

Kinetics and Mechanism of the Oxidation of Vanadium(IV) by Peroxodisulfate Ion

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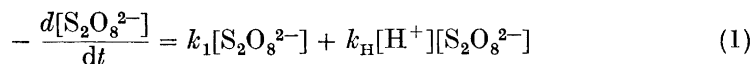
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The kinetics of the redox reaction between oxovanadium(IV) and peroxodisulfate ions in weakly acidic aqueous solution were studied between 25°C and 50°C. At hydrogen ion concentrations in the range 0.1–0.5 M the rate becomes independent of the vanadium concentration, when the concentration of vanadium(IV) exceeds about 1 mM and the peroxodisulfate is in large excess. The rate of formation of vanadium(V) was found to be twice the rate of disappearance of peroxodisulfate. The reaction is of order 1 with respect to both peroxodisulfate and hydrogen ion. The overall second-order rate constant, expressing the rate of increase of concentration of vanadium(V), was determined to be $(2.4 \pm 0.1) \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ at 25.0°C in a medium of 2.00 M (H,Na)ClO₄. The activation energy is $102 \pm 3 \text{ kJ mol}^{-1}$.

The rate-determining step is the hydrogen-ion catalyzed decomposition of peroxodisulfate ion, during which the active oxidizing agent, HSO₅⁻, is formed. Just after the redox reaction is essentially completed, the hydrogenperoxomonosulfate formed cannot decompose normally. It is suggested that the remaining small amounts of vanadium(IV) interfere by preventing the radicals formed in the uncatalyzed path of the decomposition of peroxodisulfate from taking part in the decomposition of the peroxomonosulfate.

The uncatalyzed decomposition of peroxodisulfate ion gives a pH-independent contribution to the rate of the redox reaction. An indication of a minor contribution from a direct reaction by the two reactants is also observed.

Redox reactions in aqueous solution between certain metal ions and the peroxodisulfate ion have been studied^{1,2} – mostly in acidic solution, where the thermal decomposition of peroxodisulfate ion is catalyzed by hydrogen ion according to eqn. (1):³



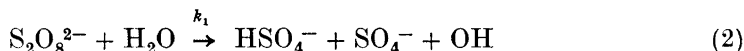
The k_{H} term becomes predominant for solutions more acidic than pH ≈ 2.

Some oxidations, like those of silver(I),¹ iron(II),¹ and chromium(II),⁴

are much more rapid than the thermal decomposition of the peroxodisulfate, and they occur by a direct reaction between the peroxodisulfate ion and the metal ion.

On the other hand, as can be seen from investigations by Fronæus and coworkers, the oxidations of cerium(III)⁵ and chromium(III)⁶ proceed at a rate much lower than the overall rate of decomposition of peroxodisulfate. In these reactions, intermediates from the k_1 path are responsible for the oxidation of the metal ion. In the latter reaction, involving a change of 3 units of oxidation number for the reductant, some intermediate from the hydrogen-ion catalyzed decomposition path also participates in the later steps of the redox reaction.

One of the basic questions concerning the oxidation mechanisms of peroxodisulfate is the thermal decomposition (*i.e.* the oxidation of water). In a paper by Fronæus and Östman,⁷ substantial evidence is put forward in favor of the mechanism suggested earlier by them for the uncatalyzed path with eqn. (2) as the primary step:



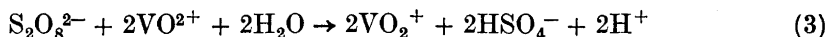
Peroxodisulfate oxidations are still studied extensively from various points of interest.⁸ The results referred to above imply that oxidations of different metal ions occur by fairly individual mechanisms. Therefore, we undertook this investigation to study the oxidation of another transition-metal ion, oxovanadium(IV).

