of a and $b(0)$ and with 500 mM HClO_4 + 500 mM NaClO_4 as additional electrolytes. $a = 0.870$ mM, $b(0) = 48.2$ mM (\bullet); $a = 1.74$ mM, $b(0) = 48.2$ mM (\circ); $a = 3.47$ mM, $b(0) = 48.2$ mM (\times); $a = 0.870$ mM, $b(0) = 98.6$ mM (\triangle); $a = 1.74$ mM, $b(0) = 98.6$ mM ($+$).

where k and a are constants. If we make use of the expression for $b(t)$, an integration of eq. (2) yields:

$$\frac{k_0}{b(0)-b(t)} \ln \frac{a}{a-x} = k - \frac{a k_0 x}{b(0)-b(t)} \quad (3)$$

For the sake of brevity we put $u = k_0 x / (b(0) - b(t))$ and the left member of eq. (3) equal to z . Then, if the rate expression proposed is correct, all the measurement series should give one and the same linear relation between u and z .

In Table 1 corresponding values of u and z have been calculated for such t -values that the differences $b(0) - b(t)$ and $a - x$ are not influenced very greatly by the experimental random errors. In Fig. 3 the function z has been plotted against u , and it is seen that a straight line is obtained. Thus, for the concentration ranges used the rate law, represented by eq. (2), is verified. The intercept on the u -axis is well defined and yields $k/a = (3.4 \pm 0.1) \times 10^{-4} \text{ min}^{-1}$, and from the slope of the line we get $a = (3.5 \pm 0.2) \times 10^3 \text{ M}^{-1}$.

In Fig. 4 the formation of cerium(IV) is represented when the additional electrolytes are perchloric acid, sodium sulphate, and sodium perchlorate. It is evident that for $a - x > 0.2$ mM x is independent of the a -value. This means that the term $a(a - x)$ in eq. (2) is $\gg 1$ in this case, and k/a can be obtained from the slope of the approximately straight-lined, first part of the curves according to the equation:

$$\lim_{t \rightarrow 0} \frac{dx}{dt} = \frac{k b(0)}{a} \quad (4)$$

Table 1. Calculated values of u and z in the different measurement series at selected values of t . Additional electrolytes:

500 mM HClO₄ + 500 mM NaClO₄.

a mM \rightarrow	0.870			1.74			3.47		
$b(0)$ mM \rightarrow	48.2			48.2			48.2		
t min	x	$u \cdot 10^3$	z	x	$u \cdot 10^3$	z	x	$u \cdot 10^3$	z
30.0	0.32	0.240	0.345	0.38	0.285	0.185	0.42	0.315	0.095
45.0	0.45	0.230	0.370						
60.0	0.57	0.225	0.420	0.71	0.280	0.205	0.80	0.315	0.100
90.0				0.99	0.280	0.235	1.10	0.310	0.105
120.0							1.34	0.305	0.110
a mM \rightarrow	0.870			1.74			x expressed in mM		
$b(0)$ mM \rightarrow	98.6			98.6					
t min	x	$u \cdot 10^3$	z	x	$u \cdot 10^3$	z	u	\rightarrow	\rightarrow min ⁻¹
15.0	0.34	0.235	0.345	0.41	0.285	0.190	z	\rightarrow	\rightarrow min ⁻¹ M ⁻¹
30.0	0.60	0.220	0.430	0.77	0.280	0.215			
45.0				1.11	0.270	0.250			

The measurements give $k/\alpha = (3.7 \pm 0.1) \times 10^{-4}$ min⁻¹. When the concentration of sodium perchlorate was increased to compensate for the decrease in ionic strength caused by the formation of hydrogen sulphate ions, we obtained $k/\alpha = (3.3 \pm 0.1) \times 10^{-4}$ min⁻¹.

