Thermal Decomposition of Sodium Carbonate Perhydrate in the Presence of Liquid Water

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A kinetic study has been made of the decomposition of sodium carbonate perhydrate, $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$, in the presence of small quantities of added water at 323-343 K. Reactions were deceleratory throughout and rates in the later stages were further reduced when the quantity of water available was insufficient to permit complete initial dissolution of the reactant solid. Rate coefficients measured for these reactions were compared with similarly determined data for the probable contributory processes. These were the decompositions, in saturated aqueous Na_2CO_3, of (i) H_2O_2 and (ii) $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$. From the pattern of behaviour observed it was concluded that the reaction of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ in water proceeds in two stages: heterogeneous dissolution of the reactant crystallites is followed by the homogenous breakdown of H_2O_2 in solution. This mechanism is distinct and different from the vacuum decomposition of the solid. It is concluded that the rate of the homogenous breakdown of H_2O_2 is probably controlled by catalytic processes involving transition-metal ions present in solution as impurities. This conclusion is supported by the observation that the present reaction was inhibited by added sodium silicate. The kinetics and mechanisms of these reactions are discussed.

The heterogeneous reaction investigated involved both a solid reactant and intermediates dissolved in the added liquid water. This combination of reactants has hitherto been the subject of relatively few detailed kinetic studies. Separate investigations of the individual steps which contribute to the overall change, in this particularly favourable system, has led to the identification of a simple reaction mechanism that is entirely consistent with the observations. The approach demonstrates the value of using complementary rate measurements to characterize the kinetics and mechanism of this decomposition involving both solid and dissolved participants.

In a recent study of the thermal decomposition of sodium carbonate perhydrate ($Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$) in vacuum[1] it was concluded that hydrogen peroxide breakdown

$$Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2 \rightarrow Na_2CO_3 + 1\frac{1}{2} H_2O + \frac{3}{4} O_2$$
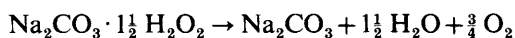
was an intracrystalline reaction proceeding within the pores of the reactant–product solid assemblage, when reaction conditions ensured that the quantity of water present was minimized. In the presence of liquid water several characteristic features of the reaction were changed. Decomposition occurred in an appreciably lower temperature interval and the rate was deceleratory throughout. This kinetic behaviour contrasts with the sigmoid-shaped yield against time curves characteristic of the isothermal vacuum reaction. The present study of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ decomposition kinetics in the presence of liquid water, and related reactions, was undertaken to determined whether this additive catalysed the solid-state process previously studied[1] in vacuum or whether this decomposition proceeded by an entirely different mechanism. Elucidation of the role of the added liquid included consideration of the possibilities that water is a solvent for the reactant solid and/or that it may catalyse H_2O_2 decomposition, besides being a reaction product and possibly a reactant impurity. We conclude, from the observations reported here, that the decomposition of sodium carbonate perhydrate in contact with liquid water proceeds through salt dissolution followed by homogenous breakdown of the H_2O_2 released[2] in aqueous solution.

Main objectives of the present study were to elucidate the kinetic characteristics of decomposition(s) proceeding in this two-phase reactant mixture and to identify the relative significances of reactions in the crystalline reactant, in solution and at the interfaces. Few detailed rate studies of solid-solution decompositions of this type have been reported. However, our results lead us to conclude that the present reaction is particularly favourable for such an investigation. While the quantitative characteriz-ation of all steps contributing to the overall chemical change has not been achieved, considerable progress towards this objective has been made. Our analysis has included simplifications which permitted the formulation of a reaction mechanism that is entirely consistent with the available rate data. Comparisons of the rates of decom-position of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ in water with parallel measurements for this reaction and for the decomposition of H_2O_2 in saturated aqueous Na_2CO_3 have permitted us to characterize the contributory steps in the overall reaction. We conclude that decomposition proceeds by the consecutive steps of heterogenous dissolution followed by homogenous reaction:

$$\text{solid reactant} \rightarrow \text{dissolved intermediate} \rightarrow \text{products.}$$
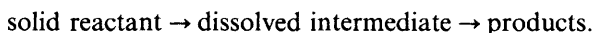
In the presence of water there is a marked increase in reactivity as compared with the higher-temperature intracrystalline rate process[1] proceeding under anhydrous conditions. These results emphasize, therefore, the importance of assessing the possible significance of even trace amounts of water when considering the reactivity of solids participating in low-temperature chemical changes. We also point out the necessity, when formulating mechanisms of complicated reactions involving solids, of investigating individually the possible contributory steps.

Citations of earlier studies concerned with decompositions of salts related to $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ were given in our earlier paper.[1] We consider it inappropriate to attempt to review here the extensive literature concerned with the catalysed and the uncatalysed decomposition of H_2O_2 in aqueuous solution. Discussions of the mechanism of the homogenous breakdown of hydrogen peroxide have not always been conclusive,[3] and at present features of this reaction remain unresolved or in dispute. There is, however, some agreement that reaction rates may be controlled by trace quantities of transition-metal ion impurities in solution.[4]

EXPERIMENTAL

METHODS

In isothermal kinetic studies of the decomposition of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ in liquid water, each measurement of the fractional reaction (α) as a function of time was made using a different sample of reactant, individually weighed [50 or 100 (± 2) mg)] into a clean, dry glass sample tube (ca. 50 mm long, 6 mm diameter and sealed at one end). A measured amount of distilled water [quantities were between 20 and 100 (± 2) mg] was then added directly to the mass of reactant, to ensure effective salt–water contact, and the tube immediately sealed. Usually some 15-20 samples were prepared concurrently and immersed together in a bath thermostatted (± 0.5 K) at the reaction temperature. Individual samples were withdrawn after appropriate measured time intervals, cooled by ice and the envelope broken open into acid solution. The available oxygen remaining ($Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ and dissolved H_2O_2) was determined by titration with standard $KMnO_4$ to provide a measure of the total quantity of unreacted H_2O_2. The effects of the variation of (i) the weight of water added to a constant weight of salt and (ii) temperature on extent of reaction–time curves were separately investigated in parallel series of experiments under otherwise standardized reaction conditions.

