

portions of methanol. The methanol solutions were poured into 40 ml. of water and the aqueous suspension was extracted with five 10-ml. portions of pentane. After drying over calcium chloride, the solvent was evaporated to give 768 mg. (90%) of crude material which was distilled, b.p. 70° (0.05 mm.), $\lambda_{\text{max}}^{\text{EtOH}}$ (of the mixture) 222 and 250 $m\mu$ (ϵ 8600 and 3500). Analysis by v.p.c. showed that the product was a 3:1 mixture of two compounds, one a tetrahydro and the other a hexahydro derivative, as indicated by mass spectral parent peaks at m/e 189 and 191, respectively. Samples of the two components were collected from v.p.c., and the major, faster eluting component was obtained pure; $\lambda_{\text{max}}^{\text{EtOH}}$ 226 and 250 $m\mu$ (ϵ 8080 and 5060); $\nu_{\text{max}}^{\text{liquid}}$ 2900(vs), 2210(m, sharp), 1650(w), 1620(m), 1420(vs), 920(m), 865(s) cm^{-1} ; n.m.r.: symmetrical triplet centered at 4.40 τ , $J = 7.3$ c.p.s.

Anal. Calcd. for $\text{C}_{13}\text{H}_{19}\text{N}$: C, 82.47; H, 10.12; N, 7.40. Found: C, 82.90; H, 9.79; N, 7.01.

The minor component was contaminated with about 25% of the other; $\lambda_{\text{max}}^{\text{EtOH}}$ 224 $m\mu$ (ϵ 7440), ϵ at 250 $m\mu$ of 1340. No further work was done with this material.

Ozonolysis of 2,3-Diethylcycloocta-1,3-diene-1-carbonitrile (20).—A sample of the pure tetrahydro derivative described above (130 mg., 0.69 mmole) was dissolved in 5 ml. of chloroform and ozone passed through the solution at -25° to -30° for 15 minutes. At the end of this time the solution had become bright green in color. The solvent was removed below 30° to leave a yellow-green oil to which was added 5 ml. of water and 1.5 ml. of 3% hydrogen peroxide (1.3 mmoles). The mixture was heated for 30 minutes on the steam-bath, during which

time most of the oil dissolved. Another 0.5 ml. of 3% hydrogen peroxide was added and the mixture left at room temperature for 45 min. Aqueous ammonium hydroxide (1 ml. of 10% solution) was then added and 20 microliters of this solution was placed on a paper chromatogram along with a comparison sample of propionic acid in ammonia. The developing system was made up by adding 1 ml. of concd. ammonium hydroxide to 100 ml. of denatured ethanol; the spray reagent was 0.05% bromphenol blue in water acidified with citric acid.³² Three spots appeared on the chromatogram of the unknown with R_f values of 0.40 (propionic acid), 0.31 (formic acid) and 0.072. The aqueous solution was made strongly basic with sodium hydroxide and extracted with three 10-ml. portions of ether. The ether solution was dried (Na_2SO_4) and evaporated to yield 21 mg. of a clear oil ($\nu_{\text{max}}^{\text{liquid}}$ 3450, 2950, 2220, 1745, 1710(sh), 1450 and 1370 cm^{-1}) which was discarded. The aqueous solution was acidified (HCl) and extracted continuously with ether for 22 hours. Drying and careful evaporation left a sharp-smelling oil which crystallized partially in a refrigerator. Two recrystallizations from 0.2 ml. of concd. nitric acid gave a compound, m.p. 152–154.4°, pure and mixed with authentic adipic acid. The infrared spectrum of the unknown (KBr) was superimposable on that of recrystallized adipic acid.

Acknowledgment.—We are indebted to the National Science Foundation (Grant G22547) for financial support.

(32) E. P. Kennedy and H. A. Barker, *Anal. Chem.*, **23**, 1033 (1951).

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE, R. I.]

Kinetics and Mechanism of the Spontaneous Decompositions of Some Peroxoacids, Hydrogen Peroxide and *t*-Butyl Hydroperoxide

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The kinetics of the decompositions of peroxoacetic acid, peroxochloroacetic acid, peroxomonophosphoric acid, hydrogen peroxide and *t*-butyl hydroperoxide have been measured in aqueous alkaline media. EDTA was added to suppress homogeneous catalysis presumably by trace metal ions. The decompositions of the peroxoacids studied were second order with respect to the peroxoacid concentrations. The dependence of rate on pH indicated that the rate of decomposition is maximum at 50% dissociation of the peroxoacids. Peroxochloroacetic acid undergoes spontaneous decomposition about 100 times as fast as does peroxoacetic acid, although the former peroxoacid oxidizes nitrosobenzene only 30 times as rapidly as does the latter peroxoacid.

The analysis of the products of decomposition of $\text{CH}_3\text{CO}^{18}\text{O}^{18}\text{H}$ showed that 83% of the heavy oxygen isotope appeared as $\text{O}^{18}\text{O}^{18}$. A reinvestigation of the aqueous alkaline decomposition of hydrogen peroxide showed that this decomposition is almost immeasurably slow when the base is purified and EDTA added to the reaction solution. Under these conditions the rate of decomposition is about one-hundredth that attributed to spontaneous decomposition alone in the literature. Mechanistic implications of these data are discussed.