There has been in the sixties a sharply rising research interest in the chemistry of vanadium, particularly the cationic oxovanadium(IV) species, VO^{2+} ,⁹ and also a few kinetic studies involving the oxidation of oxovanadium(IV) in solution have been published.¹⁰ In 1964, Espenson made a thorough investigation of the mechanism of the reaction between vanadium(IV) and chromium(VI) which starts with a rapid pre-equilibrium step leading to the formation of one VO_2^+ along with an unstable chromium(V) intermediate.¹¹ A recent study of the oxidation of oxovanadium(IV) ion by peroxodiphosphate¹² calls for a comparison with the corresponding peroxodisulfate reaction.

Rutter¹³ reported in 1907 that vanadium(IV) compounds are oxidized only slowly by acidic peroxodisulfate solutions. This has been confirmed by, among others, Berry,¹⁴ who also states that Caro's acid (peroxosulfuric acid, H_2SO_5) easily oxidizes oxovanadium(IV) quantitatively at ordinary temperatures.

The peroxodisulfate oxidations that are slow at room temperature have often been studied in the presence of a catalyst, especially silver(I) ion. The silver(I)-catalyzed oxidation of oxovanadium(IV) ion was investigated by Yost and Claussen.¹⁵ This reaction is first order in silver(I) ion, whereas the reaction rate is independent of the reductant concentration — in accord with most other silver(I)-catalyzed oxidations by peroxodisulfate.

Our aim was to elucidate the mechanism of the corresponding uncatalyzed reaction in weakly acidic aqueous solution. The overall oxidation-reduction reaction was found to follow the stoichiometry given by eqn. (3):



and can be expected to occur in a sequence of steps involving some reactive intermediate(s) from the thermal decomposition of peroxodisulfate ion.

EXPERIMENTAL

Chemicals. Solutions of oxovanadium(IV) sulfate (Merck) were converted to the perchlorate form by addition of a solution with the requisite amount of barium perchlorate, *p.a.* The resulting precipitate was filtered off. Ammonium peroxodisulfate, perchloric acid (Baker, 72 %) and other chemicals used were of analytical grade. Potassium hydrogenperoxomonosulfate was supplied as "Oxone" by duPont de Nemours. The laboratory-distilled water was redistilled twice in an all-silica apparatus.

Procedure. The vessels for the kinetic experiments were bottles of borosilicate glass kept in a paraffin-oil thermostat, generally at 40°C. To these vessels containing vanadium solution (usually 100.0 ml), a portion (usually 25.00 ml) of a thermostated peroxodisulfate solution was transferred, and the time $t=0$ was taken when the pipet was half-emptied. No change in results was observed when the ammonium peroxodisulfate was added as a solid at $t=0$. The reaction bottle also contained sodium perchlorate and perchloric acid to make the final perchlorate concentration 2.00 M. After suitable time intervals, samples were quickly withdrawn into ice-cooled flasks.

Analytical methods. For the determination of the *vanadium(V)* concentration, the absorbance of the samples was measured at the wavelength 350 nm (and occasionally at 340 nm) where the absorption of peroxodisulfate is insignificant and that of oxovanadium(IV) gives rise to a small correction term. The measurements were performed at 25°C with a Beckman model DU spectrophotometer or, in the latest measurements, a Zeiss PMQ II instrument. The internal cell length varied from 0.500 to 5.000 cm.

The vanadium(V) used for calibration was obtained by dissolving vanadium pentoxide in perchloric acid. The molar absorption coefficient for vanadium(V) in solutions of similar ionic strength and pH to the experimental solutions was $134.5 \text{ M}^{-1} \text{ cm}^{-1}$ at 350 nm and $201.0 \text{ M}^{-1} \text{ cm}^{-1}$ at 340 nm. The corresponding ϵ -values for oxovanadium(IV) were found to be $0.9 \text{ M}^{-1} \text{ cm}^{-1}$ and $2.1 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. No change in the absorbance of vanadium(V) was observed upon addition of oxovanadium(IV) to the vanadium(V) solutions (*cf.* Ref. 12).