For comparative purposes kinetic measurements were made for the following related reactions. (i) The homogenous decomposition of H_2O_2 in saturated aqueous Na_2CO_3 solution.

Samples were withdrawn from the reactant mixture at appropriate time intervals, acidified and titrated with standard $KMnO_4$. (ii) The decomposition of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ in saturated aqueous Na_2CO_3. Measured quantities of reactant solid and saturated solution (thermostatted at reaction temperature) were mixed, and after the required time the solids were separated by filtration and the available oxygen in these and in the filtrate were separately determined by acidification followed by titration with standard $KMnO_4$. (iii) A limited number of measurements were made of the rates of decomposition of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ to which small amounts of H_2O_2 had been added.

REACTANTS

Three of the five reactant preparations studied here have been described previously:[1] salts L4, W2 and W3, for which the available oxygen contents were 15.0, 13.9 and 13.7%, respectively. For each salt, the present work and the previously reported studies of the vacuum decomposition[1] were completed concurrently so that comparisons were not influenced by reactant ageing or deterioration during storage. Salt W4 was prepared in a manner similar to that described[1] for salts W1, W2 and W3. Salt F1 was a commercial product, in the form of 'abrasion-resistant particles', prepared by mixing 30% Na_2CO_3 and 20% H_2O_2 solutions with small amounts of proprietary stabilizers and the suspension dried in a hot fluidized bed containing product particles. Available oxygen contents of salts W4 and F1, again determined by $KMnO_4$ titrations, were 14.4 and 14.8%, respectively. The concentrations of heavy-metal impurities in all reactants studied[1] were low, close to our lower limits of analytical detection.

RESULTS AND DISCUSSION

To facilitate the kinetic analyses of data, the results are presented below in the sequence of increasing complexity of interpretation of observations: these are (i) H_2O_2-saturated Na_2CO_3, (ii) $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$-saturated Na_2CO_3 and (iii) $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ and water. Some other related reactions are finally described.

DECOMPOSITION OF H_2O_2 IN SATURATED AQUEOUS Na_2CO_3

50.0 cm^3 of clear saturated Na_2CO_3 solution, thermostatted at reaction temperature, were transferred to a clean, dry preheated flask and 200 ± 2 mm^3 of 30% hydrogen peroxide added. Duplicate or triplicate samples were withdrawn at appropriate time intervals, acidified, and the available oxygen measured by titration with standard $KMnO_4$. The decomposition of hydrogen peroxide in saturated Na_2CO_3 obeyed the first-order equation between $0.15 < \alpha < 0.95$ (α is the fractional reaction). There was an initial relatively rapid process when $\alpha < 0.15$ and, in consequence, extrapolated first-order plots intercepted the time axis at -3 min. Calculated Arrhenius parameters were activation energy (E) 68 ± 5 kJ mol^{-1} and frequency factor (A)$10^{9.4}$ min^{-1}. The temperature interval (323-338 K) and reactant concentration range (< 0.03 mol dm^{-3}) studied here were selected to permit comparisons with the related systems reported below. It must be remembered, however, that this reaction is believed to be particularly sensitive to the presence of trace quantities of transition-metal impurities[4] and for this reason there may not be precise agreement between decomposition rates in different reactant preparations. We have found no report, in the extensive literature, of a previous rate study for this particular reaction mixture.

DECOMPOSITION OF $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ IN SATURATED AQUEOUS Na_2CO_3

Using a method similar to that described above, 50.0 cm^3 of clear saturated Na_2CO_3 solution, thermostatted at reaction temperature, were transferred to a clean, dry and preheated flask. On the addition of salt W2 (200 ± 1 mg) with mixing a proportion of the reactant solid dissolved. A subsequent apparent change of texture of the