Introduction

The results of a kinetic study of the aqueous decomposition of Caro acid were reported in a previous paper.¹ Both the catalytic and spontaneous paths were observed for decomposition, which was shown to be homogeneous. The catalytic path was eliminated by addition of EDTA and the spontaneous decomposition found to be second order with respect to Caro acid concentrations. The dependence of rate on pH indicated that the rate law is: rate = $k_2[\text{SO}_5^{2-}][\text{HSO}_5^-]$. These results were interpreted in terms of a nucleophilic attack by the dinegative anion of Caro acid upon the peroxidic oxygen of its mononegative ion.

The decomposition of H_2O_2 is known to be catalyzed heterogeneously by the surface of the container² and homogeneously by many transition and heavy metal ions even at very low concentrations. Despite numerous kinetic studies^{3,4} it seems certain that the true rate of the spontaneous decomposition of H_2O_2 has never been measured. Duke and Haas³ were able to eliminate

successfully heterogeneous catalysis, but a reinvestigation of their system has now revealed that homogeneous catalysis must have contributed significantly to the rate attributed to spontaneous decomposition alone.

A recent study⁵ of the uncatalyzed decomposition of variously substituted peroxobenzoic acids in aqueous solutions has shown that the reaction is governed by the second-order kinetic law with maximum rates at 50% dissociation of the peroxoacids; the behavior is thus analogous to that reported for Caro acid.¹

This paper presents data on the kinetics of the decompositions of peroxoacetic acid, peroxochloroacetic acid, peroxomonophosphoric acid, *t*-butyl hydroperoxide and hydrogen peroxide. Mechanistic implications of these studies are discussed.

Results

The kinetics were measured by following the rate of disappearance of the peroxo compound iodometrically in each case. The compounds studied were of the type

ROOH , where R is H, *t*-butyl, $\text{CH}_3\text{C}-$, $\text{ClCH}_2\text{C}-$ or

(5) J. F. Goodman, P. Robson and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).

(1) D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).

(2) L. Erdy and I. Inczedy, *Acta Chim. Acad. Sci. Hung.*, **7**, 93 (1955).

(3) F. R. Duke and T. W. Haas, *J. Phys. Chem.*, **65**, 304 (1961).

(4) W. C. Schumb, C. N. Satterfield and R. L. Wentworth, "Hydrogen Peroxide," Reinhold Publishing Corp., New York, N. Y., 1955, Ch. 8 and references cited therein.

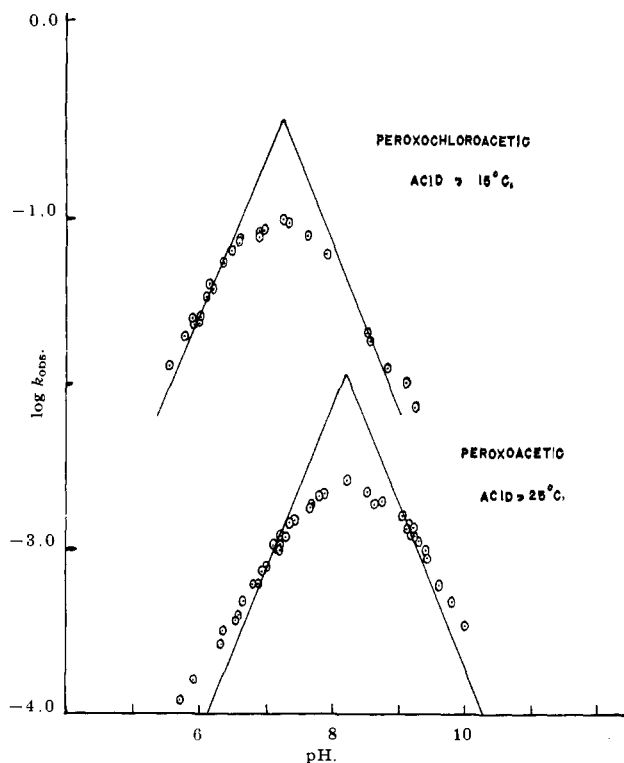


Fig. 1.—The pH dependence of the observed second-order rate constant for the decomposition of peroxyacetic acid and peroxychloroacetic acid obtained in the presence of 10^{-3} M EDTA; k is in liters/mole sec.

PO_3^{2-} . In the subsequent discussion $[\text{ROOH}]_T$ will symbolize the stoichiometric concentration of a peroxy compound and $[\text{ROOH}]_0$ its initial concentration.

Peroxyacetic Acid and Peroxychloroacetic Acid.—Preliminary experiments showed that there was serious incursion of homogeneous catalysis presumably by trace metal ions when no reagent was added to the system to complex with these metal ions and render them ineffective as catalysts. EDTA was found to be effective in this role and by measuring rates with varying concentrations of EDTA it was found that 10^{-3} M of this reagent gave optimum results. In each kinetic run 10^{-3} M EDTA was, therefore, present in the system. The decompositions, with EDTA added, were homogeneous, the rates being identical whether the reaction was carried out in polyethylene or in glass vessels.