For the determination of the *peroxodisulfate* concentration, 10.00 ml samples were used. After nitrogen had been bubbled through the sample for 10 min, an excess of standardized iron(II) solution was added, and after 20 min strong sulfuric acid was added to give a hydrogen ion concentration of 5 M.¹⁶ Then the excess of iron(II) could be back-titrated with cerium(IV) and ferroin indicator without interference from the vanadium, all of which was then present as vanadium(IV) after the reduction by iron(II). The cerium(IV) and the iron(II) solutions were standardized according to the oxalate method.¹⁷

As to samples containing both peroxodisulfate and peroxomonosulfate, the cerimetric titration gives the sum of the two species. The concentration of *peroxomonosulfate* was determined iodometrically as described by Palme.¹⁸

RESULTS

Rate of formation of vanadium(V). The appearance of vanadium(V) was followed spectrophotometrically at 350 nm with the initial concentration of vanadium(IV) ranging from *ca.* 0.5 mM to 5 mM. The peroxodisulfate was in large excess, 28–60 mM initially, during the reactions studied at 40.0°C and treated in Figs. 1–3.

As seen in Fig. 1, the initial reaction rate could easily be determined from the kinetic graphs. Such initial rates are plotted against the initial vanadium(IV) concentration in Fig. 2 for two different values of pH. The peroxodi-

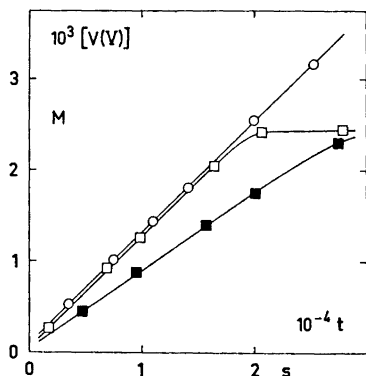


Fig. 1. Formation of vanadium(V) as a function of time at 40.0°C. The initial concentration of $S_2O_8^{2-}$ is 0.028 M. The different symbols refer to different concentrations of V(IV) according to Fig. 2. The hydrogen-ion concentration is 0.16 M (filled symbols) or 0.24 M (open symbols). The total concentration of $HClO_4$ and $NaClO_4$ is 2.00 M.

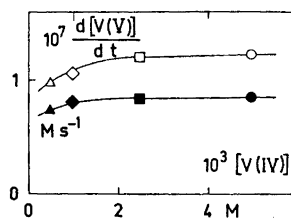


Fig. 2. Formation rate of vanadium(V) versus initial concentration of vanadium(IV) at 40.0°C and two different pH values. The composition of the solutions, see Fig. 1.

sulfate concentration is constant during this series of measurements. The rate of formation of vanadium(V) approaches a constant value at sufficiently high initial vanadium(IV) concentration (≥ 1.5 mM at the conditions valid here).

The results of Fig. 2 also indicate a first-order dependence on the hydrogen-ion concentration. This is verified by Fig. 3 which depicts measurements at two different peroxodisulfate concentrations and at high enough vanadium(IV) concentrations for the limiting rate to be reached. In addition, these measurements show that there might be a small contribution to the rate from an acid-independent reaction path, which is not appreciably larger than the experimental error.

The data of Fig. 3 also verify the expected first-order dependence with respect to peroxodisulfate.

Decomposition of peroxodisulfate ion. Stoichiometry. The decomposition of peroxodisulfate was studied by cerimetric titration. As long as the oxidation of vanadium(IV) to vanadium(V) is predominant, corresponding to the straight, sloping lines of Fig. 1, the amount of iron(II) consumed in the titration remains unchanged. This means that the peroxodisulfate disappearing is balanced by the vanadium(V) formed, so the redox reaction can be represented by eqn. (3) above.

Another indication that the stoichiometry is given by eqn. (3) was provided by a separate experiment, in which 9 mM vanadium(IV) was allowed to react with peroxodisulfate in various concentrations, 1, 2, 3, 4, and 20 mM, respectively. The final concentration of vanadium(V) was measured, and the ratio $\Delta[V^{2+}]/\Delta[S_2O_8^{2-}]$ was found to be 2.0 ± 0.1 .

