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A Kinetic and Isotope Study of the Mechanism of Decomposition of the Tetraperoxochromate(V) Ion in Basic Solution

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The decomposition of K_3CrO_8 in aqueous alkaline solution has been reinvestigated. Over the pH range from 8.0 to 11.2, the rate is first-order each in tetraperoxochromate ion and hydrogen ion concentrations. No evidence was found for any rate effect due to carbonate or phosphate buffer. Inhibition by H_2O_2, NH_3 and by ethylenediamine occurs; the nature of these rate retardations was studied. Isotope labelling of the peroxide oxygen atoms showed that all of the oxygen atoms in product O_2 originated as peroxide oxygens in the anions, and that a small but real amount of scrambling occurs. The marked complexities which obtain in this systems are discussed in terms of the kinetic and isotope data.

Introduction

The decomposition of peroxides in aqueous solution to give O_2 has attracted the attention of chemists for a great many years. Recently these systems have been the subject of renewed interest, particularly the decomposition of peroxoacids[1] and the metal- and enzyme-catalyzed decomposition of H_2O_2.[2]

To date, however, little quantitative work has been carried out on the decomposition of transition metal peroxocompounds.[3] Their decompositions can be complicated since they often contain several peroxo groups per transition metal atom. Also there is the possibility that the metal atom can be involved in redox reactions which may parallel or be an integral part of the decomposition mechanism, and there are many related rapid equilibria involving the peroxo groups.[4]

Many of the transition metals form tetraperoxoanions of the type $[M^{(n)}(O_2)_4]^{8-n}$. These include VO_8^{3-}, NbO_8^{3-}, TaO_8^{3-}, CrO_8^{3-}, MoO_8^{2-} and WO_8^{2-}, the best known being the tetraperoxochromate ion, CrO_8^{3-}. The potassium salt of this ion is stable at room temperature. The structure of the anion, which has four peroxo groups attached in a tetrahedral array about the chromium and which has eight equivalent chromium-oxygen distances, has been established[5] by X-Ray diffraction. A requirement of this structure is that an odd number of electrons must be present. The presence of one unpaired electron has been demonstrated by magnetic measurements,[6] which suggests a +5 oxidation state for the central atom. This is somewhat unusual for chromium; the tetraperoxochromate (V) ion therefore exhibits some interesting structural and chemical properties.

The decomposition of the ion in basic solution has been shown to occur according to the following equation:[7]

$$4CrO_8^{3-} + 2H_2O = 4CrO_4^{2-} + 7O_2 + 4OH^-$$

Since we shall be concerned with the rate and stoichiometric dependence on H^+, it is convenient to write this equation in the form:

$$4CrO_8^{3-} + 4H^+ = 4CrO_4^{2-} + 7O_2 + 2H_2O$$

Decomposition therefore involves simultaneous decomposition of peroxo groups and oxidation of chromium(V) to chromium(VI). Below pH 8, decomposition can occur by the above reaction but, in addition, it is reported[8] and observed here to occur partially according to the equation:

$$2CrO_8^{3-} + 12H^+ = 2Cr^{3+} + 6H_2O + 5O_2$$

Both of these pathways lead to fast decomposition in acid solution which would require special techniques (since O_2 is formed) for adequate study. The present work has also been confined to basic solution in order to avoid the change in mechanism which would follow the change in stoichiometry.

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(8) G. A. Bogdanov, *Zh. Fiz. Khim., 25,* 61 (1951).

The mechanism of decomposition in basic solution has been studied by Bogdanov[8] and by Quane and Earley.[9] The reaction was shown to be first-order in CrO_8^{3-}, and Quane and Earley obtained data for the rate dependence on pH which led them to postulate a mechanism involving unimolecular decomposition of a protonated tetraperoxochromate(V) ion:

$$H^+ + CrO_8^{3-} \overset{K_a}{\rightleftarrows} HCrO_8^{2-} \overset{k_1}{\rightarrow} \text{products}$$

Although this mechanism can explain the overall kinetics, such a simple scheme cannot completely describe the system with its complex stoichiometry. It is clear that a number of elementary steps and also a number of intermediate molecules must follow the rate-determining step. Some of the mechanistic requirements for this type of situation have been discussed.[10]