At a fixed pH, plots of the reciprocal of the stoichiometric peroxyacid concentration were linear to over 65% reaction, indicating that the uncatalyzed decompositions were second order with respect to $[\text{ROOH}]_T$. Deviations toward lower order kinetics became significant after about 65% reaction. These deviations from linearity in the second-order plots in the case of peroxychloroacetic acid may largely be attributable to its rapid hydrolysis to chloroacetic acid and hydrogen peroxide.⁶

The observed rate law at a given pH may, thus, be expressed as in eq. I

$$-d[\text{ROOH}]_T/dt = k_{\text{obs}}[\text{ROOH}]_T^2 \quad (\text{I})$$

where k_{obs} is a pseudo second-order rate constant dependent on pH. Rates of decompositions were measured at varying pH values in the range 5 to 10. Figure 1 depicts the dependence of k_{obs} on pH. The maximum observed rate of decomposition was at pH 8.2 for peroxyacetic acid ($k_{\text{obs}} = 2.7 \times 10^{-3}$ l. mole⁻¹ sec.⁻¹ at pH 8.2 and at 25°) and at pH 7.2 for peroxychloroacetic acid ($k_{\text{obs}} = 1.0 \times 10^{-1}$ l. mole⁻¹ sec.⁻¹ at 15° and at

pH 7.2). The pK_a values of these two peroxyacids were determined by potentiometric titrations and found to be 8.2 and 7.2, respectively. The maximum rate is thus observed at 50% dissociation of the peroxyacid in each case.

When EDTA was present in amounts less than 10^{-3} M, serious deviations toward lower order kinetics were noticed. In its absence the decomposition became essentially first order in $[\text{ROOH}]_T$. It was later found that Co(II) ions at concentrations as low as 10^{-6} M were effective in inducing catalytic decomposition which proved to be first order in $[\text{ROOH}]_T$. However, the Co(II)-catalyzed decomposition leads to the evolution of CO_2 and oxygen while spontaneous decomposition in the presence of EDTA yields only oxygen.⁶ EDTA was found to suppress decomposition greatly by catalytic pathways in solutions containing added transition metal ions. Further details of this catalytic decomposition will be given in a subsequent communication.

No attempts were made to maintain constant ionic strength, but variation in buffer concentration had little effect on the rate of decomposition provided appropriate amounts of EDTA were present in the system.

From the rates measured at three different temperatures, 25.0, 35.0 and 44.8°, an activation energy (E_a) of 30 kcal. mole⁻¹ was found for peroxyacetic acid decomposition.

Peroxyphosphoric Acid.—A study of the decomposition of peroxyphosphoric acid showed that its behavior was analogous to that observed for Caro acid¹ and for peroxycarboxylic acids. Maximum rate of decomposition ($k_{\text{obs}} = 7.1 \times 10^{-4}$ l. mole⁻¹ sec.⁻¹ at 35.8° and at pH $\approx 12.5 \pm 0.2$) was observed in the pH region which corresponds to its pK_{3a} ; the pK_{3a} was estimated spectrophotometrically to be 12.8 ± 0.2 .

The decomposition had to be studied in polyethylene vessels even when EDTA was present and deviations from second-order kinetics became serious as the pH of the system was shifted away from that corresponding to pK_{3a} of the peroxyacid. It seems that the catalytic pathway is not entirely suppressed. The above behavior becomes understandable if the reasonable assumption is made that the catalytic decomposition is insensitive to changes in pH and thus it makes a constant contribution to the total rate of decomposition at all pH values. In the region of pH near the pK_{3a} , where the bimolecular spontaneous process is fastest, the catalytic decomposition presumably forms a small percentage of the total observed rate. At pH values above or below the pK_{3a} region, the spontaneous pathway is adversely affected and therefore the catalytic decomposition forms a significant part of the total rate. The second-order plots were linear to over 2 half-lives at pH values near the pK_{3a} , indicating that uncatalyzed decomposition is indeed predominant in this region.

Hydrogen Peroxide.—Since the decompositions were carried out in unbuffered media and since the pH increases as the peroxide concentration decreases, the results of the studies on H_2O_2 decomposition at 35° are presented as plots of $[\text{H}_2\text{O}_2]_T$ against time.

The results obtained at various pH values (measured at the start of the kinetic runs) for two initial concentrations of hydrogen peroxide show that at $[\text{H}_2\text{O}_2]_0 = 0.1$ M the rate appears to pass through a maximum at pH $\approx pK_{\text{H}_2\text{O}_2}$, whereas at $[\text{H}_2\text{O}_2]_0 = 1$ M the rates simply decrease as the pH increases from 10.7 to 12.7.

Figures 2 and 3 show the results obtained at various pH values (measured at the start of the kinetic runs) for two initial concentrations of H_2O_2 . When $[\text{H}_2\text{O}_2]_0$

(6) E. Koubek, Ph.D. Thesis, Brown University.

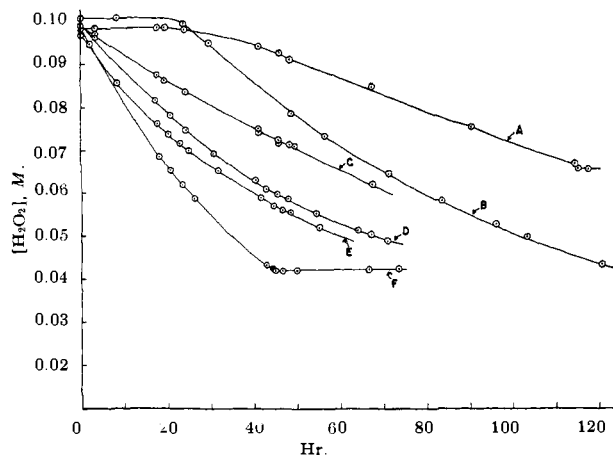


Fig. 2.—Effect of pH upon the rate of decomposition of 0.1 M H_2O_2 : initial pH of A = 11.39, B = 11.35, C = 10.54 and 11.75, D = 11.60, E = 11.19, F = 11.34. EDTA added initially in runs A and B and after 40 hr. to run F.

