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Thermal Decomposition of Sodium Carbonate Perhydrate in the Solid State

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On heating sodium carbonate perhydrate under vacuum, \sim 360-410 K, the constituent hydrogen peroxide decomposed as follows: $Na_2CO_3 \cdot 1.5H_2O_2 \rightarrow Na_2CO_3 + 1.5H_2O + 0.75O_2$. Fractional decomposition (α)-time curves were sigmoid shaped. The reaction rate in 20 torr water vapor was appreciably less than that under vacuum, behavior which markedly contrasts with the large increase in rate found when liquid water was present. It is concluded that the water accelerates the solid state reaction and escape of this product is opposed by the presence of an effective barrier phase of anhydrous Na₂CO₃ product. When water vapor was available the residual product was reorganized and the opening of channels permitted the escape of water, with a consequent reduction in the overall reaction rate.

Kinetics and mechanisms of thermal decomposition reactions of solids have often been classified¹ on the basis of two different types of behavior. The rate processes of one class are irreversible and sometimes exothermic, as exemplified by the pyrolyses of azides, permanganates, and perchlorates. In contrast, reactions of the alternative group are reversible dissociations which are frequently endothermic, including, for example, the release of water from many hydrates and of carbon dioxide from carbonates. Kinetic characteristics of reactions in the second class show features which are not found in those of the former, significant differences being that reported activation energies for salt breakdown are often close to the value of the enthalpy of dissociation and the occurrence of Smith-Topley behavior (a specific form of the dependence of reaction rate on the prevailing pressure of product, notably water, in the vicinity of the reactant, see Figures 1 and 2, also pp 213–215, in Chapter 8 of ref 1).

Not all solid state decompositions can be correctly assigned to one or other of these two classes, and the present report is concerned with a reaction which incorporates features characteristic of both types, the pyrolysis of sodium carbonate perhydrate, Na₂CO₃·1.5H₂O₂. (This salt will be referred to below by the convenient and widely used, though incorrect, name, sodium percarbonate.) The entity which undergoes exothermic and irreversible breakdown on heating, hydrogen peroxide of crystallization, is present in the reactant in a structure from which it may (at least, in principle) be released unchanged by a process analogous to water evolution from crystalline hydrates, reactions already cited as being typical reversible and endothermic dissociations. The results obtained in the present study indicate that during decomposition of sodium percarbonate under vacuum or in water vapor the hydrogen peroxide undergoes breakdown within the crystalline reactant. The mechanism operating is, however, quite different from that believed to operate when small, indeed trace amounts of liquid water, are present, since this additive exhibits a pronounced catalytic effect, increasing the rate of product formation and profoundly modifying the kinetic characteristics. Reactions occurring in the presence of liquid water will be more fully described and discussed in a future article.

The preparations, structures, and compositions of sodium carbonate perhydrates have been reported by Makarov and Chamova² and by Firsova et al.³ The thermal decomposition of sodium percarbonate has been described⁴ as proceeding through three successive stages involving different kinetic obediences. Salts related to the present reactant, for which thermal decomposition studies have been reported, include sodium and potassium peroxocarbonates,⁵ K₂CO₃·3H₂O₂,⁶ Rb₂CO₃·3H₂O₂,⁷ and Cs₂C- $O_3 \cdot 3H_2O_2$.

Experimental Section

Reactants. Sodium percarbonate samples L1, L2, and L3(Fe) were prepared^{2,3,8} in the laboratory by the addition of excess hydrogen peroxide (86% Laporte stabilized) to saturated aqueous sodium bicarbonate (Analar) at ambient temperature. After 30 min of stirring, absolute ethanol was added and the white precipitate of needle-shaped crystals filtered. This product was washed with absolute ethanol, dried overnight, and protected from light during storage. Preparations L1, L2, and L3(Fe) contained 15.0, 14.6, and 13.9 \pm 0.2% available oxygen, respectively, determined by KMnO₄ titration. Heavy metal impurities were <5 ppm in L1 and L2, while L3(Fe) contained 45 ppm of Fe³⁺, resulting from the intentional introduction of iron

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into the solution before salt precipitation.