suspended material indicated the precipitation of a solid product. Reactant solutions initially contained an appreciable proportion of the H_2O_2 originally present in the $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$, the dissolution of which must have resulted in supersaturation with respect to sodium carbonate. The precipitate progressively formed, and which remained after completion of reaction, is identified as $Na_2CO_3 \cdot H_2O$, the phase stable in contact with solution throughout the temperature range of solutions studied here. After an appropriate period at reaction temperature (± 0.5 K) each reaction mixture was rapidly filtered and cooled, both solution and solid separately acidified and the total available oxygen contents of each determined by $KMnO_4$ titrations. Measurements
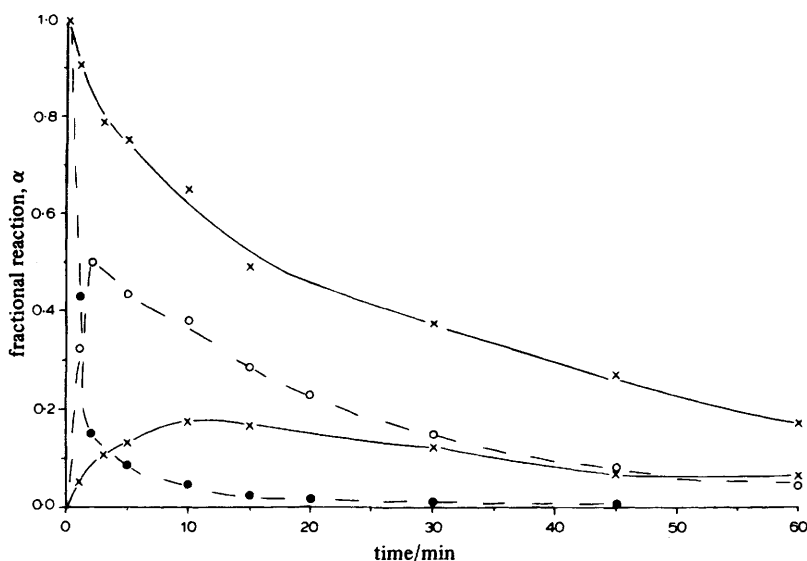

FIG. 1.—Decomposition of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ (200 mg solid) in 50 cm³ saturated aqueous Na_2CO_3 at 323 K. Available oxygen measured separately in both undissolved solid (removed by filtration) and in solution (in the filtrate) for two experiments with uncrushed ($\times$) and with crushed ($\bullet$, solid and $\bigcirc$, solution) salt W2. Following intitial dissolution of the solid the H_2O_2 concentration in solution rose to a maximum and thereafter diminished.

were performed in triplicate and (usually) for twelve appropriate time intervals for each of the isothermal reactions studied at 323, 328, 333 and 338 K. Reproducibility was very satisfactory, provided that the Na_2CO_3 solution was initially saturated and that the reactant solid was rapidly and effectively dispersed at the commencement of the experiment.

The pattern of kinetic behaviour observed was that characteristic of two-stage consecutive reactions.[5] Two typical sets of measurements are summarized in fig. 1: reactant dissolution yields H_2O_2 in solution,[2] the concentration of which initially increases to a maximum value and subsequently diminishes as reaction proceeds towards completion. Precrushing of the reactant solid resulted in a much increased initial dissolution rate, a higher maximum concentration of H_2O_2 achieved and more rapid overall decomposition.

Quantitative kinetic comparisons were made between the rates of homogeneous decomposition of H_2O_2 in saturated Na_2CO_3 (see preceding section) and (i) the rate of disappearance of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ at the maximum of the $[H_2O_2]$ against time

curve, where the known concentration of hydrogen peroxide in solution is temporarily constant, and (ii) for the crushed solid, the rate of H_2O_2 disappearance after completion of the initial rapid dissolution of the reactant. Rate coefficients for decomposition of H_2O_2 in the heterogeneous reactions, *i.e.* from the addition of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$, were $\times 0.6 \pm 0.1$ those for the homogenous reaction. Exact agreement cannot be expected for comparisons between rate processes believed to be controlled with the participation of trace impurities. This agreement is, therefore, accepted as being sufficiently close for us to conclude that the heterogeneous and the homogeneous processes proceed by the same rate-limiting step. The presence of solid $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ did not effectively enhance the reaction rate and the precipitation of sodium carbonate, consequent upon reactant dissolution, is expected to remove a proportion of the transition-metal ions believed to determine the rate of H_2O_2 decomposition.

The ready dissolution of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ in saturated Na_2CO_3 demonstrates that the present reactant is more soluble than $Na_2CO_3 \cdot H_2O$, the hydrate used to presaturate the solution and identified as the precipitate appearing progressively after dissolution of the perhydrate. The solubility of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ (S_0) may be influenced by the prevailing H_2O_2 concentration but measurements within the temperature range of interest here are not practicable for this unstable system. The notable increase in rate of reactant dissolution (shown by the very rapid initial rise of concentration of H_2O_2 in solution) caused by crushing shows that, as with many reactions of solids, kinetic characteristics are influenced by the effective area (a) of the reaction interface.[6] If the overall reaction proceeds by consecutive salt dissolution followed by H_2O_2 decomposition steps, the simplest form of the rate equations expected to be applicable is:

$$d[Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2]/dt = -k_s(S_0-S) S_0^{-1} a(1-x)^{\frac{2}{3}}$$

$$d[H_2O_2]/dt = k_s(S_0-S) S_0^{-1} a(1-x)^{\frac{2}{3}} - k_D[H_2O_2]$$

k_s and k_D are rate coefficients for the heterogeneous dissolution and homogeneous decomposition reactions, respectively. S is the concentration of salt present in solution at time t so that $k_s(S_0-S)S_0^{-1}$ provides a measure of the ease of dissolution at unit area of surface. The term $(1-x)^{\frac{2}{3}}$ is the differential form of the contracting cube equation,[6] where x is the fraction of the crystalline reactant remaining undissolved after time t. [The alternative term,[6] $(1-x)^{\frac{1}{2}}$, could well be applicable here owing to the asymmetric shape of the reactant crystallites.[1]]. The general integration and comprehensive testing of these equations is not possible because S_0 and its dependence on $[H_2O_2]$ are not known and no relationship between the variables can be identified. However, the kinetic observations are consistent with the above model.