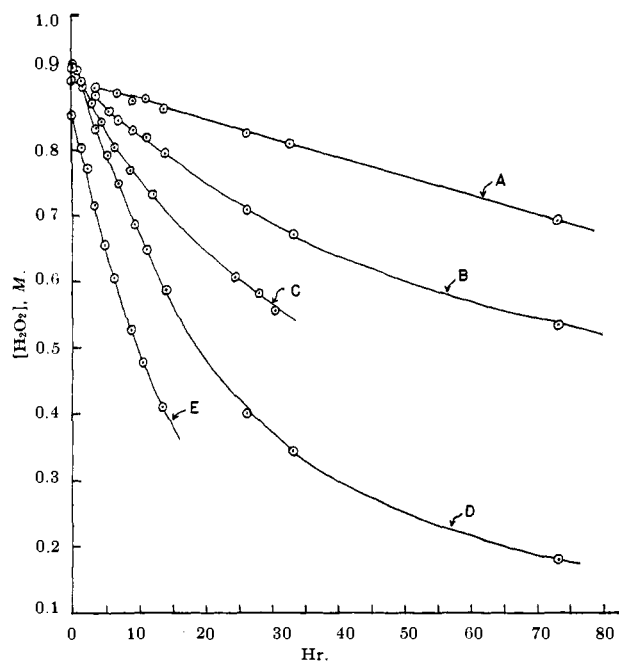


Fig. 3.—Effect of pH upon the rate of decomposition of 1.0 M H_2O_2 : initial pH of A = 12.72, B = 11.89, C = 11.54, D = 10.92, E = 10.71.

= 0.1 M , Fig. 2, the rates appear to pass through a maximum when $pH \approx pK_{H_2O_2}$, whereas at $[H_2O_2]_0 = 1 M$ (Fig. 3) the rates of decomposition decrease as the pH increases from 10.7 to 12.7.

Figure 4 shows the results, at constant initial pH and approximately constant $[H_2O_2]_0 = 1 M$, of a series of decompositions in which the effects of various combinations of NaOH purifications and EDTA additions were compared. Several important features are to be noted: (1) A comparison of runs B (purified base, no EDTA) and D (unpurified base, no EDTA) shows that purification of the NaOH solution reduces the rate of decomposition considerably. (2) Runs C and D (unpurified base, EDTA added) show that EDTA suppresses the initial rate of decomposition markedly in the presence of unpurified base. (3) A comparison of runs B, C and D reveals that addition of EDTA or purification of the base causes significant lowering of rate, the effect of EDTA being relatively shorter lived. (4) Comparing the runs A (purified base, EDTA added) and C reveals that when EDTA is added and also the

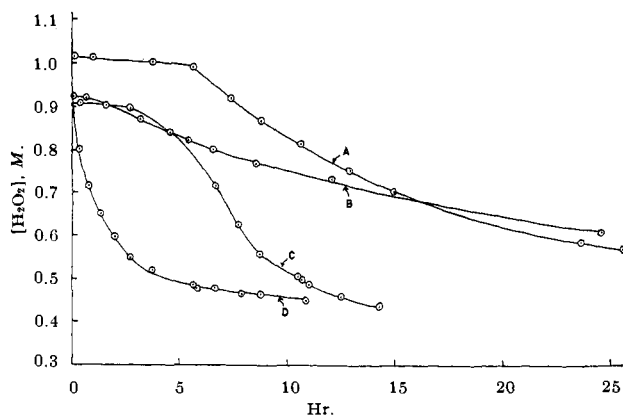


Fig. 4.—Effect of purification of NaOH on the decomposition of H_2O_2 : A, decomposition rate in purified NaOH containing $10^{-3} M$ EDTA; B, decomposition rate in purified NaOH; C, no purification but $10^{-3} M$ in EDTA; D, no purification. Initial pH of A = 11.47, B = 11.54, C = 11.48, D = 11.51.

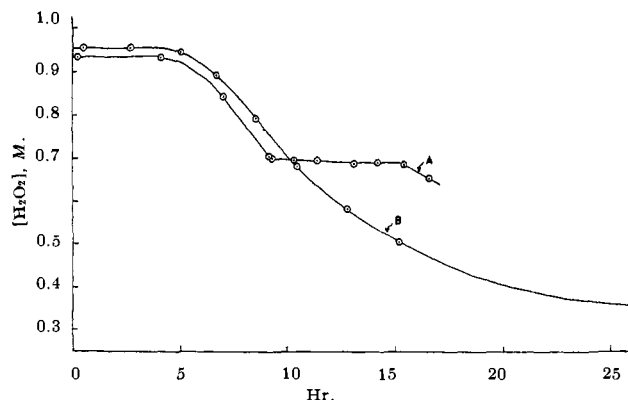


Fig. 5.—Effect of EDTA upon the rate of decomposition of 1.0 M H_2O_2 . Both A and B contained EDTA initially. EDTA was added again to run A after 10 hr. Initial pH of A = 10.94, B = 10.92.

base is purified (A) the apparent induction period, during which the decomposition is extremely slow, is much longer than when EDTA is present but the base is not purified (C).