Salt L4 was prepared on a laboratory scale by Solvay et Cie, using stabilizer-free reagents containing particularly low (<1 ppm) concentrations of heavy metal impurities. A 30% aqueous solution of sodium carbonate was added slowly (30 min) to excess 30% hydrogen peroxide at 278 K. The crystals obtained were washed twice with acetone and dried at ambient temperature. Available oxygen, also determined by KMnO₄ titration, was $15.0 \pm 0.2\%$.

Preparations W1, W2, and W3 were supplied by Laporte Industries Ltd. These were manufactured by the wet method, which is a commercial process, using a batch recycling system whereby sodium carbonate is allowed to react with 60% hydrogen peroxide; small quantities of proprietary stabilizers were present. The crystalline product was precipitated, separated in a centrifuge, and dried. Available oxygen contents of samples W1, W2, and W3, again determined by KMnO₄ titration, were 13.6, 13.9 and 13.7 \pm 0.2%, respectively.

Methods. Accumulatory Apparatus. Kinetics of salt decomposition were studied in a conventional constant volume vacuum apparatus by using ~ 8 mg samples of reactant, weighed to ± 0.1 mg. Pressures of oxygen gas evolved were measured by a McLeod gauge, separated by an 80 K cold trap from the previously outgassed reactant, which was maintained at the isothermal (± 0.5 K) reaction temperature.

Gravimetric Apparatus. Reaction rates were also studied from changes in the extension of a helical glass spring, measured by a catharometer, representing mass loss during isothermal (± 0.5 K) decomposition of (~ 40 mg samples) reactant under vacuum or in a controlled pressure of water vapor.

Unless otherwise stated, studies were concerned with the salt as prepared and data concerning crystallite shapes and sizes for the various samples of reactant investigated are given below.

Results

Stoichiometry of Reaction. The total mass losses, for each of the samples investigated in the present study, on heating within the temperature interval used for kinetic studies, 350-425 K, were 29.5-32.0%, of which 12.5-13.5%represented the noncondensable product (oxygen). The residual product was identified as anhydrous Na₂CO₃, from comparison of X-ray diffraction patterns with those given by authentic specimens. No hydrogen peroxide could be detected in the condensed volatile products by KMnO₄ titration (estimated to be capable of detecting an amount corresponding to 0.2% available oxygen). The decomposition can, therefore, be accurately represented by

$$Na_2CO_3 \cdot 1.5H_2O_2 \rightarrow Na_2CO_3 + 1.5H_2O + 0.75O_2$$

Deviations of measured values from the theoretical total mass loss for this equation (32.5%) and the oxygen yield (15.3%) are attributable to reactant impurities and deterioration during storage. Most samples underwent ~1% mass loss in the temperature interval immediately below the onset of decomposition (330-350 K), attributable to evolution of water impurity.

Kinetics of Sodium Percarbonate Decomposition. Fractional decomposition (α)-time curves for the isothermal pyrolysis of sodium percarbonate were invariably sigmoid, in the absence of water. Typical α -reduced time⁹ ($t_r = 1.00$ at $\alpha = 0.5$) data are illustrated in Figure 1, a composite plot comprised of 84 measured points from six separate isothermal reactions of salt L1 between 357-382 K, under accumulatory conditions. There was a very close similarity of the shapes of all α -time curves for reactions



Figure 1. Typical α -reduced time ($t_r = 1.00$ at $\alpha = 0.50$) data for the isothermal decomposition of sodium percarbonate. Measured points from six experiments on the reaction of sait L1 between 357 and 381 K; there was no systematic change in curve shape with reaction temperature. (\Box , 357.4 K; *, 368.0 K; O, 372.8 K; •, 373.1 K; +, 377.8 K; ×, 381.3 K.) The line is the Avrami–Erofe'ev equation (n = 3), i.e., eq 1.

of the several preparations studied by accumulatory or by gravimetric methods under vacuum or in water vapor. Reproducibility of kinetic characteristics was very satisfactory. Some small variations in rate behavior will be described below; most α -time curves showed no systematic changes of shape with reaction temperature.