The rate of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ dissolution was deceleratory throughout. An initial relatively rapid rate of dissolution diminished after the maximum $[H_2O_2]$ had been reached: this occurred for *ca.* 20% salt dissolution at 323 K and rose to *ca.* 50% at 338 K. The reduced rate of salt dissolution in the latter stages obeyed the first-order rate equation with $E \approx 40$ kJ mol^{-1}. Thus, the prevailing $[H_2O_2]$ exerts a greater control over the dissolution rate than changes in reactant surface area.

Data for the changes with the time of the overall fractional reaction [*i.e.* (H_2O_2 in reactant at time $= 0) - (H_2O_2$ in salt and solution at time $= t$)] closely obeyed the first-order equation. This obedience is regarded as empirical but the rate coefficients provide a useful comparative measure of reactivity, being $\times 0.5$ those for homogeneous H_2O_2 decomposition, and the calculated E value was 69 ± 7 kJ mol^{-1}. Fig. 2 compares overall rates of decomposition of uncrushed ($\bigcirc$) and of crushed ($\bullet$) $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ and ($\times$) the homogeneous reaction of H_2O_2, all in saturated Na_2CO_3 solution at 323 K.
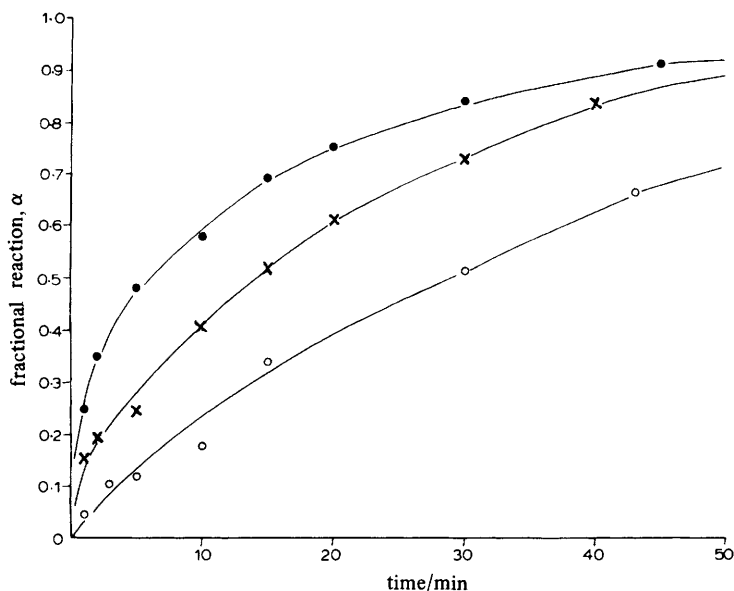
FIG. 2.—Comparison of overall decomposition rates (*i.e.* total H_2O_2 loss) of salt W2 at 323 K in saturated aqueous Na_2CO_3 for (○) uncrushed and (●) crushed salt and (×) the homogeneous reaction of similar H_2O_2 concentrations.

It is concluded that the rate-limiting step in reactions of both types is decomposition of H_2O_2 in solution, but the rate may be reduced when reactant dissolution is a necessary precursor step.

DECOMPOSITION OF $Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$ IN WATER

The high solubility of $Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$ in water made it impracticable to separate effectively solid and liquid phases for individual analyses. Thus, comparisons with other data are necessarily based on the overall extent of reaction (α, defined above), and the first-order rate equation was used as an empirical fit to the data. Two favourable factors which simplify the interpretation of observations are that the solubility of $Na_2CO_3 \cdot H_2O$ varies little[7] (*ca.* 10%) across the temperature interval studied (313-373 K) and that this solid product retains $\frac{2}{3}$ of the product water. This latter property is important when the volume of liquid H_2O added is small: results are classified below in two sections depending on whether the available water was sufficient or insufficient to dissolve completely the solid reactant. Unless otherwise stated all results reported below refer to 50 ± 2 mg samples of $Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$ reactant: this quantity was dissolved by 70 mg water (> 70 mg H_2O is referred to below as excess water).

