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A Double Isotope (^{18}O) Kinetic Study of Peroxide Group Exchange between the Tetraperoxochromate Ion and Hydrogen Peroxide in Basic Solution

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A ^{18}O labelling technique has been used to demonstrate reversible exchange of peroxide groups between H_2O_2 and the tetraperoxochromate(V) ion. The results also show that this exchange proceeds without scrambling of oxygen atoms, i.e. *the integrity of the exchanging peroxide group is conserved. The rate of exchange was proportional to $[H^+]$, in the pH range 7.87 to 11.80. The implications of these results on the mechanism of tetraperoxochromate decomposition are discussed.*

Introduction

The tetraperoxo complex of chromium(V) is one of a series of peroxidic compounds of general formula $M^{(n)}(O_2)_4^{8-n}$, others being formed with vanadium, tantalum, molybdenum and tungsten. The structure of these and other transition metal peroxo compounds and their role in the metal catalysed decomposition of H_2O_2 have been extensively reviewed by Connor and Ebsworth [1] and by Brown *et al.* [2]. In aqueous medium, decomposition of the tetraperoxochromate ion occurs spontaneously. Above pH 8, this can be represented by a single, though complex, reaction according to the equation [3]

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

This reaction has been investigated by Bogdanov [4], by Quane and Earley [5] and by Brown *et al.* [6]. The latter work confirmed that the reaction was first order in tetraperoxochromate and also established a linear dependence of the reaction rate upon $[H^+]$ in the pH range 8.0–11.2. As expected from the stoichiometry, the reaction mechanism was shown to consist of a complex sequence of steps involving several intermediates. In particular, Brown *et al.* [6] found that H_2O_2 markedly inhibited the decomposition reaction and that this inhibition was complete at sufficiently high $[H_2O_2]$. This effect was explained by suggesting that decomposition proceeds via a triperoxo species and free H_2O_2, as shown in Scheme A.

$$H_2O + Cr(O_2)_4^{3-} \rightleftharpoons Cr(O_2)_3O^{3-} + H_2O_2$$

$$Cr(O_2)_3O^{3-} + H^+ \rightleftharpoons HCr(O_2)_3O^{2-} \quad \text{Scheme A}$$

$$HCr(O_2)_3O^{2-} \longrightarrow \text{products}$$

This mechanism also explained the pH dependence of the decomposition reaction, although an equivalent mechanism involving initial protonation of the tetraperoxochromate ion could also fit the observed data. This scheme therefore involves a reversible exchange of integral peroxide groups between H_2O_2 and the chromium centre.

In view of the novelty of this postulate, in the present work we have carried out a direct kinetic study of oxygen exchange between the tetraperoxochromate ion and H_2O_2. By using double-labelled H_2O_2 (*i.e.* $H_2^{18},^{18}O_2$) it is possible not only to measure the extent of exchange, but also to determine whether peroxide groups are exchanged as integral moieties or whether significant scrambling occurs.

Experimental

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 [7]. Concentrated H_2O_2 (85% w/v) was supplied by Laporte Chemicals Ltd., U.K. $H_2^{18}O$ (97.8 atom%) was obtained from Yeda Research and Development Co. Ltd., Rehovoth, Israel. Double-

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labelled $H_2^{18},^{18}O_2$ was prepared from $H_2^{18}O$ using the gas discharge method of Edwards *et al.* [8]. All other materials were as previously described [6].

All reactions were carried out in 50 ml reaction vessels maintained at 0 °C. The exchange reaction was followed starting with label in the H_2O_2 and the reactant solutions were designed so as to obtain approximately equimolar proportions of peroxo groups derived from H_2O_2 and tetraperoxochromate. In order to prevent decomposition, tetraperoxochromate solutions were initially prepared in 0.01 *M* NaOH and maintained at 0 °C. Exchange experiments were then initiated by addition of 5 ml tetraperoxochromate solution by syringe to 7 ml ^{18}O labelled H_2O_2 in buffer [6] at 0 °C. Samples of reaction mixture (1–3 ml) were taken at appropriate time intervals and the reaction quenched by addition of excess 0.2 *M* $BaCl_2$ solution which produced a precipitate containing the barium salts of tetraperoxochromate ion and newly formed chromate ion. The sample size was varied with the extent of the reaction to ensure a working amount of undecomposed tetraperoxochromate for ^{18}O analysis. The precipitate was removed by filtration and dried at 100 °C whilst the filtrate containing H_2O_2 was acidified with 5 volumes of 5 *M* H_2SO_4 to prevent catalytic decomposition of the H_2O_2.

Molecular oxygen was released from the H_2O_2 in the acidified filtrate by reaction with ceric sulphate on a vacuum line. Details of the degassing and sampling procedure are given elsewhere [9]. Under these conditions the H_2O_2 is converted to molecular oxygen without scrambling [10]. The dried precipitate (containing barium tetraperoxochromate) was placed in a specially constructed heating chamber [9] on a vacuum line. After heating to 200–250 °C, spontaneous decomposition of the barium tetraperoxochromate occurred, with the release of molecular oxygen [6] which was collected [9] and retained for mass analysis. Mass spectra of gas samples were obtained using a AEI MS9 mass spectrometer.