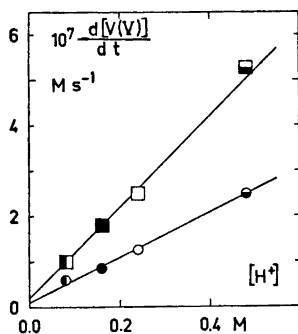


Fig. 3. Formation rate of vanadium(V) as a function of $[H^+]$ at $40.0^\circ C$. Initial concentrations are: $[S_2O_8^{2-}]_0 = 28$ mM, $[VO^{2+}]_0 = 4.9$ mM (lower graph) and $[S_2O_8^{2-}]_0 = 60$ mM, $[VO^{2+}]_0 = 1.2$ mM (upper graph), respectively.

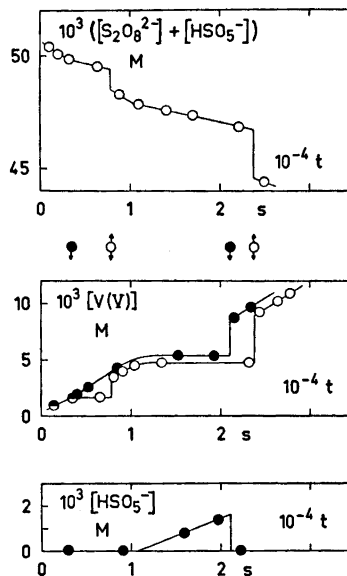


Fig. 4. Two experiments (open and filled circles, respectively) illustrating the formation of peroxomonosulfate, HSO_5^- . The arrows symbolize the addition of solid oxovanadium(IV) sulfate. The ionic medium is the same as in Figs. 1–3. $[H^+] = 0.30$ M. The temperature is $45.0^\circ C$ (*n.b.*, different from the preceding figures).

Samples withdrawn while the redox reaction is occurring, according to a 2:1 stoichiometry, consume no thiosulfate at all when titrated iodometrically as a test of peroxomonosulfate that might be present. But as soon as almost all oxovanadium(IV) has been oxidized, peroxomonosulfate appears in the sample, and its concentration increases linearly (see Fig. 4, graphs with filled circles). After a few hours, the rate of production of peroxomonosulfate is slowed down (not shown in the figure).

In the cerimetric method, giving the total concentration of peroxo species, the peroxomonosulfate shows up as a retardation in the decomposition rate immediately after the redox reaction is completed, as shown in Fig. 4 (graphs with open circles). *N.B.* The temperature referred to here is different from that of Figs. 1–3.

The period of retardation, before the rate increases again, became successively shorter as the initial concentration of vanadium(IV) was reduced to very small values. The addition of vanadium(V), instead of vanadium(IV), to the peroxodisulfate solution, however, led to a relatively long initial period of reduced rate for the disappearance of the peroxo ions determined together.

The role of peroxomonosulfate. Fig. 4 (open circles) shows the result of an experiment in which oxovanadium(IV), on two occasions, was added to a

solution of a composition typical of the period soon after the redox reaction seems to be over. At the moment of addition, an amount of vanadium(IV) corresponding to the amount of peroxomonosulfate present was oxidized to vanadium(V).

When peroxomonosulfate was added to a solution in which the redox reaction was taking place, *i.e.* at a time corresponding to, say, half-way up the sloping lines of Fig. 1, an amount of vanadium(IV) equivalent to the amount of peroxomonosulfate added was oxidized instantly. No peroxodisulfate was used up in that process.

In Figs. 1 and 4, the concentration of vanadium(V) is not zero at the time $t=0$. This is not caused by the vanadium(V) present initially, which was less than 1 % of the total vanadium, but by the fact that as soon as the peroxodisulfate is added to a thermostated solution of the desired acidity, some peroxomonosulfate appears in the solution. It amounts to less than 1 % of the peroxodisulfate present, but causes both a quick oxidation of some vanadium(IV) and, in solutions free of vanadium, a delay in the cerimetrically determined decomposition curve. Therefore, the first few minutes after mixing were not taken into account when numerical results were evaluated. This was no significant drawback, except during experiments with very low initial concentrations of vanadium(IV). However, it ruined an attempt to detect possible complex formation between the two reactants at 25°C by cation exchange and spectrophotometry performed at low concentrations of vanadium(IV).