Decompositions proceeded to completion in a single deceleratory reaction, typical results for salt W3 at 323 K in the presence of different amounts of water are illustrated in fig. 3 (*a*) (α against time plot) and 3 (*b*) (first-order plot). The variations of first-order rate coefficients with weight of water present for decompositions of salt W3 at 323 and at 333 K are shown in fig. 4. The discontinuity at 70 mg water (for 50 mg reactant) is associated with the minimum volume of added H_2O required to dissolve the solid reactant. Reactions above and below this discontinuity (and with no added water) are discussed separately in the succeeding sections.
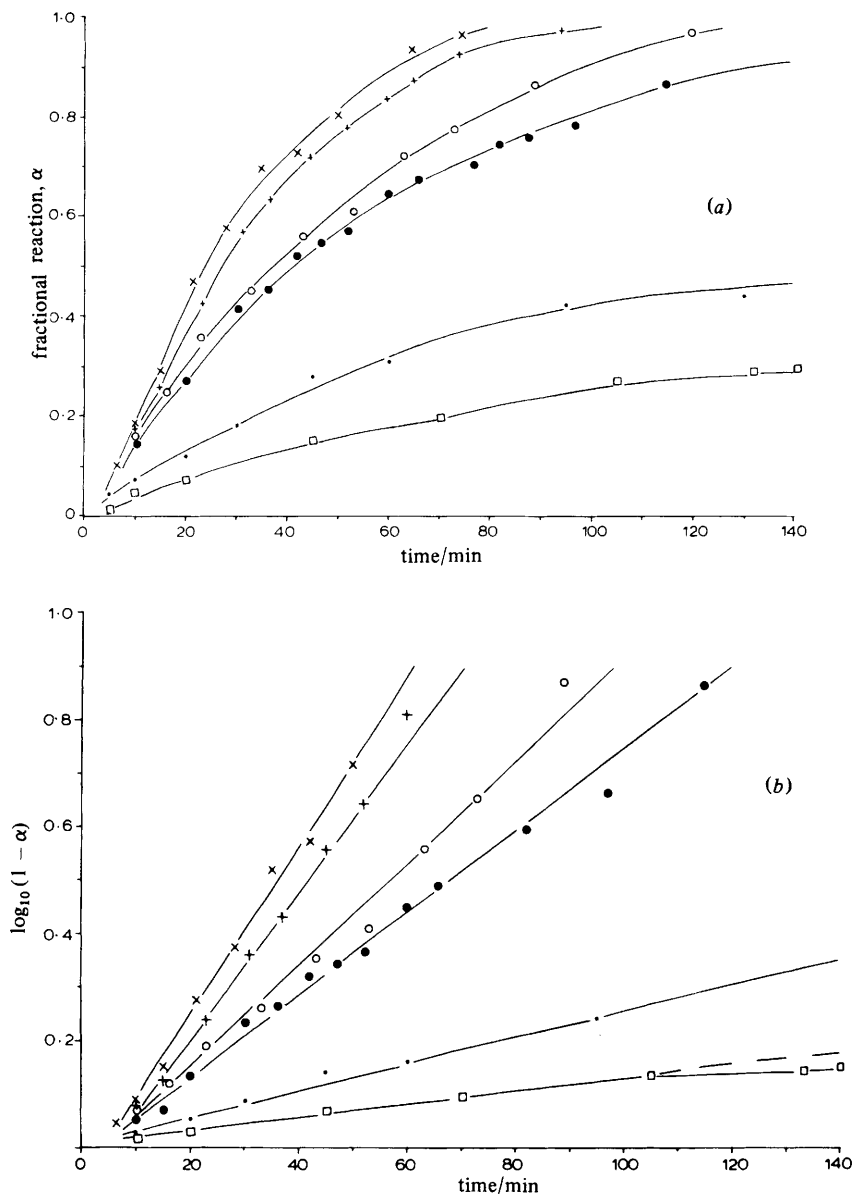
FIG. 3.—Rates of decomposition of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ (salt W3) at 323 K in the presence of the following added quantities of water (in mg): $\times$, 200; $+$, 150; $\bigcirc$, 100; $\bullet$, 80; $\cdot$, 40; $\square$, 20. (a) Fractional reaction (α) against time plots; (b) first-order plot.

EXCESS WATER

The first-order equation was obeyed between 0 and 80% reaction and rate coefficients measured for decompositions of salts W1, W2, W3 and L4 agreed within the limits of experimental accuracy. Calculated activation-energy values (for reaction with 70 mg water and also including some observations with 100 and 200 mg H_2O) were 80 ± 10 kJ mol^{-1} (313-343 K).

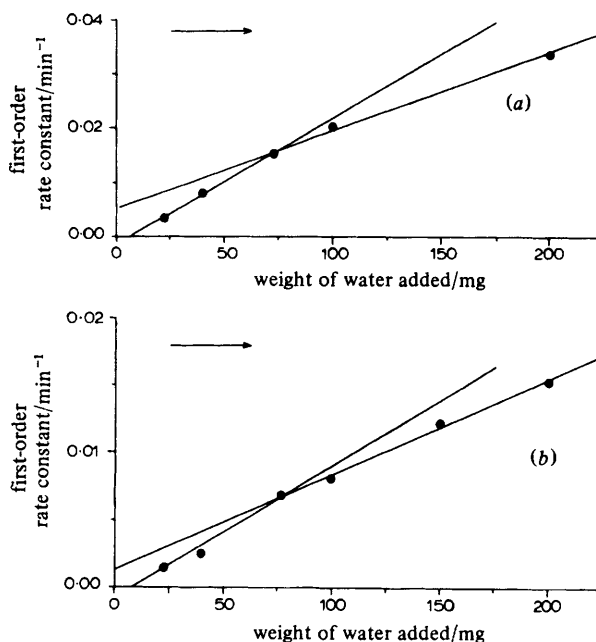FIG. 4.—First-order rate coefficients for the decomposition of $Na_2Co_3 \cdot 1\frac{1}{2} H_2O_2$ (salt W3) at (a) 333 and (b) 323 K plotted against weight of water added. The discontinuity corresponds to the minimum volume of water required to dissolve the reactant solid and the arrow specifies the first-order rate coefficient measured for the homogeneous decomposition of H_2O_2 in saturated Na_2CO_3 at the same temperature.