Experimental Section

Potassium tetraperoxochromate was prepared by treating CrO_3 with 30% H_2O_2 in the presence of concentrated KOH according to the method of Brauer.[11]

Decomposition reactions were carried out in phosphate, carbonate and ammonia buffers containing sufficient $NaClO_4$ to maintain the ionic strength constant at 0.2 *M*. Buffer components were of analytical reagent grade and were dissolved in H_2O which had been passed through a deionizing exchange unit after normal distillation. Sodium hydroxide solutions, used for stock K_3CrO_8 solutions, were purified following the method of Duke and Haas,[12] with the modification used by Koubek, *et al.*[1b] The rate of decomposition in purified NaOH, however, was found to be the same as that in alkali which had not been purified; also addition of small quantities of ethylenediaminetetraacetic acid (EDTA) did not affect the reaction rate. It was therefore concluded that the reaction was not catalyzed by trace metals, and unpurified NaOH was used thereafter. High purity 30% H_2O_2 was supplied by FMC Corp.

Spectrophotometric measurements were made with a Beckmann DU spectrophotometer. Reactions were carried out in 100-ml volumetric flasks, immersed in an ice bath at 0°. A number of reactions were started independently, but under identical conditions, by using a syringe to inject 1.0 ml of a stock solution of K_3CrO_8 directly into 50 ml of the appropriate buffer solution at 0°. The stock solutions were freshly made up by rapidly dissolving *ca.* 0.1 g K_3CrO_8 in 30 ml 0.1 *M* NaOH previously chilled to 0°. The buffer capacity was sufficiently great to overcome any effect due to added alkali. Individual reactions were stopped by quenching with a solution 0.1 *M* in NaOH and 1 *M* in $NaClO_4$. This quenching solution caused a large increase in both pH and ionic strength, both effects serving to slow down the reaction. The volume of the quenched solutions was made up to 100 ml and accurate spectrophotometric measurements made at leisure. The absorbance was measured at 372 mμ, where CrO_4^{2-} has maximal absorption with a molar absorptivity of 4.8×10^3. At 372 mμ, the molar absorptivity of CrO_8^{3-} is 1.6×10^3, *i.e.* about one-third that of CrO_4^{2-}. This technique avoided errors due to bubbling in the sample cuvette, was capable of accurate time measurements in the faster reactions and ensured that absorbance measurements were always made under the same pH conditions. pH measurements were made on a Leeds and Northrup Model 7401 meter and were, in general, precise to ±0.02 pH units.

A gas volumetric technique was used to verify the stoichiometric equation in terms of the amount of O_2 produced. The apparatus was calibrated by measuring the volume increase due to complete decomposition of a known quantity of H_2O_2 by means of a catalytic amount of MnO_2

Kinetic runs involving reactants containing small quantities of NH_3, H_2O_2, ethylenediamine, acetone, 2-propanol, N_2H_4 and EDTA were carried out as above, using carbonate buffer. The amounts of these additives were sufficiently small so that neither the pH nor the ionic strength was affected.

Attempts were made to use the gas volumetric apparatus to measure the volume of O_2 evolved when either NH_3 or H_2O_2 was present. However, this proved impossible because of a high ammonia gas pressure in the one case and evolved O_2 due to chromate-catalyzed decomposition of H_2O_2 in the other.

Double-labeled H_2O_2 was prepared from 97.8% oxygen-18-labeled water (supplied by Yeda Co,. Ltd.) using the electrical discharge method.[13] The material obtained from the discharge was diluted with 30% H_2O_2, such that the final mixture contained about 6% of the peroxo groups doubly labeled. The isotopic characteristics of the peroxide in this solution were determined by oxidizing it with ceric ion in acid solution and carrying out a mass analysis on the resulting oxygen gas, *i.e.*

$$2Ce^{4+} + H_2O_2 = 2Ce^{3+} + O_2 + 2H^+$$

This reaction proceeds without rupture of the peroxide bond,[14,2c] so that the product O_2 has the same isotopic characteristics as the peroxide. In general it was possible to prepare H_2O_2 containing more than 92% of the oxygen-18 in doubly-labeled peroxo groups. The labeled tetraperoxochromate was prepared as described above using doubly-labeled H_2O_2. Labeled water containing approximately 5% oxygen-18, was available commercially from Yeda Co., Ldt.