The rate law of the redox reaction. At high enough concentrations of vanadium(IV) and hydrogen ions, the experimental rate law consists of a simple second-order expression plus a small hydrogen ion independent term.

$$\frac{d[V(V)]}{dt} = k_2[H^+][S_2O_8^{2-}] + k'[S_2O_8^{2-}] \quad (4)$$

The concentration symbols all denote the total concentration of the respective species. From this relation the rate constant k_2 was determined to be $(1.7 \pm 0.1) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at 40.0°C and an ionic medium of 2.00 M (H,Na)ClO₄.

At very low concentrations of vanadium(IV), the rate depends on that concentration. The nature of this dependence is more complicated than would be described by a simple factor of the type $[V(IV)]/(k + [V(IV)])$ in the rate law, and it was not further investigated because of the difficulties involved in measuring the rates at very low concentrations of oxovanadium(IV).

Although the results illustrated in Fig. 2 show no significant sign of a contribution to the rate from a direct reaction between the two reactants, an indication of such an additional term in the rate law was observed during some experiments, in which the hydrogen-ion concentration was twice that of Fig. 2 and the temperature was 50°C. The rate of disappearance of peroxodisulfate ion in the absence of vanadium was found to be slightly lower than the rate during the oxidation of vanadium(IV). Under the same conditions, the rate of formation of vanadium(V) increased somewhat as the initial concentration of vanadium(IV) was increased.

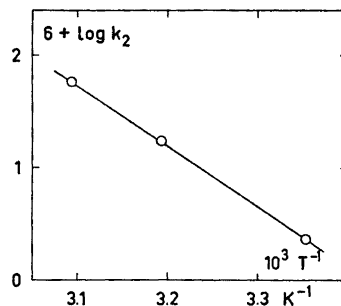


Fig. 5. Temperature dependence between 25°C and 50°C. The rate constant k_2 is defined by eqn. (4).

These observations suggest that eqn. (4) should be supplemented with an expression of the type $k''[\text{H}^+][\text{VO}^{2+}][\text{S}_2\text{O}_8^{2-}]$. But this marginal effect constitutes about 10 % of the main term in the rate law, at a vanadium(IV) concentration of 5 mM, *i.e.* only slightly outside the experimental errors. So it is impossible to tell the exact form of this additional term, particularly with regard to the pH dependence.

Effect of ionic strength and temperature. The value of the rate constant k_2 exhibits a marked dependence upon the ionic strength. This was decreased from 2.0 M to 0.5 M by the removal of sodium perchlorate at a fixed concentration of perchloric acid (0.5 M), and the effect was an increase in the rate by a factor of 1.6 at 40°C.

To determine activation data, measurements were made at three different temperatures, 25, 40, and 50°C. In Fig. 5, the logarithm of the rate constant k_2 has been plotted against $1/T$ (K^{-1}). The graph is linear within the limits of experimental errors. Accordingly, the rate constant conforms to the Arrhenius equation:

$$k_2 = A \exp(-E_a/RT) \quad (5)$$

The activation energy E_a obtained from the slope of the line is $102 \pm 3 \text{ kJ mol}^{-1}$. The value of the rate constant k_2 at 25.0°C and the same ionic medium as above was determined to $(2.4 \pm 0.1) \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$. At 50.0°C k_2 was found to be $(5.8 \pm 0.3) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$.

DISCUSSION

Dominant species. Under the conditions of these experiments, vanadium(IV) exists as VO^{2+} according to equilibrium measurements by Rossotti and Rossotti.¹⁹ Studies by the same authors show that the predominant species of vanadium(V) in these acidic solutions is the monomeric univalent cation VO_2^+ . In solutions where $[\text{H}^+] \leq 0.5 \text{ M}$, the peroxodisulfate occurs mainly as $\text{S}_2\text{O}_8^{2-}$; the acidity constant of HS_2O_8^- is reported to be $\geq 1 \text{ M}$.³