The increase in rate coefficients for reactions of 50 mg salt W3 between 70 and 200 mg water (fig. 4) is attributable to the increasing ease of reactant dissolution at the start of each experiment when the quantity of water available rises above the minimum required for solution. It was also confirmed that this rise does not, however, continue above 250 mg H_2O, where the rate is comparable to that of the homogeneous reaction of H_2O_2 in saturated Na_2CO_3 (values indicated by the arrows on fig. 4). The rate of decomposition of salt W1 was increased $\times 1.5$ by crushing before the addition of 70 mg water, an effect again attributable to an enhanced rate of reactant dissolution. This pattern of behaviour is entirely consistent with the salt dissolution followed by H_2O_2 decomposition mechanism described above. The significance of the dissolution step in controlling the overall reaction diminishes as the volume of water available is increased.

LESS WATER

Reactant mixtures containing 40 mg water or less underwent a discontinuous diminution in rate at α_B, so that first-order plots consisted of two linear regions (rate coefficients being k_1 and k_2 when $\alpha < \alpha_B$ and $\alpha > \alpha_B$, respectively). Although the reactants studied (salts F1, L4, W1, W2, W3 and W4) showed minor differences in behaviour, the values of α_B generally increased linearly with the quantity of water added. When 40 mg water was present, the magnitudes of α_B decreased with reaction temperature, being 0.45, 0.40 and 0.30 at 343, 333 and 323 K, respectively. Systematic variations were less apparent when 20 mg water was present, all values of α_B were 0.20-0.25. The behaviour of salt W4 at 373 K was exceptional in that α_B values rose

from 0.30 to 0.56 as the quantity of water added increased from 5 to 40 mg. (A possible difference at this high reaction temperature is the production of anhydrous Na_2CO_3 from the H_2O_2 containing solutions.)

Magnitudes of k_1 were directly proportional to weights of water added during reactions of salts W3 (fig. 4) and L4 but with salts F1, W1, W2 and W4 there was a relatively more rapid increase in k_1 with quantity of water present. Apparent activation energy values for decompositions of salts L4, W1, W2 and W3 with 40 mg water (k_1 values between 323-343 K) were 77 ± 5 kJ mol^{-1}, and similar magnitudes were calculated for reactant mixtures containing 20 mg H_2O, although for these the experimental uncertainty was greater.

Since k_1 and α_B values were approximately proportional to the quantity of liquid water added in the reactant mixture, it is concluded that this initial reaction is the homogeneous decomposition of H_2O_2 in aqueous solution during reactant dissolution, the rate of which diminishes as $Na_2CO_3 \cdot H_2O$ saturation is approached. Reaction rates of the several salts studied were closely similar, minor differences in behaviour being attributable to particle size variations, which can influence dissolution.

If k_1 is attributed to H_2O_2 decomposition during initial salt dissolution, the slower later process (k_2, when $\alpha > \alpha_B$) can be associated with the continued reaction when $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ can be accepted into solution only with concurrent displacement of the less soluble $Na_2CO_3 \cdot H_2O$.[7] This process is identical with that described above for reaction of sodium carbonate perhydrate in saturated Na_2CO_3, and the ratio of the first-order rate coefficients for this reaction to those for the homogeneous decomposition of H_2O_2 in Na_2CO_3 solution (relative ratios were 0.56-0.58:1.00 between 323 and 338 K) should be comparable to the k_2/k_1 ratios for the $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ in H_2O reaction. Mean k_2/k_1 values measured for salts, L4, W1, W2 and W3 (323-343 K) were 0.47 ± 0.10 with 40 mg H_2O and 0.30 ± 0.10 with 20 mg H_2O. This agreement is sufficiently close to indicate the occurrence of similar reaction types, since diffusion effects must be expected to introduce inhomogeneity within the small volumes of water added and so appreciably reduce the relative rates of reaction when $\alpha > \alpha_B$. Moreover, activation energies (*ca.* 50 kJ mol^{-1}) calculated from k_2 values were lower than those found for the homogeneous breakdown of H_2O_2 (68 kJ mol^{-1}) but nearer values characteristic of processes in which dissolution influenced decomposition rates.

Although the levels of reactivity and the kinetics of decompositions of salts F1, L4, W1, W2 and W3 were closely comparable (323-343 K), the behaviour of salt F1 differed in that k_2/k_1 ratios were small (0.2) and the activation energy, determined from the extended temperature range 323-373 K, was high (*ca.* 120 kJ mol^{-1}) for reactions in 10-40 mg H_2O. This commercial preparation is described as being comprised of 'abrasion resistant particles' and so it is concluded that the particle sizes and/or surface textures of this reactant are different from those of the other salts. Such differences can be expected to modify the kinetics of the dissolution step and, in consequence, the concentration variations of dissolved H_2O_2 and, therefore, the overall decomposition rate.

We conclude that the rates of both stages in decomposition are controlled by the homogeneous breakdown of H_2O_2 in aqueous solution: this is an identical rate-determining process to that proposed for the reactions decscribed in the preceding sections. During the initial process ($\alpha < \alpha_B$) the concentration of H_2O_2 is high owing to reactant dissolution in water. Thereafter, ($\alpha > \alpha_B$) this concentration is reduced as a consequence of the requirement that reactant dissolution necessitates displacement of $Na_2CO_3 \cdot H_2O$ from solution.

NO ADDED WATER

Rates of decomposition of the present reactants in the absence of added water, studied by the titration method after reaction periods of several days at 323-343 K, agreed well with rates obtained by extrapolations from the previous higher-temperature vacuum measurements.[1] These data confirmed that the initial stages of reaction of the dry salts were acceleratory and the addition of water increased rate coefficients *ca.* $\times 10^4$. Thus we again[1] conclude that both the levels of reactivity and the mechanisms of decomposition are different for reactions in the absence and in the presence of liquid water.