Sigmoid α -time curves for reactions of solids are frequently ascribed to mechanisms involving the nucleation and growth of a product phase.¹ From a kinetic analysis of the present observations, using the most widely accepted rate expressions,⁹ it was concluded that the Avrami-Erofe'ev equation (n = 3)

$$[-\ln (1-\alpha)]^{1/3} = k(t-t_0)$$
(1)

provided the most accurate fit to the data. To permit direct comparison of this obedience to our measurements, the theoretical line for eq 1 has been included in Figure 1. Most plots of $[-\ln (1 - \alpha)]^{1/3}$ against time were linear for $0.05 < \alpha < 0.7$ but when $\alpha > 0.7$ the reaction was completed more rapidly than theoretical expectation. Magnitudes of t_0 varied markedly, negative values being found for reactions at the lower temperatures.

Due to these shortcomings in the kinetic obedience of results to eq 1, the fit of data to alternative rate expressions was tested. The most satisfactory representation of behavior found, as adjudged by both precision and extent of fit, was afforded by the relation

$$1 - (1 - \alpha)^{1/2}]^{1/2} = k(t - t_0)$$
⁽²⁾

(The theoretical basis of this equation will be discussed below.) Typical plots of $[1 - (1 - \alpha)^{1/2}]^{1/2}$ against time for the accumulatory decomposition of sample L1 at four temperatures 355-384 K are shown in Figure 2. The results of all kinetic analyses of the present study, using eq 2, are summarized in Table I. Decomposition characteristics of samples L1 and W2 (i.e., magnitudes of k at 373 K and activation energies) measured for both salts alternatively by the accumulatory (O_2 evolution only) and by the gravimetric (loss of both O_2 and H_2O) methods agreed within experimental accuracy. The only feature of the gravimetric measurements for preparation L1, which was absent from the accumulatory observations, was the occurrence of an initial deceleratory mass loss (corresponding to $\alpha \sim 0.04$) prior to the onset of the main reaction, attributable to the release of a condensable

TABLE I: Summary of Kinetic Observations for Decomposition of Various Preparations of Sodium Carbonate Perhydrate

sample	apparatus ^a	temp, K	reaction rate at 373 K, ^b min ⁻¹	a ^c	app activatn energy, kJ mol ⁻¹
L1	A	357-384	0.013	{ 0.01-0.90, < 375 K { 0.01-0.75, > 375 K	115 ± 5
L1	G(V)	365-379	0.011	0.10-0.90	121 ± 12
L1	G(W)	365-385	0.0055	0.10-0.95	155 ± 12
L2	A	361 - 379	0.014	0.10-0.85	117 ± 5
L3(Fe)	A	357-375	0.043	0.05-0.85	115 ± 5
L4	\mathbf{A}	361-403	0.010	0.04-0.90	112 ± 5
W1	Α	373-408	0.0025	{ 0.05-0.90, <395 K { 0.02-0.75, >395 K	125 ± 10
W2	Α	359-385	0.0056	0.03-0.85	133 ± 7
W2	G(V)	371-391	0.0050	0.12-0.90	127 ± 12
$W2^d$	$\mathbf{G}(\mathbf{V})$	371-384	0.0065	0.10-0.95	127 ± 12
W2	G(Ŵ)	370-394	0.0022	0.05-0.90	159 ± 5

^a A represents the accumulatory apparatus and G, the gravimetric apparatus under (V) vacuum or (W) 20 torr of water vapor. ^b k in eq 2. ^c Range of α over which eq 2 is obeyed. ^d Reactant crushed in pestle and mortar.



Figure 2. Representative plots of $[1 - (1 - \alpha)^{1/2}]^{1/2}$ against time for the vacuum decomposition of sodium percarbonate, salt L1, at various temperatures 355–384 K.

product, probably water. The subsequent α -time data exhibited the sigmoid α -time relation characteristic of the vacuum reaction and eq 2 was obeyed $\alpha > 0.1$. Similar initial deceleratory precursor rate processes were detected in all gravimetric studies. Rates of decompositions of salts L1 and W2 in water vapor (~20 torr, excess condensed on the cooler parts of the vacuum envelope) were significantly slower (0.4–0.5 times slower, Table I) than the vacuum reaction and magnitudes of apparent activation energies were appreciably increased, from ~125 to 157 kJ mol⁻¹.

An increase in the initial period of outgassing of salt L1 from 2 to 7 h resulted in no detectable influence on the kinetics of subsequent decomposition. Accumulatory reactions of salt L1 at 353 K were interrupted at $\alpha = 0.13$ and 0.30, the reactant cooled to 288 K, and evacuated 18 h with an 80 K trap on the apparatus. On reheating to 353 K the rate of decomposition was rapidly restored to the value expected for the uninterrupted reaction and no further induction period was apparent.