For $t = 50$ min, $a = 0.87$ mM and $b(0) = 48.2$ mM we can compute $z = 1.4$ min⁻¹ M⁻¹, while the u -value is equal to k/α within the limits of the random errors. Thus, if these are taken into consideration we have $k/\alpha - u \leq 0.2 \times 10^{-4}$ min⁻¹, and then eq. (3) yields $\alpha \geq 7 \times 10^4$ M⁻¹.

It is evident that a partial exchange of perchlorate ions for sulphate ions at a constant ionic strength has no influence upon k/α , whereas the α -value increases considerably.

THE MECHANISM OF THE OXIDATION-REDUCTION REACTION

From the rate law verified it is seen at once that the reaction between cerium(III) and persulphate is not a simple bimolecular one. Neither can it be such a reaction preceded by a formation of an ordinary complex between these components, for in this case the rate law would have been of the form

$$\frac{dx}{dt} = \text{constant} \cdot \frac{(a-x)b(t)}{1 + \beta b(t)} \quad (5)$$

if β is the complexity constant, and provided persulphate is in great excess.

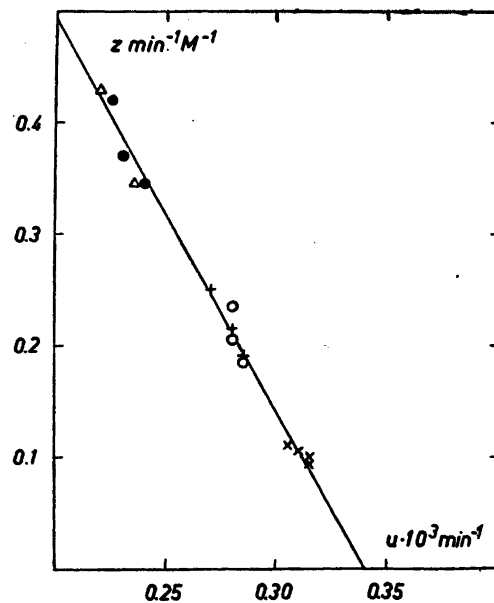


Fig. 3. z as a function of u . The signs used relate to the same concentrations as in Fig. 2.

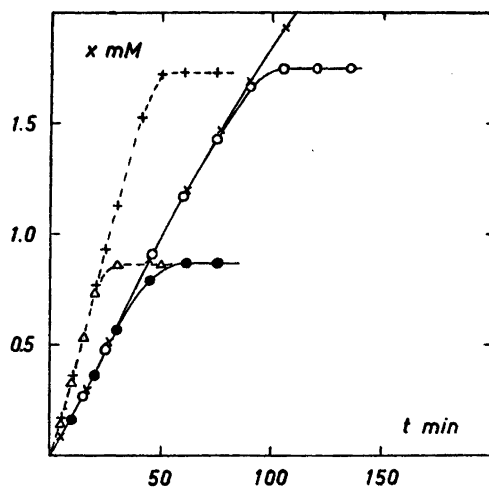
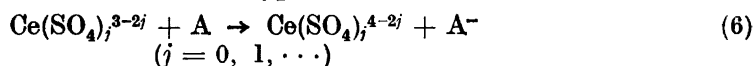


Fig. 4. The relation between x and t at different values of a and $b(0)$ and with 500 mM HClO_4 + 150 mM Na_2SO_4 + 50 mM NaClO_4 as additional electrolytes. $a = 0.870$ mM, $b(0) = 48.2$ mM (●); $a = 1.74$ mM, $b(0) = 48.2$ mM (○); $a = 3.47$ mM, $b(0) = 48.2$ mM (×); $a = 0.870$ mM, $b(0) = 98.6$ mM (Δ); $a = 1.74$ mM, $b(0) = 98.6$ mM (+).