DECOMPOSITION OF $Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$ WITH ADDED H_2O_2

It was found practicable to make only preliminary kinetic measurements for the decomposition of $Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$ with added H_2O_2 since the relatively small volumes of liquid present could not be separated from the solid for individual analyses. First-order rate coefficients for the decomposition of salt F1 (100 mg) with H_2O_2 (80 mg), 323-345 K, were comparable with the latter stages (k_2) of reaction with similar quantities of water. When the reactant mixtures consisted of 100 mg salt F1, 40 mg H_2O_2 and 40 mg H_2O the first process, corresponding to reaction of the added H_2O_2, was relatively rapid but the rate subsequently diminished. The mechanism of these reactions could not be elucidated in detail, but it seems probable that $Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$ is less soluble in H_2O_2 than in water and, therefore, reaction proceeded more slowly.

INFLUENCE OF VARIOUS ADDITIVES ON THE DECOMPOSITION OF $Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$ IN WATER

The influences of various additives, selected as probable inhibitors of the homogeneous decomposition of H_2O_2, on the reactions of $Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$ and water were investigated to determine the possible role of transition-metal-ion impurities in controlling rates of the processes studied here. The salt–water system was considered to be of greatest interest, since both dissolution and decomposition steps have been identified as influencing the overall reaction rate.

The addition of 5 mg of NH_4Cl or of $(NH_4)_2SO_4$ to salt W3 (50 mg) and H_2O (40 mg) did not change the pattern of kinetic behaviour, although reaction rates were increased $\times 3$. Thus the NH_4^+ ion in solution apparently does not possess the inhibitory effect found[1] for NH_3 gas on the solid-state reaction. The addition of 5 mg montmorillonite or of 0.08 mg Fe^{3+} dissolved in the added water of the same reaction mixture composition also produced a similar increase $(\times 3)$ in reaction rate. The presence of 5 mg of the molecular sieves NaY, NH_4Y or HY, again in the same mixture of reactants, resulted in a just detectable $(\times 1.5)$ rise in reaction rate. It seems probable that the promoting effect of all these additives could be a consequence of the presence of trace amounts of transition-metal-ion impurities concurrently introduced into the aqueous solution in which reaction proceeds.

In contrast, sodium silicate, urea and sodium chlorate each exhibited appreciable inhibitory effects that are separately described below.

SODIUM SILICATE

Comparative studies were made of the rates of decomposition of salt W3 (100 mg), water (80 mg) and sodium silicate (0.0, 0.2, 1.0 or 10.0 mg: approximate composition $2Na_2O \cdot 0.5SiO_2$, and containing *ca.* 100 ppm Fe impurity) between 333-363 K. The pattern of kinetic behaviour was unaltered by the additive, typical α against time plots
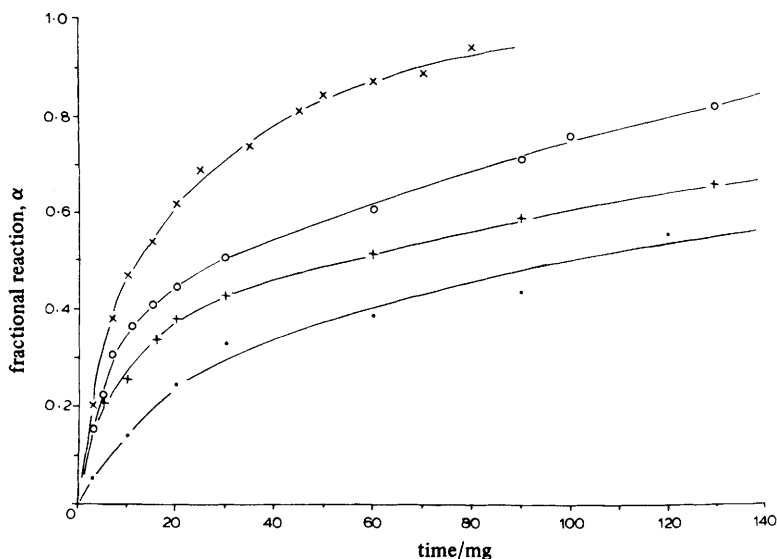
FIG. 5.—Plots of α against time for the decomposition of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ (100 mg salt W3) and 80 mg H_2O at 343 K to which the following quantities of sodium silicate had been added (in mg): $\times$, 0; $\bigcirc$, 0.2; +, 1.0; $\cdot$, 10.0.

for reactions at 343 K are shown in fig. 5, and reaction rates were progressively diminished by increasing amounts of added sodium silicate. When 0.2 or 1.0 mg additive was present α_B values were relatively low (0.07-0.17) but increased again ($\alpha_B \approx 0.35$) when 10.0 mg was added. Similar behaviour was observed at 353 and 363 K. 0.2 and 1.0 mg additions of sodium silicate caused only slight reductions in k_1 values ($\times 0.91 \pm 0.03$ of that when water only was present), but the reduction in k_2 was significantly greater ($\times 0.25$). With 10.0 mg sodium silicate the reductions in both (k_1 and k_2) values were appreciable ($\times 0.2$ and $\times 0.16$) at 343 K and (0.5 and 0.25) at 363 K, compared with rates of reactions in pure water. Activation-energy values calculated for reactions in the presence of sodium silicate were larger (100-110 kJ mol^{-1}) than those found when water only was added (*ca.* 80 kJ mol^{-1}).