Isotopic analyses were made on both product O_2 and product CrO_4^{2-} as follows. For the preliminary experiments a glass bulb with a side arm into which K_3CrO_8 could be weighed was constructed to allow reaction of the solid with water under vacuum. All solutions were thoroughly degassed and the pressure taken down to that of water vapor before allowing

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the solid to come into contact with the water. Dissolution was rapidly attained by vigorous magnetic stirring, and samples of the product O_2 taken for mass analysis. When the decomposition was complete, the product CrO_4^{2-} was precipitated with $BaCl_2$ and the precipitate filtered and dried at 120°C. The $BaCrO_4$ was transferred to a quartz vessel and strongly heated with an oxygen flame, when the O_2 evolved was collected for mass analysis. All other experiments were carried out in carbonate buffer with a freshly prepared solution of double labeled K_3CrO_8 in 0.1 *M* NaOH, once again using a glass bulb with a side arm to assure complete degassing before mixing.

Results

Decomposition Rate. Gas volumetric measurements showed that 1.76 moles of O_2 were evolved per mole of CrO_8^{3-} decomposed. Also, it was found spectrophotometrically that 0.98 moles of CrO_4^{2-} were produced for every mole of CrO_8^{3-} decomposed. The stoichiometry of decomposition was thereby confirmed.

For the kinetic data the reactions were usually followed for at least two half lives.

The first-order dependence of the reaction on $[CrO_8^{3-}]$ was confirmed by the linearity of the plots of $2.3\log(A_\infty - A_t)$ against time, where A is the absorbance at 372 $\mathrm{m\mu}$. All first-order rate constants were determined from the slopes of such plots. At fixed pH the rate is therefore

$$-\frac{d[CrO_8^{3-}]}{dt} = k'[CrO_8^{3-}]$$

where k' is a pseudo-first-order rate constant.

Table I. Dependence of Observed k′ Value on pH [a]

pH	Buffer	k′(min^{-1}×10^3)
8.07	Carbonate	132.40
8.07	Phosphate	2700 [b]
8.71	Phosphate	436
9.10	Carbonate	168
9.30	Carbonate	92.0
9.60	Carbonate	51.2
10.02	Carbonate	20.2
10.39	Carbonate	8.40
10.84	Carbonate	2.58
11.20	Carbonate	1.17
8.70	Ammonia	132
9.30	Ammonia	33.2
9.62	Ammonia	18.8
9.80	Ammonia	13.2
10.40	Ammonia	4.4

[a] At 0° and ionic strength = 0.2 *M*. [b] Owing to the very fast rate at pH 8, this value is subject to considerable error.

The hydrogen-ion dependence of the decomposition rate in the pH range 8.0 to 11.2 is shown in Table I, for the buffer systems carbonate, phosphate and ammonia. This is plotted on a log-log scale in Figure 1. It is apparent from this graph that in carbonate and phosphate buffers the same linear relationship between log k' and pH holds. This dependence somewhat differs from that reported by Quane and Earley whose data suggested curvature in this pH range. The slope of the line in Figure 2 representing the relation for both phosphate and carbonate buffers is 1.03, showing that the decomposition is first-order in $[H^+]$ in this pH range. Therefore,

$$k' = k[H^+]$$

where k is a second-order rate constant, and the rate law becomes

$$-\frac{d[CrO_8^{3-}]}{dt} = k[H^+][CrO_8^{3-}]$$

The mean value of k calculated from this data is $2.10 \times 10^8\ M^{-1}\ \mathrm{min}^{-1}$ at 0°. Using the same rate law, Quane and Earley obtained a value of $k = 1.25 \times 10^8\ M^{-1}$ at 30°C in 3.0 *M* $NaClO_4$. This is in general