Then the only possible explanation of the reaction is that the oxidizing agent is an intermediate species A, formed in the thermal decomposition of persulphate. The rate constant for the formation of A is denoted by k_1 , and depending on whether the ions (or molecules) A are formed in the uncatalyzed decomposition reaction or in the one catalyzed by hydrogen ions, the value of k_1 must be equal to either $3.5 \times 10^{-4} \times n \text{ min}^{-1}$ or $1.00 \times 10^{-2} \times [\text{H}^+] \times n$ (that is approximately $k_0 \times n$) min^{-1} , where n is an integer, indicating how many A are formed from one persulphate ion.

In the absence of cerium(III) A reacts under the liberation of oxygen, and for this partial process we introduce the rate constant k_2 . In the presence of cerous ions and cerous sulphate complexes (*cf.* Fronæus²) we have a set of simultaneous redox reactions of the type



Then for the rates of formation of A and cerium(IV) the following equations can be expected to be applicable.

$$\frac{dy}{dt} = k_1 b(t) - k_2 y - k_3 (a-x) y \quad (7)$$

$$\frac{dx}{dt} = k_3 (a-x) y \quad (8)$$

Here the coefficient k_3 is a function of the sulphate ion concentration, if the cerous ion and the cerous sulphate complexes have different individual rate constants for the redox process (6).

If $k_3(a-x)$ is a quantity that is negligible in comparison with k_2 the system of differential equations (7, 8) has a simple solution. Then, if $y = y_0$ when $t = 0$ (the time at which cerium(III) is added), and we apply the relation $b(t) = b(0) e^{-k_0 t}$ verified before, the simplified equation

$$\frac{dy}{dt} + k_2 y = k_1 b(t) \quad (9)$$

has the solution

$$y = \left(y_0 - \frac{k_1 b(0)}{k_2 - k_0} \right) e^{-k_2 t} + \frac{k_1 b(0)}{k_2 - k_0} e^{-k_0 t} \quad (10)$$

If the condition $k_2 \gg k_0$ is fulfilled the last term in the right member of eq. (10) will be the dominating one a short time after the starting of the redox reaction and we have approximately: $k_2 y = k_1 b(t)$. Comparing this expression with eq. (9) we find that for such t -values dy/dt is a quantity negligible in comparison with $k_2 y$. This is the steady-state approximation.

When $k_3(a-x)$ cannot be neglected, $k_2 + k_3(a-x)$ varies with time, but provided this sum is $\gg k_0$, it is obvious that the steady-state approximation must still be applicable, giving us: $y\{k_2 + k_3(a-x)\} = k_1 b(t)$. Combining this expression with eq. (8) we obtain

$$\frac{dx}{dt} = \frac{k_1 k_3 (a-x) b(t)}{k_2 + k_3 (a-x)} \quad (11)$$

With $k_1 = k/\alpha$ and $k_3/k_2 = \alpha$ this differential equation is identical with the rate law (2), experimentally verified.

Thus k_1 has the value $3.4 \times 10^{-4} \text{ min}^{-1}$, independent of the variation in $[\text{H}^+]$ accompanying the partial exchange of perchlorate for sulphate ions. Since this value within the limits of experimental random errors is equal to the rate constant of the uncatalyzed thermal decomposition of persulphate but much smaller than k_0 , we can conclude that the species A is formed in this reaction, and that *only one* A is formed from every persulphate ion decomposing in this way.

Furthermore, the great increase in k_3/k_2 on the addition of sulphate ions must certainly be due to an increase in k_3 , since this change in the ionic medium of a constant ionic strength cannot possibly cause a very great decrease in the activity coefficients included in k_2 . This means that the cerous sulphate complexes have greater values for the rate constant of the redox process (6) than the free hydrated cerous ion.