It is apparent from the above results that small quantities (0.2 and 1.0 mg) of sodium silicate were effective in reducing only the rate of the second and slower stage of reaction (k_2), whereas larger amounts (*e.g.* 10 mg) were required to influence the earlier stage (k_1). This trend can be qualitatively identified in fig. 5. The addition of small quantities of Fe^{3+} in solution (10 ppm) to reactant mixtures also containing sodium silicate resulted in no appreciable increase in reaction rates, suggesting that the silicate present is capable of suppressing the catalytic properties of the impurity transition-metal ion.

UREA

Rates of decomposition of salt F1 (50 mg) were measured from comparative series of experiments with 10, 20 or 40 mg water and 5 or 10 mg urea (323-373 K). Behaviour patterns were identical with those found with water alone, except that all rate coefficients (k_1 and k_2 values) were reduced $\times 0.7 \pm 0.1$. Activation-energy values were unchanged, 109 kJ mol^{-1}.

SODIUM CHLORATE
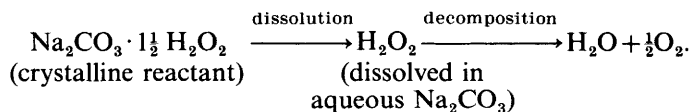
The initial stage (k_1) of reaction of salt F1 (100 mg) with 40% solution of $NaClO_3$ (80 mg) was almost entirely suppressed ($\alpha_B < 0.05$) and the rate of the subsequent reaction (k_2) was reduced $\times 0.5$.

MECHANISMS OF INHIBITION

The reductions in reaction rates in the presence of the above three inhibitors are attributable to the suppression of a catalytic process promoting the homogeneous H_2O_2 decomposition: this is the usual explanation of negative catalysis. Transition-metal ions, participating in electron-transfer processes, are regarded as the most probable catalysts in the homogeneous reaction.[4] Indeed the three effective inhibitors mentioned above can be envisaged as reducing the activities of these impurities, although by three distinct effects. (i) Sodium silicate is expected to remove from solution transition-metal ions by the formation of most insoluble compounds. The promotional effect of Fe^{3+} ions, intentionally introduced, was removed when sodium silicate was also added. (ii) Urea may be expected to complex with transition-metal ions, thereby changing the relative stabilities of the different valence states and thus the relative ease of participation in electron-transfer interactions. (iii) While the chlorate ion, ClO_3^-, is not expected to complex with transition-metal ions, the strongly oxidizing properties of this additive could be expected to maintain transition-metal ions in their highest valence state (perhaps also involving interactions with the intermediates of H_2O_2 breakdown). This must reduce the effectiveness of such catalysts in electron-transfer processes.[8] These three modes of inhibition (precipitation, complex formation and oxidation) are consistent with control of H_2O_2 decomposition by electron-transfer processes involving participation of multivalent ionic impurities.

CONCLUSIONS

Evidence has been given above that the decomposition of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ in the presence of liquid water proceeds by a mechanism that is quite different from that of the solid-state reaction[1] in vacuum. The two rate processes occur in different temperature intervals and exhibit very different kinetic characteristics. When reactant mixtures contained small amounts of water, decomposition rates were approximately proportional to the volume of liquid present and this increased towards the value characteristic of the independently measured rates of the homogeneous reaction when sufficient solvent was present to effect complete solution. This pattern of behaviour indicates that $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ first dissolves and H_2O_2 decomposes homogeneously in solution:

$$Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2 \xrightarrow{\text{dissolution}} H_2O_2 \xrightarrow{\text{decomposition}} H_2O + \tfrac{1}{2}O_2.$$
$$\text{(crystalline reactant)} \qquad \text{(dissolved in} \atop \text{aqueous } Na_2CO_3\text{)}$$

The arrows represent controlling processes in the two consecutive steps, both of which exerted some control upon overall reaction rate, under the conditions studied here. The rate of dissolution was increased, and became less significant in determining the decomposition rate, if either the quantity of water available or the surface area of the salt was increased.

Separation of the products for individual analyses was impracticable for the salt–water reaction mixtures owing to the solubility of $Na_2CO_3 \cdot 1\frac{1}{2} H_2O_2$ and the rapid

decomposition process. However, the first-order equation provided a satisfactory empirical measure of the rate of the overall process and comparisons showed that the levels of reactivity of the several preparations studied were closely similar. Moreover, the present system was found to be particularly amenable to kinetic analysis and is of interest because few such 'mixed-phase' solid and liquid reactions involving heterogeneous and homogeneous steps have previously been the subject of quantitative rate studies. Favourable features here include the availability of independently measured kinetic data for the several closely related systems, the almost constant volume of water present and the almost constant solubility of product $Na_2CO_3 \cdot H_2O$ (where formed). However, it was not possible to resolve completely all absolute rates of the two contributory reaction steps.

Although it was not a primary objective of our study, the results are consistent with a model of H_2O_2 decomposition in aqueous solution controlled by transition-metal-ion catalysts presumably involving electron transfer. This satisfactorily explains the inhibiting effects reported above. The appreciable activity shown by even minute amounts of impurity in these reactions makes it difficult to formulate a mechanism for the decomposition of H_2O_2 alone and, in the literature, more interest has been directed to the mode of action of various catalysts.

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