451. *Peroxy-complexes of Inorganic Ions in Hydrogen Peroxide–Water Mixtures. Part II.* Decomposition by Chromate Ions.*

By P. Flood, T. J. Lewis, and D. H. Richards.

The measurement of pH, optical absorption, and decomposition rate has provided information on the reversible and the irreversible reactions involving the chromate ion in hydrogen peroxide–water mixtures. At acid and alkali concentrations $<2 \times 10^{-3}$M there exists an equilibrium between a peroxide and a non-peroxide derivative of the chromate ion. The former species is partially ionised and catalytically active, whereas the latter is non-ionised and inert. The observed kinetics indicate a first-order decomposition of the peroxide non-ionised form and two second-order reactions between the peroxide ionised component and either a water molecule or a hydroperoxide ion.

EARLY work on the decomposition of dilute hydrogen peroxide by the chromate ion has been reviewed by Baxendale.[1] Spitalsky[2] postulated a cyclic oxidation–reduction mechanism between the sexivalent and the tervalent chromium ion; Kobosev and

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* Part I, preceding paper.

[1] Baxendale, *Adv. Catalysis*, 1952, **4**, 75.

[2] Spitalsky, *Z. anorg. Chem.*, 1908, **56**, 72.

Galbreich[3] suggested a cyclic mechanism involving a peroxy-complex of the chromate ion, without invoking reduction to Cr^{3+}. Haggett, Jones, and Wynne-Jones,[4] in work where measurements were extended to concentrated hydrogen peroxide, also indicated the presence of peroxy-complexes and suggested that the maximum in the curve of decomposition rate against hydrogen peroxide concentration observed by all the investigators for comparatively dilute peroxide (about 10%) is due to the maximum formation of a highly active monoperoxy-complex, and that the fall in rate at higher peroxide concentrations is due to the formation of a comparatively inactive diperoxy-complex. The formation of the diperoxy-complex is inhibited in acid solution, and here no maximum in the rate curve is observed. They found further that over a considerable solvent range the ratio of the mole fraction of water to that of hydrogen peroxide ($C_{H_2O}/C_{H_2O_2}$) was linearly proportional to the decomposition rate in acid solution and to the reciprocal of this rate in slightly alkaline solution. This they interpreted as an example of the competition of solvent molecules for a place in the solvation shell of the catalytic ion, as in the catalytic decomposition of hydrogen peroxide by ferric salts.[5] In the present investigation the more detailed study of the variations in the properties of the system with acidity have led to conclusions differing in a number of respects from those of Wynne-Jones and his co-workers.

EXPERIMENTAL

Materials.—Hydrogen peroxide was obtained by distilling Laporte's commercial 87% non-stabilised " high-test peroxide " at 13 mm. without fractionation. Dilutions were made with conductivity water. For very concentrated hydrogen peroxide, 99·5% electrolytic non-stabilised material, supplied by Laporte Chemicals Ltd., was used without purification.

Potassium dichromate and sodium hydroxide were of " AnalaR " quality. Perchloric acid was obtained by the appropriate dilution of " AnalaR " 60% material. Sodium perchlorate was prepared by neutralisation of " AnalaR " perchloric acid with sodium hydroxide.

Units.—The practices of the preceding paper are continued, for the reasons given there. In the rate equations time is expressed in minutes.

Techniques.—Solutions were prepared in series with variable acidity and constant hydrogen peroxide concentration. Ionic strength was maintained at 0·01 by addition of sodium perchlorate. A catalyst concentration 2×10^{-4}M was used throughout. Thus the mole fraction of the catalyst changed with solvent composition but, since the total chromate concentration appears in all derived equilibrium and rate equations, allowance could be made for this variation.

Decomposition rates were obtained by measuring the oxygen evolved in a given time by means of conventional gas burettes. Samples (50 ml.) of the reaction mixtures were contained in Pyrex tubes, previously cleaned with nitric acid, and immersed in a thermostat-bath at 22°. This temperature was chosen to facilitate comparison with optical-absorption studies which were carried out at room temperature, estimated as 22° ± 1°.

Absorption measurements were carried out in a Unicam S.P. 500 spectrophotometer with 4-cm. glass cells. Interference by oxygen bubbles was greatly reduced by placing the cells under vacuum for a few minutes immediately before use.

The measurement of pH involved the use of the E_0 figures of Mitchell and Wynne-Jones.[6] Several types of cell were used but the most reliable was simply the immersion of the glass electrode and the dip-type saturated calomel electrode in the test solution held in an open beaker. The assembly was contained in a constant-temperature cabinet at 25°. E.M.F.s were recorded on a Cambridge Instrument Co. pH meter.