Results and Discussion

The exchange reaction could be studied either by measuring the loss of label from H_2O_2 or the gain in label by tetraperoxochromate. These measurements should, in principle, be complementary and the final enrichment reached at equilibrium should be the same both in H_2O_2 and in tetraperoxochromate. However, in practice, measurements on the H_2O_2 are more reliable. This is chiefly because of partial decomposition of the barium tetraperoxochromate during the drying process and also because the barium precipitate sometimes contained carbonate (from the buffer) which produced CO_2 on heating. Both of these effects resulted in relatively small oxygen samples for the mass spectrometer. For these reasons, quantitative kinetic measurements were made using the loss of label from H_2O_2 as an index of exchange, the more limited data from the tetraperoxochromate being used mainly as a check on the fate of label from H_2O_2.

Figs. 1(a) and 1(b) show exchange data at pH 7.87 and 10.41 respectively. It is evident that, at both pH values, extensive exchange is occurring as required by the mechanism proposed by Brown *et al.* [6]. In Fig. 1(a), exchange is almost complete after 40 s, as indicated by the loss of label from H_2O_2. The equilibrium enrichment reached corresponds to approximately half of the initial enrichment, as required by the initial proportions of H_2O_2 and tetraperoxochromate, although the small, but significant decom-

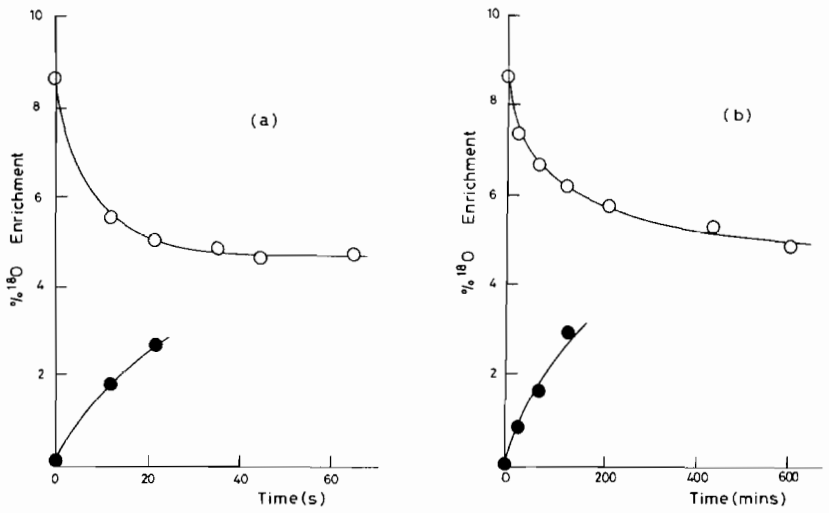

Fig. 1. Peroxide exchange between H_2O_2 and the tetraperoxochromate(V) ion. Variation of residual ^{18}O enrichment (○) in tetraperoxochromate and incorporation of ^{18}O into H_2O_2 (●) with time at pH 7.87 (a) and pH 10.41 (b).

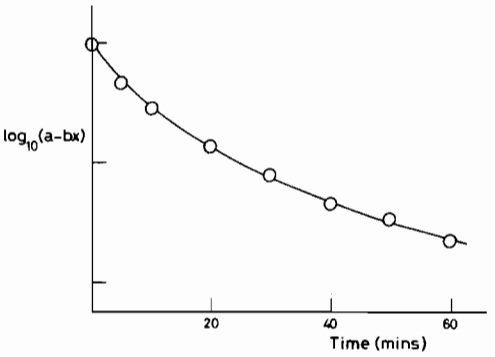

Fig. 2. Plot for determination of gross rate of exchange (R) at pH 10.41. The value of R was determined by constructing a tangent at the origin (see the text).

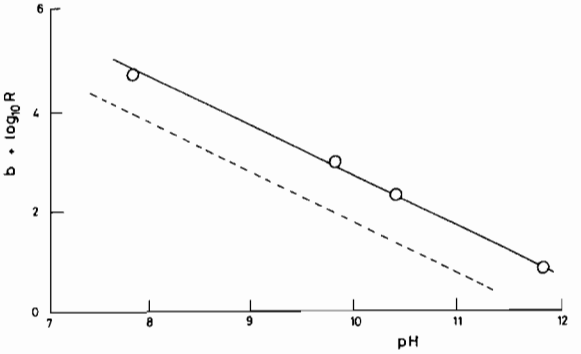

Fig. 3. pH dependence of gross rate of exchange. The broken line represents the initial rate of tetraperoxochromate decomposition under the same conditions.

position of tetraperoxochromate expected during this time [6] precludes more accurate analysis of the equilibrium condition. Also, within the limitations of the data, it may be seen that tetraperoxochromate progressively takes up label, corresponding to the loss of label from H_2O_2. Fig. 1(b) shows similar effects at pH 10.41. However, the rate of exchange is less by several orders of magnitude, indicating a pronounced pH dependence of the kinetics of exchange. Similar exchange reactions but with differing rates, were also observed at pH 9.84 and pH 11.80. It was not possible to extend measurements to higher pH values because of the very slow rates of exchange and complications caused by decomposition of the H_2O_2 [11].