Figure 2 also illustrates the effects of introducing EDTA into solutions with $[H_2O_2]_0 = 0.1 M$. If the chelating agent is added at the start of the reaction (A and B), the apparent induction period lasts for about 30 hr. As run F of Fig. 2 indicates, the reaction can be virtually stopped at any time during a run by the addition of EDTA. Similar behavior was observed when the $[H_2O_2]_0 = 1 M$ (see Fig. 5). Presumably the slow oxidation of EDTA by H_2O_2 prevents it from suppressing the catalytic decomposition indefinitely.

Of particular importance is the fact that the initial rate calculated from run D of Fig. 4 (purified base, no EDTA) is about one-fourth to one-sixth as fast as the rate of decomposition reported by Duke and Haas,³ but when the base is purified and also EDTA added (A in Fig. 4) the initial rate is about one-hundredth their rate. Since the rate of spontaneous decomposition cannot be faster than the slowest observed rate (assuming a bimolecular polar mechanism), it is clear that catalytic decomposition formed a major factor of the rate which these authors³ attributed to spontaneous decomposition alone.

***t*-Butyl Hydroperoxide.**—Preliminary experiments on the base-catalyzed decomposition of *t*-butyl hydroperoxide showed no appreciable change in either the hydroperoxide concentration or in pH over a period of 3

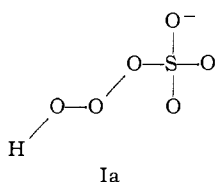
weeks at 38.5°. At 55.1° and at pH 12.8 and with added EDTA a half-life of about 40 days was observed for decomposition. In the absence of EDTA, the half-life was reduced slightly. The reaction appeared to be first-order in $[ROOH]_T$. Several kinetic runs with varying pH values between 2.1 and 12.2 yielded similar results. Since the reaction was too slow to furnish useful data, it was not investigated further.

Discussion

Summary of Results.—(1) In all the cases studied, previously^{1,5} and now, the uncatalyzed decompositions when observed obey the second-order kinetic law at fixed pH; the rates show a maximum in each case at a pH at which $[ROOH] = [ROO^-]$. (2) Peroxochloroacetic acid undergoes decomposition at a rate which is faster, by at least a factor of 100, than the rate of decomposition of peroxyacetic acid. Toward nitrosobenzene, however, peroxochloroacetic acid is only 30 times as effective as its unsubstituted analog.⁶ (3) The decomposition of H_2O_2 is virtually stopped when purified base is used with added EDTA. The question whether the extremely slow decomposition during the apparent induction period is occurring by a spontaneous process, through a catalytic pathway or by both processes cannot be answered with any amount of certainty. *t*-Butyl hydroperoxide is similarly too sluggish in its decomposition to give reliable kinetic data. (4) The analysis of the products of the decomposition of

peroxyacetic acid, containing $CH_3CO^{18}O^{18}H$, showed that 83% of the heavy oxygen isotope appeared as $O^{18}O^{18}$.

The kinetic behavior, which appears to be common for these decompositions, suggests that the rate-determining transition state is composed of a molecule of the undissociated species ROOH and a molecule of its ionized form, ROO^- .^{1,5} Ball and Edwards,¹ who first observed this kinetic behavior for the decomposition of Caro acid, interpreted their results in terms of a bimolecular nucleophilic attack by the anion ROO^- upon the outer peroxidic oxygen of the undissociated molecular ROOH; the resulting reactive intermediate which would then break down into products in a rapid step was pictured as Ia.



Since there is strong evidence for the peroxidic oxygen acting as an electrophilic site in the oxidation of a large number of nucleophiles^{7,8} and since anions of the type ROO^- (where $R = H$ or CH_3) are known to possess exceptionally high nucleophilic reactivity,⁹ the mechanism of Edwards and Ball¹ appears to be reasonable. It ascribes, at least in a qualitative sense, the very low rates of decompositions of H_2O_2 and *t*-butyl hydroperoxide to the high basicity of OH^- and *t*- BuO^- which causes them to be very poor leaving groups in the transition states leading to the intermediates of the type Ia. The differences between the reactivities of the variously substituted peroxobenzoic acids⁵ and between the two

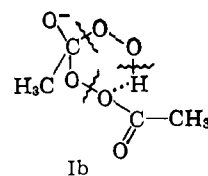
peroxyacetic acids also are understandable on similar grounds.