RESULTS AND DISCUSSION

pH *Measurements.*—pH measurements, by indicating the degree of hydrolysis of the various ions which are present, give information on the nature of the equilibria involving the chromate ion in hydrogen peroxide–water mixtures.

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[3] Kobosev and Galbreich, *Acta Physicochem. U.R.S.S.*, 1945, **20**, 479.
[4] Haggett, Jones, and Wynne-Jones, *Discuss. Faraday Soc.*, 1960, **29**, 153.
[5] Jones, Kitching, Tobe, and Wynne-Jones, *Trans. Faraday Soc.*, 1959, **55**, 1959.
[6] Mitchell and Wynne-Jones, *Trans. Faraday Soc.*, 1955, **51**, 1090.

Little change in pH occurs when potassium dichromate is added to neutral hydrogen peroxide. Hence under these conditions the anion, whether a simple chromate ion or a peroxy-complex, has a single negative charge, since no hydrogen ions are involved in such equilibria as $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-$ and $HCrO_4^- + H_2O_2 \rightleftharpoons HCrO_5^- + H_2O$. The anion may be assumed to be monomeric in view of the first-order relation between decomposition rate and total chromium concentration.[1,4]

Addition of sodium hydroxide up to 2×10^{-3}M to the neutral chromate solution brings about pH changes which are the same as those produced when no chromate is present. On the other hand, the addition of perchloric acid to neutral chromate solutions results in the presence of fewer hydrogen ions than the total stoicheiometric amount added, indicating that in acid solutions the univalent hydrogen chromate ion adds a further proton and becomes uncharged chromic or perchromic acid.

The apparent acid dissociation constant of chromic acid may be calculated at a particular hydrogen peroxide concentration from the measured pH of the system. The difference between the stoicheiometric amount of hydrogen ions added and that amount recorded as present by the pH meter is taken as the total concentration of undissociated chromic and perchromic acid in the system. The difference between the latter figure and that of the total chromate present is taken as the total concentration of the singly charged chromate or perchromate anions. Then the apparent ionisation constant is defined as

$$K_{ap} = \frac{\text{Total concentration of chromate and perchromate ions} \times [H^+]}{\text{Total concentration of un-ionised chromic and perchromic acid}}.$$

The variation of K_{ap} with hydrogen peroxide concentration may be explained by postulating two equilibria:

$$H_2CrO_4 + H_2O_2 \xrightleftharpoons{K_1} H_2CrO_5 + H_2O \qquad (1)$$

$$H_2CrO_5 \xrightleftharpoons{K_2} H^+ + HCrO_5^- \qquad (2)$$

Then

$$K_{ap} = \frac{C_{H^+}C_{HCrO_5^-}}{C_{H_2CrO_5} + C_{H_2CrO_4}}$$

$$= \frac{C_{H^+}C_{HCrO_5^-}}{C_{H_2CrO_5} + C_{H_2CrO_5}a_{H_2O}/K_1a_{H_2O_2}}$$

$$= K_2(1 + 1/K_1\theta)^{-1}$$

Hence

$$1/K_{ap} = 1/K_2 + 1/K_1K_2\theta, \qquad (3)$$

where C_{H^+} is the concentration of the hydrogen ion, $C_{HCrO_5^-}$ that of the $HCrO_5^-$ ion, etc., a_{H_2O} and $a_{H_2O_2}$ are the respective activities of the water and hydrogen peroxide components of the solvent mixture, calculated from the vapour pressure data of Scatchard *et al.*[7] and $\theta = a_{H_2O_2}/a_{H_2O}$. A plot of $1/K_{ap}$ against $1/\theta$ gives a straight line of intercept $1/K_2$ and slope $1/K_1K_2$. No term involving the solvent concentration has been introduced into equation (2). This question will be discussed later.

Fig. 1 shows $1/K_{ap}$ plotted against $1/\theta$. The values calculated from the slope and the intercept of this line are $K_1 = 1{\cdot}4$, and $K_2 = 0{\cdot}5 \times 10^{-4}$. From the value of K_2 it may be calculated that in neutral and alkaline solution all the chromate is present in the ionised peroxide form. This result is confirmed in the spectrophotometric and decomposition-rate experiments described below.