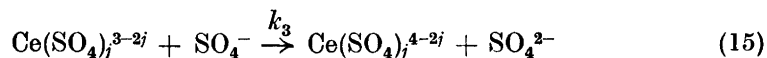
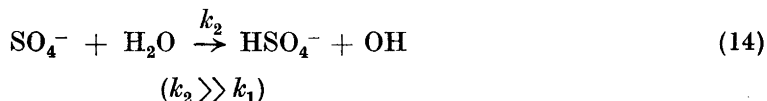
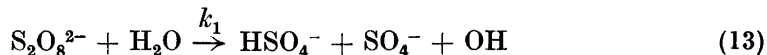
DISCUSSION

For the uncatalyzed thermal decomposition of persulphate in aqueous solutions Bartlett and Cotman³ have proposed the following rate-determining step

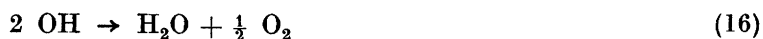


followed by a reaction between the radical ion SO_4^- and water, giving the intermediate radical OH and finally oxygen. This mechanism, involving a symmetrical dissociation of the persulphate ion, has been accepted by Kolthoff and Miller¹. There is also much evidence in other investigations^{4,5} that SO_4^- is the strongly oxidizing agent formed in the uncatalyzed thermal decomposition of persulphate ions, but no urgent reasons for the acceptance of all steps in this mechanism exist.

It is evident that our intermediate species A is equal to the radical ion SO_4^- , and then another mechanism, consistent with our conclusion that only one SO_4^- can be formed from one persulphate ion, must be introduced. For the uncatalyzed thermal decomposition and the redox reaction with cerium(III) we propose the following mechanism.



$$(j = 0, 1, \dots)$$



Bartlett and Nozaki⁵ have shown that in alkaline solutions the rate constant of the decomposition of persulphate increases considerably (more than eight-fold at 80° C), if the solution is saturated with ethyl acetate. This makes it very plausible that the rate-determining step is a bimolecular reaction involving the solvent, as we have assumed in (13).

Since our kinetics data do not indicate any reduction of the cerium(IV) formed in the step (15), we must conclude, if the mechanism proposed is correct, partly that the radical OH cannot reduce cerium(IV) in these solutions, partly that OH does not form hydrogen peroxide. The first of these conclusions is consistent with results obtained by Milling, Stein, and Weiss (*cf.* Weiss⁶), and the second conclusion is supported by an investigation of Milling and Weiss (*cf.* Weiss^{6,7}). The reaction (16) must not be interpreted as a simple step, it only indicates that the OH radical yields free oxygen.

The mechanism is also in agreement with the results of Kolthoff and Miller¹, *e. g.* that the oxygen liberated by the uncatalyzed decomposition of persulphate comes from the water and not from the persulphate.

When it is a question of explaining the result obtained that cerous sulphate complexes are oxidized more rapidly than the free hydrated cerous ion, several factors should be taken into consideration.

It is seen at once that the Coulomb forces between the reactants in step (15) must be of little significance for the reaction rate, since this attraction decreases or is changed into repulsion by the coordination of sulphate ions.

On the other hand, the application of the Franck-Condon principle⁸ to the redox step (15) can give a conceivable explanation. Since the cerous and ceric ions have different energies of hydration, the rearrangement of the hydration atmosphere connected with the electron transfer involves an energy barrier to the reaction. By the coordination of sulphate ions the energies of hydration and the barrier certainly are decreased, and thus the reaction rate can be increased.

It is also conceivable that by the coordination of sulphate ions the 4f electron is promoted to a 5d electron, which should increase the probability for electron transfer.

Finally we will discuss the ability of the ligands to act as electron conductors. If the reaction step (14) occurs with a water molecule coordinated to a cerous ion the reaction does not proceed to oxidation of the central ion, since according to our mechanism above OH does not react with cerium(III). On the other hand, when an electron is transferred from a coordinated sulphate ion to a radical ion SO_4^- the oxidizing agent comes close to the central ion, and the redox reaction (15) can occur. Thus we must conclude that in the present case the sulphate ligand is a better electron conductor than the water ligand, and an increased rate of the redox reaction by the coordination of sulphate ions is to be expected.

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