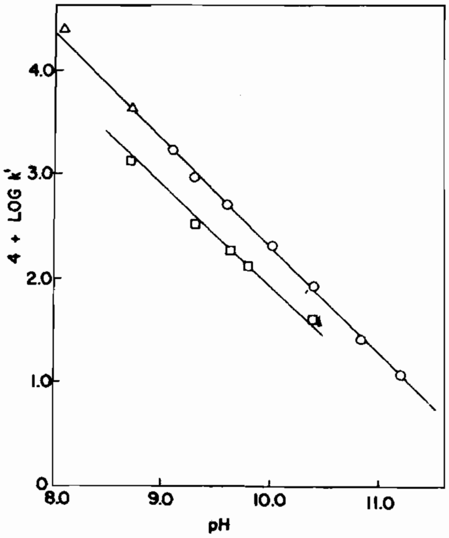

Figure 1 . Decomposition of tetraperoxychromate(V) ion in various buffer solutions at 0°. Effect of pH on rate (all solutions 0.2 *M* total ionic strength): Δ, phosphate buffer; ○, carbonate buffer; □, ammonia buffer.

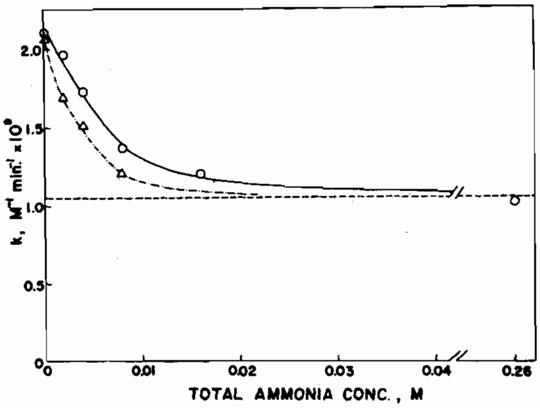

Figure 2. Decomposition of tetraperoxychromate(V) ion in ammonia buffer at 0°. Effect of total ammonia concentration on rate (all solutions 0.2 *M* total ionic strength, pH 10.40): ○, $[CrO_8^{3-}]_0 = 1.47 \times 10^{-4}\ M$; Δ, $[CrO_8^{3-}]_0 = 0.83 \times 10^{-4}\ M$.

agreement with our value, considering the differences in temperature and ionic strength and the use of glass electrodes to measure [H^+].

The activation energy for the decomposition was determined to be 20 kcal/mole.

Effect of NH_3 on Decomposition Rate. A remarkable feature of Figure 1 is that the points obtained for ammonia buffers lie on a straight line, but one which is almost parallel to and displaced downward from that corresponding to phosphate and carbonate buffers. In the presence of ammonia, decomposition still involves complete conversion of CrO_8^{3-} to CrO_4^{2-}. The amount of oxygen evolved under these conditions could not be readily checked, however, since the ammonia gas is in large excess over oxygen pressure. The value of k calculated from these points is $9.0\times10^7\,M^{-1}$ min^{-1}, *i.e.* approximately one-half that for phosphate and carbonate buffers. Quane and Earley have demonstrated similar rates in reactions in carbonate buffers and in unbuffered solutions. We assume, therefore, that the relative displacement of the lines in Figure 1 is due to inhibition by NH_3 and not to carbonate or phosphate catalysis. This inhibition by NH_3 is also shown in Figure 2, which shows the effects of addition of increasing amounts of NH_3 on the value of k. These additions were sufficiently small so that neither pH nor ionic strength were changed appreciably. It is clear from Table I, Figure 1 and Figure 2, that the value of k is about half its normal value when the ammonia concentration is greater than 0.02 M. This inhibition appears to be a specific action of NH_3 and could not be due to a medium effect. Figure 2 also shows that the magnitude of the inhibition is dependent on initial tetraperoxochromate concentration, and thereby suggests some competition between NH_3 and CrO_8^{3-} in the reaction sequence.

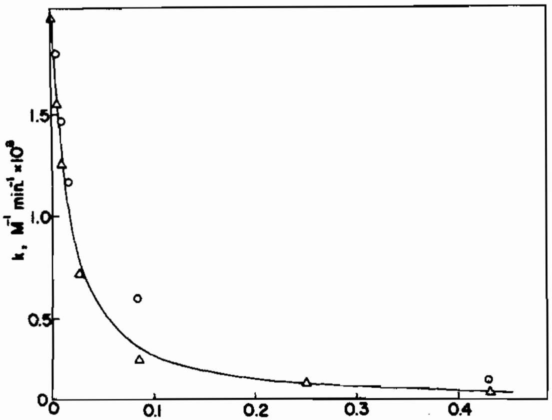

Figure 3. Decomposition of tetraperoxychromate(V) ion in carbonate buffer at 0°. Effect of hydrogen peroxide addition (total ionic strength 0.2 M): ○, pH 10.40; △, pH 9.40.