It must be made clear, however, that none of the techniques used by us fully characterises the species postulated in equations (1) and (2). Derivatives of the acids H_2CrO_4 and H_2CrO_5 have been written for convenience, but any two species related by the equation, $H_2CrO_n + H_2O_2 \rightleftharpoons H_2CrO_{n+1} + H_2O$, would suffice. There is some

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[7] Scatchard, Kavenagh, and Ticknor, *J. Amer. Chem. Soc.*, 1952, **74**, 3715.

evidence that two higher peroxy-species are indeed involved. The ionisation of H_2CrO_4 has been found in the present investigation to be immeasurably small, whereas in the literature the most reliable value for this in water is about 2×10^{-2} in terms of mole fractions,[8] a figure several powers of ten larger than that calculated here for K. It seems probable that two new species are involved, both of which have a dissociation constant far lower than that of H_2CrO_4 in water. Also it is known that when small amounts of hydrogen peroxide (less than 0·5%) are added to a solution of chromium trioxide in water (naturally acid owing to hydrolysis to the $HCrO_4^-$ ion) the hydrogen-ion concentration of the system falls almost to that of the neutral point. Either a non-dissociated peroxy-complex is formed, or the introduction of small amounts of hydrogen peroxide causes a large change in the basicity of the medium.[9] The final evidence for the formation of two higher peroxy-complexes comes from the ultraviolet spectrum of chromate solutions. The prominent absorption peak at 350 mμ which is due to the $HCrO_4^-$ ion in water disappears on addition of a small amount of hydrogen peroxide. Since the same effect cannot be reproduced by making the aqueous solution strongly acid and forming the un-ionised H_2CrO_4 molecule a new complex is probably formed even in very dilute hydrogen peroxide solutions, in which case the two related acids on which all calculations in this paper are based are not H_2CrO_4 and H_2CrO_5, but two similarly related higher peroxy-complexes.

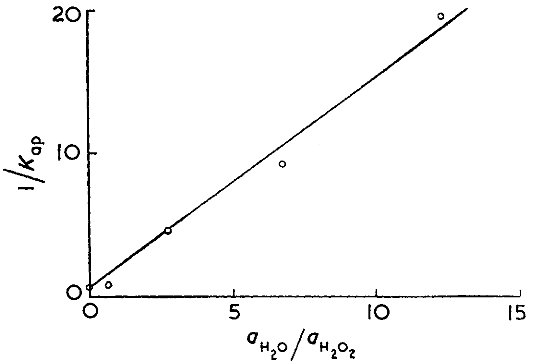

FIG. 1. Plot of $1/K_{ap}$ against $a_{H_2O}/a_{H_2O_2}$.

Spectrophotometric Experiments.—Spectrophotometric studies have confirmed the existence of the equilibria (1) and (2), and an independent determination of K_1 and K_2 has been obtained.

It was found that the chromate ion in hydrogen peroxide gives a broad absorption band with a maximum at 510 mμ. In neutral and slightly alkaline conditions (up to 2×10^{-3}M-sodium hydroxide) the height of the peak was found to be independent of both hydrogen peroxide and HO_2^- concentration, but addition of perchloric acid to a neutral solution caused a sharp decrease in the absorption maximum and a weakening of the familiar purple colour of the solutions. A selection of curves showing the effect on the peak height of the addition of perchloric acid and sodium hydroxide at various hydrogen peroxide concentrations is shown in Fig. 2.

The constant peak height in neutral and alkaline solutions indicates that all the chromate is present as the absorbing species, which by inference from the pH experiments may be taken as $HCrO_5^-$. The extinction coefficient for this ion at the maximum (510 mμ) is 595.

The values of K_1 and K_2 may be obtained from the variation in optical density with perchloric acid concentration.

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[8] Tong and King, *J. Amer. Chem. Soc.*, 1953, **75**, 6180.
[9] Maggs, personal communication.

Solution of equations (1) and (2) gives

$$C_{\mathrm{HCrO_5^-}} = \frac{C_{\mathrm{Cr}} K_1 K_2 \theta}{K_1 K_2 \theta + C_{\mathrm{H^+}}(1 + K_1\theta)}, \tag{4}$$

where C_{Cr} is the total concentration of chromate of all species. Then if $HCrO_5^-$ is the only ion absorbing at 510 mμ it may be shown that