However, there were certain observations made during the present investigations which were hard to reconcile with the above mechanism. Thus, for example, peroxochloroacetic acid oxidizes nitrosobenzene about 30 times as fast as does peroxyacetic acid. This difference in their reactivities is almost certainly ascribable to the greater ability of the chloroacetate ion as a leaving group relative to the acetate ion. If the mechanism of their spontaneous decompositions is analogous to that suggested for the peroxyacid oxidation of nitrosobenzene,¹⁰ then the expected difference between the rates of their decompositions would be a factor of about 30 (if $ClCH_2COO^-$ and CH_3COO^- are assumed to have comparable nucleophilic reactivity) or less than a factor of 30 (if the chlorine atom in $ClCH_2COO^-$ reduces the electron density at the nucleophilic center significantly and consequently decreases its nucleophilicity). The observed rate of decomposition of peroxochloroacetic acid is at least 100 times as fast as that of the decomposition of peroxyacetic acid. The indication was that the electrophilic site might not be the outer peroxidic oxygen atom and that instead it might be the carbonyl carbon atom in the decomposition of the two peroxyacetic acids studied. The substitution of the chlorine atom in a position adjacent to the electrophilic center, then, would be expected to exert a much greater accelerative influence on the decomposition rate,¹¹ than when the outer peroxidic oxygen is assumed to be the electrophilic site.

In addition, HOO^- is about 200 times as effective a nucleophile as OH^- toward carbonyl carbon in esters.⁹ This exceptionally high nucleophilic reactivity has been ascribed to the operation of the "Alpha Effect."¹² It seems reasonable to assume, then, that the peroxyacetate ion will exhibit nucleophilic reactivity toward the ester carbonyl carbon comparable to that of HOO^- and greater than that of OH^- . Also it is reasonable to expect that both HOO^- and CH_3COO^- will maintain their superior nucleophilic reactivities (relative to OH^-) toward the carbonyl carbon in peroxycarboxylic acids. Since the basic hydrolysis of peroxyacetic acid and peroxochloroacetic acid were found to be very facile reactions, it is hard to explain why during their spontaneous decompositions the anions would attack the peroxidic oxygen to the complete exclusion of the attack on the carbonyl carbon.

In order to obtain more definitive evidence as to whether the peroxidic oxygen or the carbonyl carbon is the electrophilic site, the products of the decomposition

of peroxyacetic acid containing about 4% $CH_3CO^{18}O^{18}H$ were analyzed. The nucleophilic attack by ROO^- upon the outer peroxidic oxygen¹ would demand that the O^{18} appear predominantly as $O^{16}O^{18}$ (almost complete scrambling), while the attack upon carbonyl carbon (*via* intermediate Ib) predicts that



(7) J. O. Edwards in "Peroxide Reaction Mechanisms," edited by J. O. Edwards, Interscience Publishers, Inc., New York, N. Y., 1962, pp. 67-106.

(8) K. M. Ibne-Rasa and J. O. Edwards, *J. Am. Chem. Soc.*, **84**, 763 (1962).

(9) W. P. Jencks and J. Carriolo, *ibid.*, **82**, 1778 (1960).

(10) K. M. Ibne-Rasa, C. G. Lauro and J. O. Edwards, *ibid.*, **85**, 1165 (1963).

(11) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 317.

(12) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

O^{18} appear as $O^{18}-O^{18}$ (no scrambling). The experiment showed that 83% of the heavy oxygen isotope appeared as $O^{18}-O^{18}$. The 17% scrambling might arise from the attack upon the peroxidic oxygen (*via* intermediate Ia) or at least part of it might be due to interference by catalytic decomposition, where scrambling can occur.

The above data thus establish that in the decomposition of peroxocarboxylic acids the dominant mode of reaction is *via* intermediate Ib, *i.e.*, the electrophilic site is carbonyl carbon rather than the peroxidic oxygen. If the uncatalyzed decompositions of other peroxoacids also occur by a similar mechanism, as suggested by the analogous kinetic behavior of the cases studied, the sulfur atom in Caro acid and phosphorus atom in peroxomonophosphoric acid are implicated as the preferred electrophilic sites in their decompositions.

The postulated attack of an anion of the type ROO^- upon phosphorus is not novel; in the reaction of HOO^- with isopropoxymethyl phosphoryl fluoride (Sarin) the suggested mechanism^{13,14} involves a nucleophilic attack by this ion on the phosphorus atom of Sarin, with a reaction rate which is considerably greater than that when OH^- is the nucleophile.

The observed extreme reluctance of *t*-butyl hydroperoxide to undergo uncatalyzed decomposition presumably stems from the fact that the tertiary carbon atom is sterically too hindered to allow the approach of the incoming nucleophile and from the unavailability of a site to accommodate the negative charge in the expected intermediate. The latter reason also explains the almost negligible rate at which H_2O_2 undergoes spontaneous decomposition, if at all.

A kinetic study of the uncatalyzed decomposition of peroxobenzoic acids by Goodman, Robson and Wilson⁵ appeared in the literature when the present work was near completion. Although these authors postulated the nucleophilic attack of the peroxobenzoate ions upon the carbonyl carbon of the neutral molecules giving rise to an intermediate of the type Ib, no definite evidence was reported which could discriminate between the two probable mechanisms. The evidence presented here does provide this discrimination and favors the mechanism they have proposed.

Experimental

Materials.—Except where otherwise stated, reagent grade chemicals were used without purification.

Laboratory distilled and de-ionized water was used in preparing solutions. De-ionized water was obtained by passing distilled water through a Barnstead bantam demineralizer, model BD-1, using a Barnstead mixed resin cartridge.