Effect of H_2O_2 on Decomposition Rate. Figure 3 shows the effect of H_2O_2 on the rate constant k. The data shown are for pH values of 10.40 and 9.40. It is clear that peroxide strongly inhibits the decomposition but in a different fashion than does NH_3. In this case the rate of loss of CrO_8^{3-} approaches zero at high H_2O_2 concentration. Figure 3 also demonstrates that the inhibition is virtually independent of pH. The effect of initial tetraperoxochromate concentration on peroxide inhibition is shown in Figure 4. It is seen that this inhibition is not a function of initial tetraperoxochromate concentration and therefore the inhibition appears to involve no competition between H_2O_2 and CrO_8^{3-} for an intermediate. Additional experiments showed that the mixing of H_2O_2 and CrO_4^{2-} under the same conditions as those of the tetraperoxochromate decomposition produced no detectable amount of CrO_8^{3-}. Evidently, therefore, the effect of H_2O_2 is not merely to cause the regeneration of CrO_8^{3-} from the CrO_4^{2-} formed by the decomposition.

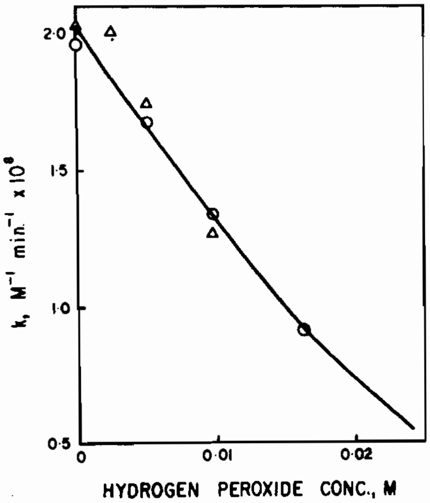

Figure 4. Decomposition of tetraperoxychromate(V) ion in carbonate buffer at 0°. Effect of hydrogen peroxide addition (total ionic strength 0.2 M); △, $[CrO_8^{3-}]_0 = 1.95\times10^{-4}\,M$, ○, $[CrO_8^{3-}]_0 = 0.67\times10^{-4}\,M$, pH = 10.40.

Effect of other Additives. The addition of 2-propanol or acetone had no effect on the decomposition rate. The effect of hydrazine (or EDTA in significant quantity) was to cause a reduction of chromium to Cr(III) and therefore to change the stoichiometry completely. We examined the reaction of N_2H_4 and CrO_8^{3-} in some detail and observed second-order kinetics, *i.e.*,

$$\frac{d[Cr(III)]}{dt} = k_H[N_2H_4][CrO_8^{3-}]$$

This reaction even at low concentrations of N_2H_4 is faster than the tetraperoxochromate decomposition showing that it is a direct redox process rather than an interaction between N_2H_4 and some decomposition intermediate.

The results obtained with ethylenediamine as an additive were interesting. With small amounts, the decomposition rate dropped markedly; further addition however reversed the trend and the rate increased. The lowest rate corresponds to about 60% of the rate in the absence of inhibitor, which fact suggests that the action of ethylenediamine may be related to that of NH_3.

Isotope Distribution. From ^{18}O tracer work with double-labeled H_2O_2 it is possible to detect whether the product O_2 was formed from one peroxo group without O–O bond cleavage, or whether each oxygen atom in the O_2 came from a different peroxide group, the latter case being designated scrambling.[15] The percentage scrambling of the product O_2 is given in Table II. The scrambling is calculated on the basis that for every peroxo–^{18}O–^{18}O bond broken, two oxygen ^{16}O–^{18}O molecules are formed. These results show an average of about 9% scrambling with a slight pH dependency. The low scrambling percentage indicates that, for the most part, molecular oxygen is formed without rupture of peroxide bonds.