$$D_0/D - 1 = C_{\mathrm{H^+}}(1/K_2 + 1/K_1K_2\theta), \tag{5}$$

where D_0 is the optical density in neutral solution, and D the optical density at a hydrogen-ion concentration $C_{\mathrm{H^+}}$. Hence if $D_0/D - 1$ is plotted against $C_{\mathrm{H^+}}$ a straight line passing through the origin should be obtained with a slope equal to $(1/K_2 + 1/K_1K_2\theta)$. Then by plotting this slope against $1/\theta$, a further straight line should be obtained with intercept equal to $1/K_2$ and slope equal to $1/K_1K_2$. Fig. 3 shows plots of $D_0/D - 1$ against $C_{\mathrm{H^+}}$ for the four curves of Fig. 2. Straight lines are obtained, showing that $HCrO_5^-$ is the only absorbing species. More detailed analysis showed that if the ionisation of the non-peroxide species were appreciable the curves would have a positive intercept on the $D_0/D - 1$ axis, whereas in practice the curves have, if anything, a small intercept on the $C_{\mathrm{H^+}}$ axis. This is the most direct evidence for ignoring the ionisation of H_2CrO_4 in the equilibrium picture.

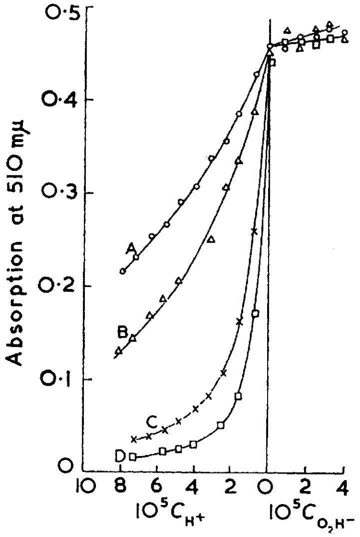

FIG. 2. Plot of absorption against added perchloric acid and sodium hydroxide.
$C_{H_2O_2}$: A, 0·749; B, 0·492; C, 0·258; D, 0·124.

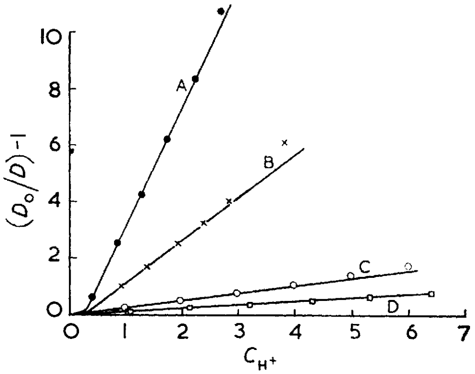

FIG. 3. Plot of $(D_0/D) - 1$ against $C_{\mathrm{H^+}}$.
$C_{H_2O_2}$: A, 0·124; B, 0·258; C, 0·492; D, 0·749.

Fig. 4 shows the slopes of these graphs plotted against $1/\theta$. A straight line is obtained from which the following values are calculated: $K_1 = 0{\cdot}73$ and $K_2 = 0{\cdot}9 \times 10^{-4}$.

Decomposition-rate Experiments.—If in addition to the equilibria described by equations (1) and (2) certain irreversible decomposition processes are postulated, the whole kinetic picture may be explained. In this section a general empirical equation relating decomposition rate to the concentrations of the chromate, hydrogen, and hydroperoxide ions, and of the hydrogen peroxide, is first derived; it is then related to the theoretical equation calculated from the postulated processes.

The first-order dependence of decomposition rate on total chromate concentration recorded by previous workers[1,4] has been confirmed. This enabled decomposition rates for a constant mole fraction of catalyst to be calculated from the observed rates in which the molarity of the catalyst was held constant.

Three typical series of decomposition-rate experiments are shown in Fig. 5. Each represents the effect of changing hydrogen- and hydroperoxide-ion concentration on decomposition rate at a constant hydrogen peroxide concentration. It can be seen that there is always a discontinuity in the curve at the neutral point of the hydrogen peroxide, that the decomposition rate increases linearly with hydroperoxide-ion concentration up to $C_{O_2H^-} = 4 \times 10^{-5}$, and that the decomposition rate alters linearly with hydrogen-ion concentration up to 4×10^{-5}, but that the sense and magnitude of the latter variation depend greatly on the hydrogen peroxide concentration. At peroxide concentrations below a mole fraction of about 0·5 the relation between rate and hydrogen-ion concentration is no longer linear. At hydrogen-ion concentrations greater than 4×10^{-5} the decomposition rate always falls off, but this region, where possibly Cr^{3+} is formed in some quantity, has not been studied in detail.