Kinetics of Sodium Percarbonate Decomposition in the Presence of Liquid Water. A kinetic study was made of the isothermal decomposition of salt W2 in the presence of added water. Weighed individual samples of reactant $(50 \pm 2 \text{ mg})$ sodium percarbonate and 20, 40, or 70 mg of distilled water (measured by micropipet) were sealed in small glass ampules (~50 mm length and 6 mm diameter). These were reacted at 323, 333, or 343 (±1) K, each for an appropriate time interval and the quantity of available oxygen remaining in the product determined by KMnO₄



Figure 3. Typical α -time plots for the isothermal decomposition of sodium percarbonate (salt W2) at 333 ± 1 K in the presence of added liquid water (50 mg of salt W2 and 20 (X), 40 (O) or 70 (\bullet) mg of water).



Figure 4. Typical α -time plots for the isothermal decomposition of sodium percarbonate (salt W2) in the presence of added liquid water (50 mg of salt W2 and 40 mg of water: 323 (X), 333 (O), and 343 (\odot), \pm 1 K).

titration. Typical α -time curves are shown in Figures 3 and 4, from which it is apparent that when liquid water is available the reaction proceeds in a lower temperature range than the vacuum decomposition (see data for salt W2 in Table I) and that the rate process is deceleratory throughout. This notable increase in reactivity, the dependence of reaction rate on quantity of added water, and marked change in kinetic characteristics must be attributed to the occurrence of an alternative reaction mechThermal Decomposition of Sodium Carbonate Perhydrate

anism, differing from that operating under vacuum conditions. The simplest explanation, consistent with the data available, is that hydrogen peroxide undergoes homogeneous decomposition following reactant dissolution in the aqueous phase, known to be present here but believed to be absent during the vacuum reaction with which the present article is primarily concerned.

Mechanical Pretreatment of the Reactant. Salt L2 was compressed between teflon disks (20 MN m⁻² for 2 min) to form a coherent pellet which was decomposed at 364 K. The induction period to reaction (15 min) was shorter than that of untreated salt (27 min) and subsequently eq 2 was obeyed for $0.10 < \alpha < 0.95$; the magnitude of the rate constant was just perceptably larger (1.2 times) than that of uncompacted salt. Crushing salt L2 in pestle and mortar reduced the induction period to reaction at 361 K from 32 to 5 min and the acceleratory portion of the α -time curve was reduced in relative significance, through completion of the initial increase in rate by $\alpha = 0.1$. The rate of the first portion of the deceleratory process (between $\alpha = 0.1$ and (0.4) was greater (6 times) than that characteristic of the prepared salt, though this relative enhancement diminished to 2 times in the later stages. The influence of mechanical pretreatment on reaction rates varied with severity, the increase in reaction rate became less pronounced after a longer time of crushing.

In contrast with the behavior described above for salt L2, crushing exerted remarkably little influence on the kinetics of decomposition of salts L3(Fe) and W2. Mechanical treatment reduced (0.5 times) the induction period to decomposition of salt L3(Fe), while the rate of decomposition of salt W2 was slightly increased (Table I), though the shape of the α -time curve was not significantly changed.

Effects of Additives. The effects of the following additives ($\sim 20\%$ by weight) as possible inhibitors for the decomposition of salt W2 at 386 ± 2 K were investigated: sodium silicate, sodium phosphate (both are inhibitors for the decomposition of liquid H_2O_2 , urea (which forms a molecular complex with H_2O_2), quinol (which quenches free radical reactions), montmorillonite (a clay which absorbs water), ammonium nitrate, ammonium acetate, ammonium phosphate, and acetamide. These additives (simply mechanically mixed as fine powders to avoid the complex effects which result from crushing and compaction) caused remarkably little change in the kinetics of sodium percarbonate decomposition; α -time curves were almost identical with those of the pure salt and eq 2 was obeyed for $0.07 < \alpha < 0.97$. Urea was exceptional in that, when present, the value of k was reduced (~ 0.65 times). Induction periods were increased in the presence of ammonium salts and quinol by the approximate time required for the additive to be removed from the reaction vessel by sublimation. Ammonia gas (15 torr) appreciably reduced $(\sim 0.6 \text{ times})$ the reaction rate.