Table II. Results on Scrambling in Product Oxygen

pH	Added Ammonia, *M*	% Scrambling
[a]	None	8.0
[a]	None	10.0
10.1	None	8.8
8.9	None	10.5
[a]	<0.04	5
10.1	0.05	1.3
10.1 [b]	0.04	1.3

[a] Preliminary experiments, unbuffered and therefore alkaline. All other runs buffered with carbonate buffer. [b] Also 0.04 *M* in NaCl.

Table III. Analysis of Oxygen from Tetraperoxochromate[a] in Presence of H_2O_2 [b] [c]

Time (mins)	$^{18}O/^{16}O$ in product oxygen	$^{18}O/^{16}O$ in product chromate
1	0.043	—
5	0.043	—
9	0.044	—
14	0.044	—
23	0.044	—
	—	0.027

[a] 0.07 g K_3CrO_8. [b] 0.2 ml of 4.0 M H_2O_2 with $^{18}O/^{16}O$ = 0.104. [c] Ambient temperature.

Since the scrambling could have occurred in one step of the chain sequence, it was of interest to investigate the effect of NH_3 on the scrambling figure. In several experiments with small amounts of added NH_3, the percentage scrambling observed was significantly lower than in the uninhibited case.

Mass analysis of the oxygen in product chromate showed that approximately one-third is derived from solvent H_2O and the remaining two-thirds retained from CrO_8^{3-}. Using double-labeled K_3CrO_8 having an initial $^{18}O/^{16}O$ ratio of 0.039 in unlabeled water gave product chromate with an $^{18}O/^{16}O$ ratio of 0.025. Unlabeled K_3CrO_8 in labeled water having an initial $^{18}O/^{16}O$ ratio of 0.058 gave product chromate with an $^{18}O/^{16}O$ ratio of 0.019. The results agree well with each other giving a 2:1 ratio for the source of the oxygen in the product chromate. Thte conditions were such that no exchange of oxygen atoms with water was expected.

Table III shows the $^{18}O/^{16}O$ values in O_2 evolved from decomposition of CrO_8^{3-} in the presence of double-labeled H_2O_2. Under the conditions used, chromate catalysis of H_2O_2 decomposition is not significant. It is clear that a constant $^{18}O/^{16}O$ value is established in the first minute, *i.e.*, before decomposition has proceeded significantly. The value of $^{18}O/^{16}O$ obtained by assuming complete exchange between all peroxide groups (four groups per tetraperoxo-chromate ion and one group per H_2O_2 molecule) is approximately 0.046 as compared to the measured constant value of 0.044. These results demonstrate the existence of an exchange of peroxo groups between H_2O_2 and CrO_8^{3-}. This exchange must be rapid since it is complete before appreciable decomposition of CrO_8^{3-} takes place. We are presently investigating the exchange reaction in more detail and the results will be reported elsewhere.

Discussion

The decomposition of the tetraperoxochromate ion has been shown here to be a much more complicated reaction than that indicated by its rate law. This is not surprising when we take into consideration that we are dealing with a chromium atom in an intermediate oxidation state, bonded with four peroxo-groups, and also the stoichiometry (please note the magnitudes of the coefficients) of the reaction.

The general mechanism proposed here will be consistent with the following experimental observations:

1) The rate law, which is first-order each in $[CrO_8^{3-}]$ and in $[H^+]$.

2) The stoichiometry, which is complicated and which has high values for the stoichiometric numbers (*e.g.*, seven moles of O_2 are produced from four moles of CrO_8^{3-}).

3) The rate inhibition by ammonia, which is observable at low $[NH_3]$, which cuts the overall rate of reaction down by a limiting factor of 2, and which involves a step wherein NH_3 and CrO_8^{3-} apparently compete for an intermediate.

(4) The rate inhibition by hydrogen peroxide, which is observable at low $[H_2O_2]$, which effectively cuts the rate down to a negligible value, and which seems to be independent of pH and initial $[CrO_8^{3-}]$.

5) The results of isotope tagging, which show that the oxygen atoms in product O_2 are derived from the peroxide oxygen atoms in the reactant, and which show that the oxygen atoms in the product CrO_4^{2-} are derived partly from peroxidic oxygen atoms of the reactant and partially from the oxygen atoms of solvent water.