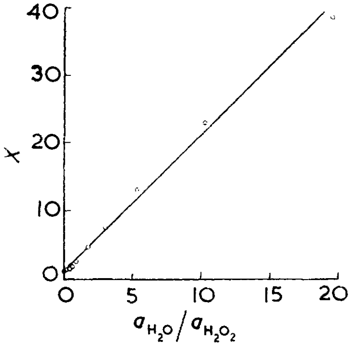

FIG. 4. Slope of lines of Fig. 3 plotted against $a_{H_2O}/a_{H_2O_2}$.

$$X = 10^{-4}\left(\frac{1}{K_2} + \frac{a_{H_2O}}{K_1K_2a_{H_2O_2}}\right).$$

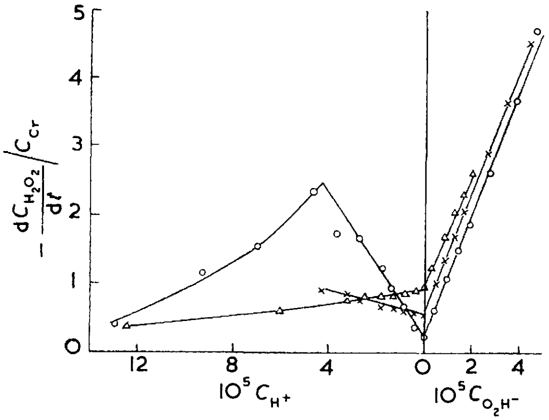

FIG. 5. Decomposition rate as a function of the concentration of the H_3O^- and O_2H^+ ions.
$C_{H_2O_2}$: ○, 0·967; ×, 0·706; △, 0·568.

An empirical equation of the following form may be used to represent these results:

$$-\frac{dC_{H_2O_2}}{dt} = C_{Cr}(A + BC_{H^+} + CC_{O_2H^-}), \qquad (6)$$

where C_{Cr} is the total chromate concentration, and A, B, and C are functions of the solvent composition only. Table 1 shows the variation of A, B, and C with hydrogen peroxide concentration in the more concentrated range. A more refined treatment for dilute hydrogen peroxide is given below.

TABLE 1.

$C_{H_2O_2}$	0·967	0·860	0·743	0·706	0·568	0·488	0·409	0·331	0·258
A	0·196	0·348	0·443	0·569	1·16	1·81	2·40	3·22	3·80
$10^{-5}B$	0·53	0·28	0·10	0·08	−0·11	−0·14	−0·35	−0·75	−1·27
$10^{-5}C$	1·00	1·02	1·08	0·96	1·14	0·99	1·00	1·03	

Function C remains constant over this concentration range of hydrogen peroxide. This is consistent with the pH and spectrophotometric evidence that only one peroxy-complex, written tentatively as $HCrO_5^-$, is present in neutral and slightly alkaline solutions.

This ion enters into a direct reaction with a hydroperoxide ion, and this results in evolution of oxygen.

Fig. 6 shows the plot of A against the concentration and activity of water in the solvent mixture. Although no linearity exists between decomposition rate in neutral solution and the mole fraction of the water component, the plot of A against activity of water approximates to a straight line. Since only one peroxy-complex is present it seems clear that the activity of water enters into an irreversible rate equation. Under these conditions it does not enter into an equilibrium equation relating two different peroxy-complexes, as has been postulated by Wynne-Jones and his co-workers.[4] Not only do the pH and the spectrophotometric work point conclusively to one peroxy-complex, but the constancy of function C over a wide hydrogen peroxide range is further confirmation, since unless their rate constant with the hydroperoxide ion were the same the existence of two peroxy-complexes would cause C to change linearly with A.

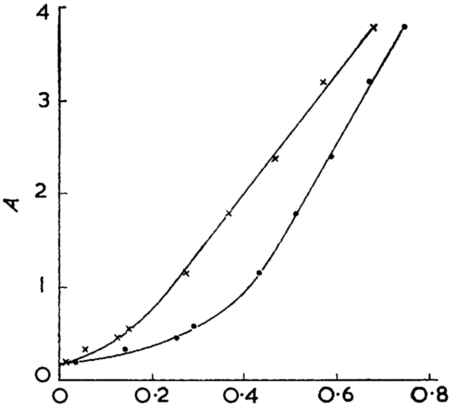

FIG. 6. Plot of A against (●) C_{H_2O} and (×) a_{H_2O}.