The disodium salt of ethylenediaminetetraacetic acid dihydrate (EDTA) was a G. Frederick Smith commercial product. In the CH_3CO_3H , $ClCH_2CO_3H$ and H_2O_2 decompositions, the EDTA was recrystallized according to the method of Blaedel and Knight.¹⁵

Potassium peroxodiphosphate, from which peroxomonophosphoric acid was obtained, was prepared electrolytically using the procedure described by Fichter and Gutzwiller¹⁶ as modified by Crutchfield.¹⁷ The procedure outlined by Chulski¹⁸ for the conversion of the potassium salt to the lithium peroxodiphosphate tetrahydrate, was then followed. The $Li_4P_2O_8 \cdot 4H_2O$ was airdried until free flowing. Yields from such preparations, based on the original potassium phosphate electrolyzed and converted to $Li_4P_2O_8 \cdot 4H_2O$, were approximately 50%.

The purity of the salt, after recrystallization, was determined by iodometric analysis of the active oxygen present. The analysis showed the product to be 99.5% $Li_4P_2O_8 \cdot 4H_2O$.

In alkaline solutions it was necessary to exclude lithium ion since lithium phosphate was found to precipitate under the conditions employed. This exclusion was accomplished by converting stock solutions of $Li_4P_2O_8$ to $Na_4P_2O_8$ using an ion-exchange technique described by Crutchfield.¹⁷

Peroxoacetic acid was prepared as follows: 46.0 g. of B and A 30% H_2O_2 were slowly added to 70.0 g. of concentrated H_2SO_4 immersed in an ice-bath. To this mixture 20.4 g. of acetic anhydride was added dropwise with constant stirring. After standing overnight, the CH_3CO_3H formed was distilled under a reduced pressure of 25 mm. and at a temperature of $30.5 \pm 0.5^\circ$. The distillate contained approximately 75% peroxoacetic acid; smaller amounts of H_2O_2 (~3%) and CH_3CO_3H (~15%) were also present. These two impurities had no significant effect on the decomposition under investigation; further purification was, therefore, not carried out.

Shortly before use these samples were diluted to form a stock solution. Analyses were carried out according to the procedure outlined by Greenspan and MacKellar.¹⁹

Peroxoacetic acid was prepared in a similar manner to CH_3CO_3H except that the peroxoacid was extracted with anhydrous methylene chloride instead of fractionally distilled. Details of the preparation are: 11.5 g. of B and A 30% H_2O_2 was slowly added to 30.0 g. of cold (0°) concentrated H_2SO_4 ; 9.5 g. of chloroacetic acid was then added with stirring. After standing for at least 24 hr., 30 ml. of methylene chloride, redistilled from CaH_2 , was added and the $CH_2Cl_2-ClCH_2CO_3H$ layer removed. The extract was immersed in an ice-bath and the CH_2Cl_2 evaporated under reduced pressure, precautions being taken to exclude moisture. The clear, viscous liquid remaining (density 1.5, m.p. $< 0^\circ$) contained 60% $ClCH_2CO_3H$ (as shown by iodometric analysis) and small amounts (1–5%) of H_2O_2 (by ceric ion analysis); the remainder was chloroacetic acid; 1 ml. of this liquid was then added to 50 ml. of buffer solution.

t-Butyl hydroperoxide, obtained from K and K Laboratories, was purified^{20,21} by fractional distillation under a reduced pressure of 20 mm. The distillate boiling at $39-39.5^\circ$ was collected; a modified technique of iodometric analysis²² showed it to be 97.3% pure. Solutions of 0.1 M *t*-butyl hydroperoxide of various pH values were prepared, EDTA being added to some samples.

Stock solutions of hydrogen peroxide were prepared by dilution with de-ionized water of BECCO 98% unstabilized H_2O_2 . No purification of this material was undertaken. Analyses were carried out using both Ce(IV) and $I_2-Na_2S_2O_3$ standard techniques.

Phosphate, carbonate, and, in the case of H_3PO_3 decomposition, borate buffers were used in the studies on H_3PO_3 , CH_3CO_3H and $ClCH_2CO_3H$. The buffer salts were recrystallized (for the H_3PO_3 and labeled CH_3CO_3H decompositions) from conductivity water, a small quantity of EDTA ($\sim 10^{-3}$ M) being added in the first recrystallization.

The NaOH solution used in the H_2O_2 decompositions was an A.R. Mallinckrodt 50–52% solution diluted to 10 and 5 M stock solutions. The base was purified according to the method of Duke and Haas⁸ with one modification: The addition of $Fe(NO_3)_3$ as a co-precipitating agent was omitted.

Peroxoacetic acid, doubly labeled with O^{18} , was prepared in the following manner. $Na_2O_2^{18,19}$ was synthesized as outlined by Anbar²³; 7 ml. of cold 2 M $HClO_4$ solution in water of natural isotopic composition was used to hydrolyze the $Na_2O_2^{18,19}$ to $H_2O_2^{18,19}$; 2.9 ml. of this labeled H_2O_2 solution was then mixed with 0.505 ml. of BECCO 98% H_2O_2 solution; 2.94 ml. of the resulting peroxide solution was added slowly with stirring to 2.0 ml. of cold (0°) concentrated H_2SO_4 ; finally, 0.9 ml. of acetic anhydride was added dropwise. The procedure for the preparation of $ClCH_2CO_3H$ was then followed, three 15-ml. portions of CH_2Cl_2 being used for the extraction. After evaporation of the CH_2Cl_2 , 9 ml. of de-ionized water was added to the small volume (~ 1 ml.) of liquid finally obtained.