Since peroxide groups in these experiments were either unlabelled or double-labelled, exchange without cleavage of the peroxide (O–O) bond (scrambling) would produce oxygen peaks at only m/e 32 and m/e 36 in the mass spectrometer (after correction for the naturally abundant peak at m/e 34). The intensity of the peak at m/e 34 is therefore a sensitive measure of any cleavage and reformation of the peroxide O–O bond occurring during the exchange reaction, defined as

$$\% \text{ scrambling} = \frac{\text{peak height (m/e 34)} \times 100}{\text{peak height (m/e 34)} + \text{peak height (m/e 36)}}$$

In all of the exchange experiments carried out, the scrambling increased slightly above zero but never increased over 5%. It is clear from these data, therefore, that peroxide group exchange readily occurs between H_2O_2 and the tetraperoxochromate ion, that such exchange occurs almost without loss of the integrity of the peroxide O–O bond and that the reaction is significantly pH dependent.

The kinetics of the peroxide group exchange may also be examined using the present data. Using the general theory of exchange reactions and considering the peroxide group as a single moiety, which may be labelled or unlabelled, it may be shown [12, 13, 14] that

$$\log_{10}\left\{\frac{(y_oT + x_oP)}{(y_o - x_o)T} - \frac{x(T+P)}{(y_o - x_o)T}\right\} = -\frac{(T+P)\cdot R\cdot t}{2.303\ \ T\cdot P} \quad (1)$$

where x_o, x are the fractions of the H_2O_2 molecules (total concentration, P) labelled at time zero and time t respectively, y_o is the fraction of tetraperoxochromate peroxide groups (total concentration T) labelled at time zero and R is the gross rate of exchange of peroxide groups including contributions involving both ^{18}O labelled groups and non-labelled groups.

Equation (1) may be simplified to

$$\log_{10}(a - bx) = -cRT \quad (2)$$

where a, b and c are constants whose values may be readily determined from the initial conditions in any experiment. This treatment assumes that in any experiment there is no net chemical change and that R is therefore a constant for any set of initial conditions. This is strictly true only in the initial part of the exchange reaction in the present work, since the onset of tetraperoxochromate decomposition significantly reduces its concentration (see below).

Fig. 2. shows a typical plot according to Equation (2) for the data at pH 10.41. This is clearly non-linear, presumably because of deviations due to increasing decomposition of tetraperoxochromate and the value of R was therefore determined from a tangent to the curve at time zero as shown in Fig. 2. Similar plots were made at other pH values studied. Since the initial conditions (except for pH) were identical for each experiment, the values of R obtained may be compared directly with one another. Fig. 3 shows the pH dependence of these R values, plotted logarithmically. Within experimental error, this plot is linear, with a slope of −1 showing that R

is directly proportional to $[H^+]$ within the pH range 7.87–11.80. The pH dependence of the exchange reaction is therefore the same as that of the decomposition of tetraperoxochromate [6].

The initial rate of decomposition of tetraperoxochromate under the conditions used in the present work may readily be calculated from the data of Brown *et al.* [6]. The pH variation of the initial rate calculated in this way is shown in Fig. 3 along with the exchange data. It is clear that the exchange rate is significantly higher than the decomposition rate. This is consistent with Scheme A which requires that decomposition occurs via a pre-equilibrium formation of a triperoxo- complex which then undergoes further decomposition. If the rate of exchange had been slower than decomposition, then Scheme A would not be a viable one. The present data are also consistent with the inhibition of tetraperoxochromate decomposition by H_2O_2 previously observed [6]. However, the exchange rate is faster than the decomposition rate by less than one order of magnitude. In view of the additional fact that four exchangeable peroxide groups are removed for each tetraperoxochromate ion decomposed, it is therefore not surprising that decomposition causes deviations of the type seen in Fig. 2.

Since the pH dependence of the rate of the exchange reaction is the same as that of the decomposition reaction, it appears that the protonation step must precede the exchange reaction. Scheme A should therefore be modified as follows.

$$Cr(O_2)_4^{3-} + H^+ \rightleftharpoons HCr(O_2)_4^{2-}$$

$$HCr(O_2)_4^{2-} + H_2O \rightleftharpoons HCr(O_2)_3O^{2-} + H_2O_2$$

$$HCr(O_2)_3O^{2-} \longrightarrow \text{products}$$

Scheme B

From Scheme B, it appears that the decomposition sequence is initiated by protonation of tetraperoxochromate anion. The protonated species appears to be able to lose a peroxide moiety much more readily than the non-protonated ion and the resulting triperoxo intermediate may combine with H_2O_2 (thus explaining H_2O_2 inhibition and the exchange reaction) or may irreversibly decompose to give products. It seems possible that protonation followed by loss of a peroxide group may represent a more generalised mechanism for decomposition of the tetra and diperoxides of transition metals.

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