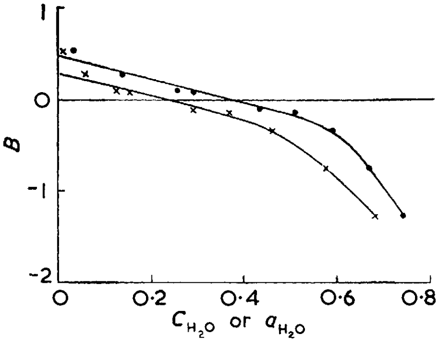

FIG. 7. Plot of B against (●) C_{H_2O} and (×) a_{H_2O}.

Fig. 7 shows the variation of function B with the concentration and activity of the water constant of the solvent. From a positive value in very concentrated hydrogen peroxide the value of B decreases linearly with water activity, being negative at hydrogen peroxide concentrations below about 0·65.

The full empirical equation for the decomposition of hydrogen peroxide by the chromate ion is therefore:

$$-\frac{dC_{H_2O_2}}{dt} = C_{Cr}\{aa_{H_2O} + (b - ca_{H_2O})C_{H^+} + dC_{O_2H^-}\}, \tag{7}$$

where a, b, c, and d are constants independent of the acid or hydrogen peroxide concentration.

Equation (7) may be derived by postulating in addition to the equilibria (1) and (2) three irreversible decomposition steps:

$$HCrO_5^- + O_2H^- \xrightarrow{k_1} \text{Products} \tag{8}$$

$$HCrO_5^- + H_2O \xrightarrow{k_2} \text{Products} \tag{9}$$

$$H_2CrO_5 \xrightarrow{k_3} \text{Products} \tag{10}$$

If the activity coefficients of all species present except the solvent molecules are taken as unity, solution of (1) and (2) gives

$$C_{\mathrm{HCrO_6^-}} = \frac{C_{\mathrm{Cr}}K_1K_2\theta}{K_1K_2\theta + C_{\mathrm{H^+}}(K_1\theta + 1)}, \tag{11}$$

and

$$C_{\mathrm{H_2CrO_6}} = \frac{C_{\mathrm{Cr}}K_1C_{\mathrm{H^+}}\theta}{K_1K_2\theta + C_{\mathrm{H^+}}(K_1\theta + 1)} \tag{12}$$

At sufficiently low $C_{\mathrm{H^+}}$ a state is reached where $K_1K_2\theta \gg C_{\mathrm{H^+}}(K_1\theta + 1)$, *i.e.*, that $C_{\mathrm{HCrO_6^-}} \approx C_{\mathrm{Cr}}$. This condition is apparently reached in neutral and alkaline solution where the irreversible decomposition steps (8) and (9) then give rise to the observed variations of A and C with hydrogen peroxide concentration, *i.e.*,

$$-\frac{\mathrm{d}C_{\mathrm{H_2O_2}}}{\mathrm{d}t} = C_{\mathrm{Cr}}(k_2a_{\mathrm{H_2O}} + k_1C_{\mathrm{O_2H^-}}). \tag{13}$$

The equation governing decomposition in acid solution is obtained by combining equations (11) and (12) with (9) and (10).

$$-\frac{\mathrm{d}C_{\mathrm{H_2O_2}}}{\mathrm{d}t} = C_{\mathrm{Cr}}\left\{\frac{k_2K_1K_2\theta a_{\mathrm{H_2O}} + k_3K_1\theta C_{\mathrm{H^+}}}{K_1K_2\theta + (K_1\theta + 1)C_{\mathrm{H^+}}}\right\} \tag{14}$$

$$= C_{\mathrm{Cr}}\left\{\frac{K + LC_{\mathrm{H^+}}}{M + NC_{\mathrm{H^+}}}\right\},$$

where $K = k_2K_1K_2\theta a_{\mathrm{H_2O}}$, $L = k_3K_1\theta$, $M = K_1K_2\theta$, and $N = K_1\theta + 1$.

The value of B of equation (6) is calculated from the difference between the rate R at hydrogen-ion concentration $C_{\mathrm{H^+}}$ and the rate R_0 in neutral solution where the hydrogen-ion concentration may be regarded as effectively zero.

Hence, since R_0 is given by

$$R_0 = C_{\mathrm{Cr}}K/M,$$

$$R - R_0 = \Delta R = C_{\mathrm{Cr}}C_{\mathrm{H^+}}(LM - KN)/M(M + NC_{\mathrm{H^+}}),$$

and

$$B = (LM - KN)/M(M + NC_{\mathrm{H^+}}). \tag{15}$$

Equation (15) is the most general form of the function B of equation (6) and shows that B is not strictly independent of $C_{\mathrm{H^+}}$. In practice, deviations from linearity in the relation between R and $C_{\mathrm{H^+}}$ become large at hydrogen peroxide concentrations below about 0·5, and the values in this range are dealt with below by direct application of equation (12). The form of B recorded for higher hydrogen peroxide concentrations in the empirical equation (7) may be obtained by making certain simplifications.