Infrared Measurements. The infrared spectra of the residues from decomposed ($\alpha = 1.00$) salts L4 and W1 were indistinguishable from those of authentic Na₂CO₃ (consistent with the X-ray diffraction identification of the solid reaction product). No additional features could be discerned for samples of salt partially decomposed to $\alpha = 0.35$ and 0.70.

Surface Area Measurements. Surface areas of samples of salt decomposed completely ($\alpha = 1.00$), or partially to a preselected α value, were determined ($\pm 1.0 \text{ m}^2 \text{ g}^{-1}$) by application of the BET equation to the nitrogen adsorption isotherm at 80 K. Results are summarized in Table II and Figure 5. Salt decomposed "under vacuum" was heated

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TABLE II: Surface Area $(m^2 g^{-1})$ of Residues from Decomposition of Sodium Carbonate Perhydrate under Vacuum and in Water Vapor^a

	area of residue from decomposition			
salt	under vacuum in	1 20 torr H ₂ O		
L4	11.5	2.8		
W1	25.3	8.7		
W2	31.4	5.8		

^a Measured by the BET method. Each recorded value is the mean of duplicate measurements.



Figure 5. Variation of surface area of sodium percarbonate (preparations L4 and W2) with α , measured from nitrogen adsorption at 80 K, using the BET method.

during maintained evacuation to ensure the rapid removal of all volatilized products. During reactions "in 20 torr of H_2O " the products were not withdrawn from the reaction vessel, and water condensed on the cooler parts of the glass envelope.

The total surface areas of salts L4 and W2 progressively increased with extent of vacuum reaction; the effect was relatively greater as α approached unity, Figure 5. After exposure of the residue from vacuum decomposed salt W2 to water vapor for 18 h at 293 K, the surface area diminished from 31.4 (Table II) to 10.2 m² g⁻¹.

Examination of the Salt by Electron Microscopy. Since sodium percarbonate is unstable in the electron beam, it was necessary to use a replication technique and, therefore, only surface textural features could be examined.

Salt L1 consisted of elongated, fiberlike crystals having maximum dimensions 10–30 μ m and major-minor axes ratios of ~3–10:1. These were aggregated in coherent parallel alignment groupings and surfaces characteristically included striations parallel to the major axis. Pitting and cracking of surfaces of the unreacted salt was rare but with progressive decomposition (samples were examined at $\alpha = 0.06, 0.27, 0.63, \text{ and } 1.00$) there were textural changes, including surface roughening, pore development, and particle disintegration. Crystal sizes and shapes in salt L4 were generally similar to those of salt L1, but here there was some cracking and pitting of surfaces of the unreacted material ($\alpha = 0.00$). Due to the diversity and variability of textures apparent in the individual crystals of each sample, no systematic changes in appearance with α could

be recognized. Salts W1 and W3 were composed of approximately spherical granules with generally smooth surfaces, though there were also local irregularities. There were indications that a pore structure was developed during decomposition.

No surface feature was identified, in any of the series of samples examined, that could be used for the unambiguous recognition of either the reactant or the product phase or to permit a positive distinction to be made between them. Any changes of textural appearance occurring during reaction were insufficient to provide information concerning the existence of a reaction interface or to characterize the reaction as a nucleation and growth process. The results of this electron microscopic study must, therefore, be regarded as inconclusive.

Discussion

The present report is exclusively concerned with sodium percarbonate decomposition in the absence of liquid water. When this solvent is available the kinetics and mechanism of the reaction were profoundly modified and a report of the distinct and different rate process will be published elsewhere.

Since the kinetic characteristics of sodium percarbonate decomposition measured by volumetric (O_2 evolution only) and by gravimetric (production of both O_2 and H_2O) methods were identical and since no detectable quantity of H_2O_2 was volatilized unchanged, it is concluded that the reaction

 $Na_2CO_3 \cdot 1.5H_2O_2 \rightarrow Na_2CO_3 + 1.5H_2O + 0.75O_2$

occurs in the solid state. The initial minor deceleratory process, detected in gravimetric studies but absent from volumetric measurements, and varying in extent between the several preparations, is attributable to water release; preparations of sodium percarbonate always contain appreciable quantities of impurities and deteriorate during storage. Oxygen contents are invariably below the theoretical maximum (15.3% for Na₂CO₃·1.5H₂O₂); available oxygen in the present samples ranged from 13.6 to 15.0%.