6) The double-isotope-label data, which indicate that about 9% of the O_2 molecules are scrambled during decomposition in the absence of NH_3, and

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[15] J. O. Edwards and P. D. Fleischauer, *Inorg. Chim. Acta - Reviews*, 2, 53 (1968).

that less scrambling occurs during decomposition when NH_3 is present.

The rapid peroxide group exchange may be important to the decomposition mechanism, however it is not necessarily involved.

The mechanism must involve a sequence of steps. We shall make the reasonable assumption that none of these steps will have a molecularity greater than three. Further it seems unlikely that more than one O_2 molecule is evolved in any one step. It is then seen that there are at least seven steps in the sequence. Further, the simplicity of the rate law indicates that most of these steps follow the rate-determining step. In such case, there must be a number of intermediates after the rate-determining step. These intermediates are designated as A, B and C in the mechanism, as none of them has so far been identified. It is possible to imagine a number of different species for each intermediate, any or all of which could exist, and ultimately give the same overall results.

Of the variety of possible mechanisms, one that fits the results well will be proposed here. This is

$$H_2O + CrO_8^{3-} \rightleftharpoons Cr(O_2)_3O^{3-} + H_2O_2 \qquad (I)$$

$$Cr(O_2)_3O^{3-} + H^+ \rightleftharpoons HCr(O_2)_3O^{2-} \qquad (II)$$

$$HCr(O_2)_3O^{2-} \xrightarrow{k_r} A + O_2 (+\text{ Other Products}) \qquad (III)$$

$$A + Cr(O_2)_4^{3-} \longrightarrow B + O_2 (+\text{ Other Products}) \qquad (IV)$$

$$B + Cr(O_2)_4^{3-} \longrightarrow C + O_2 (+\text{ Other Products}) \qquad (V)$$

where $Cr(O_2)_3O^{3-}$, $HCr(O_2)_3O^{2-}$, A and B are intermediates and where C reacts in such a way as to ultimately involve one or more CrO_8^{3-}, three more H^+ and to yield the other CrO_4^{2-} and O_2 product molecules. As required by the rate law, the transition state (in the proposed rate-determining step (III)) has one chromium atom, one hydrogen atom, a charge of –2, plus other oxygen atoms.

The inhibition by hydrogen peroxide is explained by means of the first step, which is postulated to be the replacement of a peroxide ion by an oxide ion in the chromium coordination sphere.

Not only is this step an important part of the mechanism, but this step provides a natural explanation for the observation of rapid peroxo group exchange between CrO_8^{3-} and H_2O_2. Further, the species which is postulated to undergo significant decomposition is the triperoxochromium species $HCr(O_2)_3O^{2-}$; this is in good accord with the results of Haggett[2d,16] who found it necessary to postulate that a triperoxochromium species was an active intermediate in the chromate-catalyzed decomposition of H_2O_2 in solutions of low alkalinity. At higher concentrations, he[16] observed that the decomposition rate was slower and this was relatable to the formation of the more stable tetraperoxochromate species.

The rapid exchange of peroxo groups indicates that step (I) is a rapid equilibrium; the known rapid rates of proton transfer and the lack of general acid catalysis indicates that step (II) is a rapid equilibrium. The rate of decomposition is then established by step (III) for which one can write the rate law

$$\frac{d[CrO_4^{2-}]}{dt} = 4k_r[HCr(O_2)_3O^{2-}] \qquad (1)$$

where the factor 4 is introduced to take into account the fact that four CrO_8^{3-} are used up and four CrO_4^{2-} are formed as a stoichiometric consequence of each reactive act. Using the law of mass conservation for peroxochromates, we have

$$[CrO_8^{3-}]_T = [CrO_8^{3-}] + [Cr(O_2)_3O^{3-}] + [HCr(O_2)_3O^{2-}] \qquad (2)$$

where T represents the total (*i.e.*, analytical) peroxochromate. By substitution into (2) of the appropriate equilibrium constant expressions for K_I and K_{II}, the equation

$$[CrO_8^{3-}]_T = [HCr(O_2)_3O^{2-}]\left\{\frac{[H_2O_2]}{K_IK_{II}[H^+]} + \frac{1}{K_{II}[H^+]} + 1\right\} \qquad (3)$$

is obtained. Substitution of (3) into (1) gives

$$\frac{d[CrO_4^{2-}]}{dt} = 4k_r[CrO_8^{3-}]_T\left\{\frac{K_IK_{II}[H^+]}{[H_2O_2] + K_I + K_IK_{II}[H^+]}\right\} \qquad (4)$$