Good linearity between decomposition rate and hydrogen-ion concentration is obtained at hydrogen peroxide concentrations above 0·5 and at hydrogen-ion concentrations below 2×10^{-5}. In this range it may be said that $NC_{\mathrm{H^+}}$ is considerably smaller than M, and hence

$$B \approx (LM - KN)/M^2$$

$$= k_3/K_2 - k_2a_{\mathrm{H_2O}}/K_2 - k_2a_{\mathrm{H_2O}}/K_1K_2\theta, \tag{16}$$

which at even lower $a_{\mathrm{H_2O}}$ values reduces to

$$B = k_3/K_2 - k_2a_{\mathrm{H_2O}}/K_2. \tag{17}$$

This is the form taken for B in the expanded empirical equation (7), and hence the rate equations (8—10) coupled with the equilibria (1) and (2) will explain the observed kinetics of decomposition in neutral, weakly acid, and weakly basic solutions.

All the rate and equilibrium constants except K_1 may now be calculated from the kinetic data. k_1 is directly related to C of Table 1, k_2 is obtained from the slope of Fig. 6, K_2 from the slope of Fig. 7, and k_3 from the intercept of Fig. 7 at $a_{H_2O} = 0$. The following values are obtained: $K_2 = 5{\cdot}6 \times 10^{-5}$; $k_1 = 1 \times 10^5$; $k_2 = 7$; and $k_3 = 3{\cdot}7$. All are calculated on the basis of mole fractions except k_2 which involves the activity of the water component.

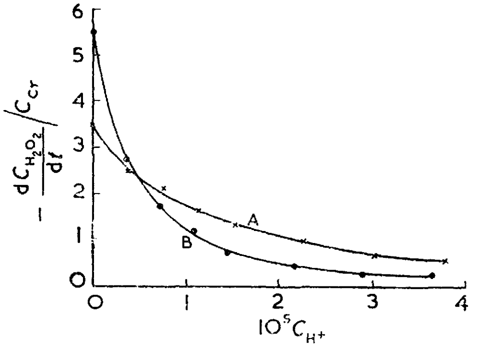

FIG. 8. Decomposition rate plotted against hydrogen-ion concentration at low hydrogen peroxide concentrations.
$C_{H_2O_2}$: A, 0·258; B, 0·124.

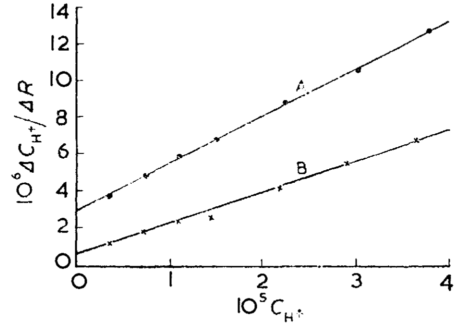

FIG. 9. Plot of $\Delta C_{H^+}/\Delta R$ against C_{H^+} for the curves of Fig. 4.
$C_{H_2O_2}$: A, 0·258; B, 0·124.

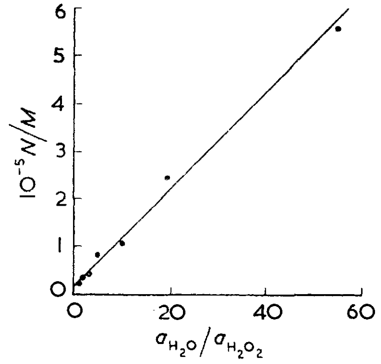

FIG. 10. Plot of N/M against $a_{H_2O}/a_{H_2O_2}$.

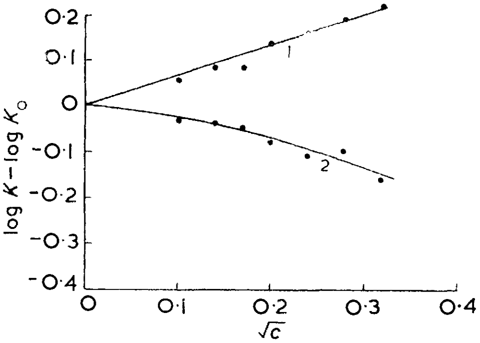

FIG. 11. Salt effects in the decomposition of hydrogen peroxide by chromate.
(1) $C_{NaOH} = 2 \times 10^{-5}$. (2) $C_{HClO_4} = 2 \times 10^{-5}$.