While there appears to be conclusive evidence that the unstable constituent (H_2O_2) undergoes irreversible breakdown within the reactant crystal, there is less direct information concerning the course of the contributory chemical steps. The microscopic examinations yielded only a very qualitative indication that reaction was accompanied by some crystallite cracking and surface roughening. There was no positive evidence that decomposition occurred at a reaction interface or that the mechanism involved the nucleation and growth of a product phase. In the absence of reliable observational information, the analysis of kinetic data provides the most secure foundation for mechanistic interpretation.

The fit of rate measurements to eq 1 was not regarded as acceptable and eq 2 was used in Table I as an empirical relation for the quantitative comparison of the reactivities of the different sodium percarbonate preparations studied. A theoretical basis for eq 2 is provided by a reaction model based on the following assumptions. (i) Reaction proceeds inward from crystal surfaces. If a diffuse interface is developed within reactant particles and the rate of advance is constant, the contracting area expression $[1 - (1 - \alpha)^{1/2} = kt]$ will be obeyed approximately for the decomposition of cylindrical crystals.⁹ The two-dimensional character of the reaction geometry may also (or alternatively) be a consequence of the layer-type lattice of the salt.^{10,11} (ii) Water is an effective catalyst for H₂O₂ breakdown and the availability of H₂O in the reaction zone is envisaged as increasing as the effective thickness of the barrier layer (Na₂CO₃ product), through which it must diffuse to escape, systematically rises. Combination of the contracting area equation with an appropriate form of Ficks law, applied to allow for the decreasing ease of removal of the active catalyst, yields eq 2. The shape of the α -time curve demonstrates that the autocatalytic effect is sufficient to produce a pronounced initial acceleratory reaction interval and, even after the point of inflection, the deceleratory period is less marked than that characteristic of eq 1.

The present model, attributing autocatalytic behavior to barrier layer opposition of *escape* of the active product, represents an inversion of the well-known and widely used kinetic expression based on increasing opposition offered by the barrier layer to reactant *contact* in gas-solid processes. The latter treatment is familiar in discussions of metal oxidation^{12,13} where the parabolic law and the Jander equation,⁹ both involving the diffusion law, have found extensive application.

The above kinetic model provides an acceptable rate equation and is consistent with the promoting effect of liquid water on sodium percarbonate decomposition. The inhibitory effect of H_2O vapor on reaction (Table II) is identified as a consequence of the water-promoted recrystallization of the solid product, whereby escape of volatile substances from the active zone is facilitated by the development of pores and channels in the barrier layer during the area reduction (Table II) of the residual phase. Studies of Smith-Topley behavior¹ have found marked dependences of rates of many dehydrations on water vapor pressure which may also control the texture of solid products. Since the water vapor pressure used here resulted in an inhibition of reaction, it is concluded that the effective pressure within the reaction zone must be appreciably greater than 20 torr. Equation 2 was developed to make allowance for an influence exerted by the volatile product on the overall reaction rate through recrystallization of the residual solid; such a parameter is not incorporated in most topochemical rate equations.

The intracrystalline reaction mechanism proposed above is consistent with our observation that most of the solid additives studied here (some inhibit homogeneous decomposition of H_2O_2) did not significantly influence the reaction rate, since these additives were unable to approach internal reaction sites. However, small molecules (such as water product) may be expected to penetrate the fine pores of the composite reactant-product crystallites. The reduction in rate of sodium percarbonate decomposition caused by NH₃ gas may result from chemical interaction with participants in the H_2O_2 decomposition processes inside the reaction zone. The influence of the ammonium salts tested is also believed to arise through the ammonia molecules released on dissociation. Urea was the only additive found here for which an inhibitory effect was maintained throughout reaction. This was not attributable to separation of $(NH_2)_2 \cdot CO \cdot H_2O_2$ since appropriate experiments characterized the pure molecular compound as being less stable than sodium percarbonate; it decomposed, with melting, between 338 and 368 K. The reduction in reactivity of sodium percarbonate which resulted from the addition of NH₃ and urea may be a consequence of their ability to enter temporarily the disorganized lattice at the reaction zone and form hydrogen bonds^{10,11} stabilizing the labile constituent of the reactant.