Assuming that the third term in the denominator is negligible, the rate expression

$$\frac{d[CrO_4^{2-}]}{dt} = 4k_r[CrO_8^{3-}]_T[H^+]\left\{\frac{K_IK_{II}}{[H_2O_2] + K_I}\right\}$$

is obtained. This is the form demanded by the observed kinetics and by the behavior of the peroxide inhibition, and the value of K_I is calculated from the intercept on Figure 5 to be 0.013 *M*.

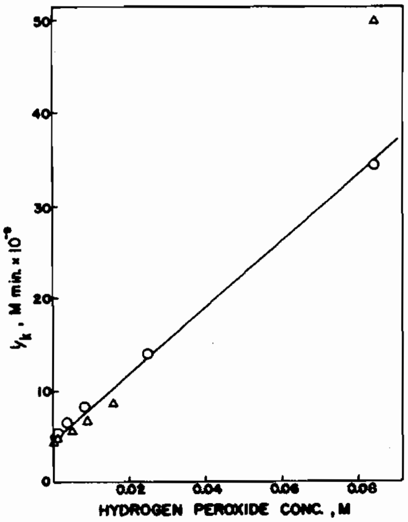

Figure 5. Decomposition of tetraperoxychromate(V) ion in carbonate buffer at 0°. Reciprocal of rate constant. *k* as a function of $[H_2O_2]$.

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(16) M. L. Haggett, Ph.D. thesis, King's College, Newcastle upon Tyne, England, August 1961.

The inhibition by NH_3 is quite different. The limiting decrease in rate by a factor of two strongly suggests that the ammonia changes the sequence of steps after the rate step. The kinetic consequence of this type of inhibition is that the number four in equation (1) is changed to 1, 2 or 3 depending on where and how the NH_3 reacts. The simplest way of writing such a mechanism is to postulate that the NH_3 reacts with an intermediate present in the sequence after the second CrO_8^{3-} ion has participated. In our mechanism then, this intermediate would be B and the inhibition step can be written as

$$B+NH_3 \longrightarrow CrO_4^{2-}+O_2\,(+\text{ Other Products}) \qquad \text{(VI)}$$

It can thus be seen that steps (V) and (VI) are competitive with B reacting with CrO_8^{3-} and NH_3 respectively. This competition is clearly seen in Figure 2. The rate of reaction in the presence of NH_3 can be put into equation form as

$$\frac{d[CrO_4^{2-}]}{dt} = \left\{ 2+2\,\frac{k_5[CrO_8^{3-}]}{k_5[CrO_8^{3-}]+k_6[NH_3]} \right\}$$
$$\frac{k_r K_I K_{II}[CrO_8^{3-}][H^+]}{[H_2O_2]+K_I}$$

The entry of the oxygen isotope into CrO_4^{2-} from water is a further consequence of the first step of the mechanism. Under conditions of our experiments, no significant exchange of oxygen atoms between CrO_4^{2-} and water is expected, thus the isotope must have entered the chromate coordination sphere during the decomposition sequence.

The results of the double-labeling experiments show that oxygen-oxygen bond integrity is maintained for the most part during decomposition. An interesting aspect of the double-label study is the observation that much of the scrambling is eliminated by the NH_3 inhibition. This means that the bulk of the scrambling occurs in step V or some later step.

A feasible intermediate could be that reached when the decomposition is at the stage where two peroxo-groups remain associated with the chromium center. Work now being carried out in this laboratory on the decomposition of triamminediperoxochromium(IV) does not substantiate this possibility. The decomposition of $(NH_3)_3Cr(O_2)_2$ in solutions of low alkalinity leads to different products to those formed from CrO_8^{3-} under the same conditions, and is a slower reaction.

The present mechanism is incomplete; this is largely due to the fact that much more evidence as to the number and nature of the intermediates and steps would be required for completion. The formulation of the constitution of the intermediates (such as A, B etc.) which are formed in the reaction sequence is a difficult process which is not possible with the available data. Further study of inhibitors might prove fruitful.

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