At hydrogen peroxide concentrations below about 0·5 the plot of decomposition rate against hydrogen-ion concentration becomes progressively more curved. Typical curves are shown in Fig. 8. Direct application of equation (15) must be made.

By simple re-arrangement

$$C_{H^+}/\Delta R = M(M + NC_{H^+})/(LM - KN). \qquad (18)$$

Hence if $C_{H^+}/\Delta R$ is plotted against C_{H^+} a straight line should be obtained. The ratio of the slope to the intercept of this line equals N/M which is equal to the function $(1/K_2 + 1/K_1K_2\theta)$. Hence, by plotting Slope/Intercept against $1/\theta$, both K_1 and K_2 may be calculated. Fig. 9 shows the plot of $C_{H^+}/\Delta R$ against C_{H^+} for the curves shown in Fig. 8. Although theoretically this procedure may be applied to all hydrogen peroxide concentrations, in practice it was effective only up to $C_{H_2O_2} = 0{\cdot}5$ since in this dilute region the value of $1/\theta$ is altering most widely. At higher peroxide concentrations $1/K_2$ becomes much larger than $1/K_1K_2\theta$, and N/M tends to a limiting value.

The graph of N/M against $1/\theta$ is shown in Fig. 10. The values calculated from the slope and the intercept are $K_2 = 6{\cdot}7 \times 10^{-5}$ and $K_1 = 1{\cdot}8$.

A study of salt effects in both acid and alkaline solution at one hydrogen peroxide concentration has provided further evidence relating to the nature of the reactions taking place. Fig. 11 shows the effect of ionic strength on the rate of catalytic reaction in 2×10^{-5}M-acid and 2×10^{-5}M-alkaline solution. In alkaline solution the salt effect is positive and linearly related to the square root of the ionic strength. This is typical of the primary salt effect on a reaction involving two ions of similar charge, and the magnitude of the effect here observed corresponds to that calculated for two singly charged ions of the same sign.[10] This supports the other evidence to the effect that a saturation level of $HCrO_5^-$ ion builds up in alkaline solution (precluding any possibility of a secondary salt effect) and that the decomposition involves direct interaction between this ion and hydroperoxide ion.

In acid solution a negative salt effect is observed. This is interpreted as a secondary salt effect, causing an increase in the value of K_2. The formation of $HCrO_5^-$ at the expense of H_2CrO_5 would otherwise be obtained by reducing the hydrogen-ion concentration of the system, and it is known that under the conditions of the experiment this would reduce the rate of oxygen evolution. Hence a similar change in the relative concentrations of H_2CrO_5 and $HCrO_5^-$ produced by the addition of sodium perchlorate would also be expected to reduce the decomposition rate, and this provides further evidence that the reaction scheme described is essentially correct.

Conclusions.—All three techniques indicate the existense of an equilibrium between a partially ionised chromate peroxy-complex and a un-ionised species having one less oxygen atom. Kinetic measurements have shown that both the ionised and the un-ionised form of the higher peroxy-complex take part in decomposition reactions, the former by direct reaction with either a hydroperoxide ion or a water molecule and the latter by a first-order decomposition process. The constants are collected in Table 2.

TABLE 2.

Method	K_1	10^4K_2	10^5k_1	k_2	k_3
pH	1·4	0·5			
Absorption	0·73	0·9			
Kinetics (high $C_{H_2O_2}$)..................		0·56	1	7	3·7
,, (low $C_{H_2O_2}$)	1·8	0·67			

The difference between the equilibrium constants obtained from the spectrophotometric experiments and those from the other techniques may be due to the fact that absorption is a function of concentration whereas the kinetic and pH experiments measure the activities of the species involved.

The behaviour of the chromate ion in hydrogen peroxide–water mixtures may be explained only by assuming the acid dissociation constant K_2 to be independent of solvent composition, *i.e.*, the basicity of the solvent is independent of peroxide concentration. Similar effects have been noted by us for the analogous dissociations of the peroxy-complexes of the ferric and molybdate ions [11,12] and by Wynne-Jones and his co-workers for the ferric ion.[5] This behaviour contrasts with the ionisation of indicators in similar hydrogen peroxide–water mixtures,[13] and will be discussed in a later paper.

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