While the relatively rapid rate of decomposition of salt L3(Fe) can be ascribed to the catalytic influence of the incorporated iron, the observed obedience to eq 2 over the wide interval $0.05 < \alpha < 0.85$ is not so readily explained. The constant level of promotion could result from the

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homogeneous dispersal throughout the reactant of Fe³⁺ ions, each of which can act as a local catalyst for decomposition when the advancing reaction zone reaches it, thereby conferring mobility on H_2O_2 molecules in the neighborhood. It is alternatively possible that within a diffuse reaction zone enhanced mobility of both Fe³⁺ and H₂O₂ ensures contact and subsequent decomposition of the latter.

Comparison of the relative reactivities of the six salts for which kinetic data are available (Table I) suggests that reaction rates may be determined by the effective concentrations of the free transition metal impurities present. The low concentrations involved (<1 ppm), possible inhomogeneities, and the presence of inhibitors makes it impracticable to attempt quantitative confirmation of this supposition by analytical methods. The most stable preparations (W1 and W2) were manufactured containing stabilizers. The laboratory preparations (L1, L2, and L4), where the possibility of contamination was probably greater, were slightly more reactive, though, significantly, the sample (L4) prepared from the purest materials was the least reactive of this group. The incorporation of iron (L3(Fe)) increased the decomposition rate. If transition metals participate as promoting catalysts, controlling all reactions, the inhibiting effects of NH_3 and urea could be ascribed to competition with H₂O₂ toward complex formation at the active impurity ion.

The various effects of mechanical pretreatment must be interpreted with care, since impurities may be introduced. A reduction in particle sizes is expected to result in conflicting kinetic influences, since the acceleration resulting from an increase in the effective area of initiation of reaction (reactant surface) may be offset by a reduction in the thickness of the product layer ultimately generated. The irregular behavior observed is consistent with the operation of complex controls; the general acceleration of the onset of reaction apparent in crushed material is consistent with some promotion of the initiation process during the severe pretreatment.

We are reluctant to identify the activation energy, calculated from the temperature coefficient, for sodium percarbonate decomposition with any particular bond redistribution step in H₂O₂ breakdown. Within the same temperature interval the apparent values for reaction in 20 torr of H_2O were ~30 kJ mol⁻¹ greater than those for the same reaction under vacuum. This behavior may arise through variations in the effective concentrations of active precursors to and participants in the chemical steps proceeding within the reaction zone, including availabilities of H_2O_2 , H_2O (including species derived therefrom), and transition metal ions, and the influence of water on product phase reorganization. If the concentrations of participants in a heterogeneous process are not independent of temperature, the activation energy found is not necessarily to be identified with that of a single rate-limiting step.¹⁴ We cannot be sure that the value found here has fundamental or mechanistic significance. The value for sodium percarbonate pyrolysis (120 kJ mol⁻¹) is slightly larger than that reported for the reaction of sodium peroxocarbonate $(\sim 90 \text{ kJ mol}^{-1})$ within the same temperature interval.

Our kinetic observations show significant differences from data reported by Nagaishi et al.⁴ which may be due to the use of alternative salt preparations but is more probably a result of a change of experimental technique. We believe the measurements obtained in our isothermal methods to be the more reliable, particularly in view of the great sensitivity of kinetic characteristics to the presence of even trace quantities of liquid water, since we have taken care to exclude the possibility of its formation.

Conclusions

The solid state decomposition of sodium percarbonate is an autocatalytic rate process; the kinetic characteristics of the pyrolyses of several different preparations were closely similar. Although liquid water strongly accelerates salt breakdown, the vapor exerted an appreciable inhibitory effect, which we believe to be a consequence of textural reorganization of the solid product. Since evidence concerning the existence of a reactant-product contact interface was not obtainable, little progress could be made toward characterizing the mechanism of hydrogen peroxide breakdown, identified here as an intracrystalline process involving the participation of water and possibly also transition metal ions as catalysts, even when such metals are present in trace quantities.

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Supplementary Material Available: The derivation of eq 2 and comments on the mechanism of the water-catalyzed decomposition of hydrogen peroxide (2 pages). Ordering information is available on any current masthead page.

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