Type of mechanism. The oxidation of oxovanadium(IV) by peroxodisulfate ion proceeds at a relatively slow rate compared to the well-known peroxodisulfate oxidations that are first order with respect to both the metal ion

and the oxidant.¹ In contrast to the parallelism between electron transfer reactions of vanadium(IV) and iron(II) observed by Rosseinsky and Nicol,²¹ the kinetics of the reaction studied in the present paper do not resemble those of the oxidation of iron(II) by peroxodisulfate.¹ Nor has the experimental rate law much in common with that of the reaction between chromium(VI) and vanadium(IV).¹¹

The oxidation of vanadium(IV) by peroxodiphosphate¹² is much faster than the reaction dealt with in the present paper. The type of mechanism proposed, an inner-sphere mechanism with the transition state written as $VP_2O_8 \cdot xH_2O$, reveals kinetics that are quite different from those of the peroxodisulfate oxidation. On the other hand, vanadium(IV) is oxidized much more rapidly by peroxodisulfate than are cerium(III)^{5,7} and chromium(III),⁶ the oxidations of which are governed by the uncatalyzed decomposition of peroxodisulfate ion, *i.e.* the k_1 term of eqn. (1).

The rate of reaction in the present study is approximately the same as the decomposition rate for peroxodisulfate ion according to the k_H path. This fact, together with the hydrogen ion dependence (Fig. 3) and the zero-order behavior with respect to the reducing agent (Fig. 2), indicates that at the $[H^+]$ -values used an intermediate formed in the hydrogen-ion catalyzed decomposition of peroxodisulfate ion is responsible for the oxidation of vanadium(IV) to vanadium(V).

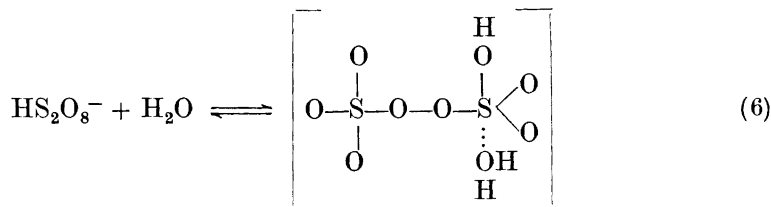
The influence of ionic strength is similar to the observations by Kolthoff and Miller for the k_H reaction path,³ so a reaction between the peroxodisulfate ion and an oxonium ion is likely to start the reaction sequence.

Activation parameters. The activation energy found is close to that reported by Kolthoff and Miller for the acid-catalyzed path of the peroxodisulfate decomposition.³ This gives further support to a mechanistic proposal based on this decomposition path.

The activation enthalpy is obtained by subtracting the term RT from E_a , the activation energy. This leads to: $\Delta H^\ddagger = 100 \pm 3 \text{ kJ mol}^{-1}$ at 25°C.

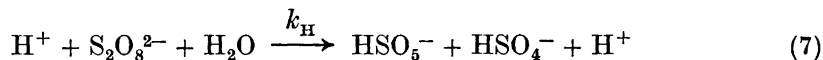
The activation entropy, finally, was calculated from transition state theory.²² The following value was found: $\Delta S^\ddagger = -17 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$ at 25°C.

The mechanism proposed. The activated complex probably consists of a peroxodisulfate ion together with a proton and a solvent molecule:

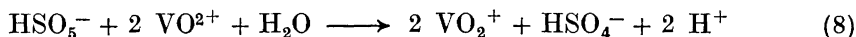


One of the products formed in the succeeding primary steps of the decomposition is then effective in the oxidation of vanadium(IV). The nature of this reactive species has been the subject of some speculation. Kolthoff and Miller³ suggested SO_4 , and Yablonsky²³ proposed a 5-coordinated hydrated form of this molecule. We shall, as earlier,⁶ follow the proposal of Wilmarth and

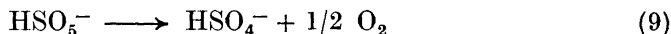
Haim,¹ eqn. (7), involving the breaking of an O-S bond, on the right-hand side of eqn. (6):



The steps subsequent to reaction (7) involve a rapid oxidation of two oxovanadium(IV) ions by each HSO_5^- ion formed. These elementary steps can be summarized by the following expression:



The intermediate, HSO_5^- , is the hydrogenperoxomonosulfate ion, the corresponding base to "Caro's acid". This ion is known to form from peroxodisulfate at high acidities, $[\text{H}^+] \geq 2 \text{ M}$.³ At lower concentrations of hydrogen ion than about 0.5 M, and in the absence of a reducing agent, the peroxomonosulfate formed is reported to decompose rapidly to hydrogensulfate and oxygen gas:



In the present investigation, no peroxomonosulfate was detected in solutions free from vanadium, apart from the small amount that forms during the first few minutes after mixing and then remains in the solution, until an oxidizable species, like oxovanadium(IV), is added. When enough vanadium(IV) is present, any peroxomonosulfate formed is instantly reduced according to eqn. (8).

A comparison between this mechanism and the experimental results implies that the experimentally determined rate constant, k_2 , is equal to $2 k_{\text{H}}$. It was experimentally verified that the rate of decomposition of peroxodisulfate, in the absence of vanadium, is in accord with this conclusion, apart from a small deviation that could be accounted for by an additional term in the rate law (see above and below). The value of k_{H} at 50°C was found to be $(2.9 \pm 0.1) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. This is in good agreement with the results of Kolthoff and Miller,³ who reported this rate constant in a medium of 0.1 M perchloric acid to be $8.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, corresponding to a value of about $3.0 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at an ionic strength of 2.0 M.

Formation of peroxomonosulfate. During a certain period just after the redox reaction is essentially completed, the rate of disappearance of peroxo species (di- and monosulfate together) is reduced to about one third the rate during the redox reaction. At the same time, the rate of formation of peroxomonosulfate is two thirds the rate of decomposition during the redox reaction (Fig. 4). Thus, during this period of time, the peroxodisulfate decomposes at the original rate, while the peroxomonosulfate cannot decompose normally according to eqn. (9).

Tsao and Wilmarth²⁴ suggested that the radicals formed in the uncatalyzed decomposition of peroxodisulfate, SO_4^- and OH , play a catalytic role in the decomposition of the hydrogenperoxomonosulfate ion. During the latter stages of the redox reaction between peroxodisulfate and oxovanadium(IV), when the rate of reaction (8) has become very low, the small amounts of vanadium(IV) still present seem to be able to scavenge effectively radicals

needed for the normal decomposition of the peroxomonosulfate formed. This proposal is substantiated by the observation that when the initial concentration of oxovanadium(IV) is decreased to very small values, the period of relatively rapid formation of peroxomonosulfate is decreased accordingly. The fact that this period is pronounced in a solution of peroxodisulfate to which vanadium(V) has been added, shows that such a solution contains minute amounts of vanadium in a lower oxidation state than V.

Reaction paths of minor importance. The experimental results imply that species from the pH-independent decomposition path also participate in the oxidation of vanadium(IV). This might be expected, since the radicals formed according to eqn. (2) are very reactive. The contribution from the k_1 path should involve the oxidation of two oxovanadium(IV) ions for each peroxodisulfate ion decomposed according to eqn. (2), *i.e.* the constant k' of eqn. (4) should be equal to $2k_1$.

The rate constant k_1 was determined by Kolthoff and Miller to be $1.0 \times 10^{-6} \text{ s}^{-1}$ at 50°C , independent of ionic strength.³ From the activation energy given by Kolthoff and Miller, we find that the value of this rate constant at 40°C is $2.0 \times 10^{-7} \text{ s}^{-1}$. Therefore, the calculated contribution to the rate of formation of vanadium(V) is $4.0 \times 10^{-7} \times [\text{S}_2\text{O}_8^{2-}] \text{ M s}^{-1}$, which is consistent with the intercepts on the rate axis of Fig. 3, within experimental errors.

As mentioned above there is also an indication of a contribution from a reaction that is first order in each of the two reactants. The rate constant of the direct reaction between oxovanadium(IV) and peroxodisulfate is, however, several powers of ten lower than that of the oxidation of iron(II) by the peroxodisulfate ion.

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