$O_2^{18,19}$ (98.07 atom % O^{18}) was supplied by Yeda Research and Development Co., Israel.

Prepurified nitrogen was obtained from Air Reduction Co.

Equipment.—Polyethylene bottles were used as reaction vessels in studying the kinetics of the decompositions of H_3PO_3 , *t*-BuOOH and H_2O_2 ; glass vessels were adequate for the CH_3CO_3H and $ClCH_2CO_3H$ decompositions. The reaction vessels were immersed in constant temperature ice- or water-baths ($t \pm 0.05^\circ$). Spectrophotometric measurements were carried out at 25° using a Beckman model DK-1 recording spectrophotometer.

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pH Measurements were made using Beckman model G pH meters. These instruments were standardized before use with commercial certified buffer solutions.

Procedures.—Peroxomonophosphoric acid was prepared for each kinetic run by acid hydrolysis of $\text{Na}_4\text{P}_2\text{O}_8$ as follows: To 20.0 ml. of 0.10 *M* $\text{Na}_4\text{P}_2\text{O}_8$ in a test-tube was added 2.00 ml. of 6.00 *M* HClO_4 . The resulting solution was heated for 35 min. in an oil-bath at 50°. Under these conditions 60 to 70% of the peroxodiphosphate was hydrolyzed to peroxomonophosphoric acid. The remainder of the total active oxygen was present predominantly as peroxodiphosphoric acid with only a small concentration of H_2O_2 (<1% of the total active oxygen). The solution was then cooled rapidly to about 35° and, noting zero time, added to a polyethylene reaction vessel which contained a known volume of quenching solution. The vessel was immediately placed in a constant temperature bath at $35.8 \pm 0.05^\circ$. The quenching solution contained a known amount of standard sodium hydroxide (to neutralize the acidity of the hydrolysis mixture and to fix approximately the pH of the resulting solution), a known amount ($\sim 10^{-4}$ *M*) of either EDTA or α, α' -dipyridyl and, in some instances, a known volume of buffer solution.

Aliquots of the reaction solutions were withdrawn at appropriate time intervals and analyzed iodometrically for peroxomonophosphoric acid. Because of the considerable concentration of peroxodiphosphate present, the analyses were carried out in acetate buffers at pH 4.6; no interference from the oxidation of iodide ion by peroxodiphosphate was noted at this pH.

The decompositions of $\text{CH}_3\text{CO}_3\text{H}$, $\text{ClCH}_2\text{CO}_3\text{H}$ and H_2O_2 were started by adding the required volume of peracid or peroxide solution to a buffer or NaOH solution, of the required pH, to which EDTA ($\sim 10^{-3}$ *M*) had been added. As previously, aliquots were withdrawn by pipet periodically and analyzed, the analyses for $\text{CH}_3\text{CO}_3\text{H}$ and $\text{ClCH}_2\text{CO}_3\text{H}$ being carried out in phosphate buffers of pH 3.5.

The prepared *t*-BuOOH solutions were immersed in a constant temperature water-bath and aliquots taken at intervals of 24 hr. and analyzed by an iodometric method.²²

The pH of all reaction solutions was measured at the start and at the end of a kinetic run. In buffered solutions the pH was usually constant to ± 0.1 pH unit.

Samples, for mass spectrometric analysis, of the oxygen evolved in the base-catalyzed decomposition of the labeled peroxyacetic acid were collected as follows: 5 ml. of labeled $\text{CH}_3\text{CO}_3\text{H}$ solution was added to the side arm of a 100-ml. reaction vessel. Contained within the same flask was 45 ml. of a carbonate buffer solution ($\sim 10^{-3}$ *M* in EDTA) which maintained a pH near 8.2, the pK_a of peroxyacetic acid. The purity

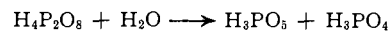
of this buffer had been previously determined by following the spontaneous decomposition of ordinary peroxyacetic acid.

The reaction flask and its contents were then attached to a vacuum line and thoroughly flushed with a stream of prepurified nitrogen. After passage of nitrogen gas for at least 1 hr., a sample was taken from above the liquids, and the nitrogen flow terminated. Mass spectral analysis of the blank sample demonstrated the efficiency of this process. Following this the reaction vessel was turned into a position enabling the two liquids to mix. After a period corresponding to ca. 70% reaction, a representative sample of gas (now nitrogen and oxygen) was taken.

The remaining 0.4-ml. portion of the hydrogen peroxide used initially to prepare the labeled peroxyacetic acid was diluted with 9.6 ml. of de-ionized water. One-half of this solution was oxidized with an excess of acid ceric ion in the same apparatus and according to the same procedure used for the spontaneous decomposition.

A repeat of this experiment was carried out with the remaining H_2O_2 solution. Since it is known^{23,24} that the O—O bond of H_2O_2 is not broken on oxidation by an excess Ce(IV) , these experiments gave the relative amounts of H_2O_2 ^{16,16}, H_2O_2 ^{16,18} and H_2O_2 ^{18,18}. It was assumed that the $\text{CH}_3\text{CO}_3\text{H}$ was labeled in the same relative amounts.²⁵

A spectrophotometric method²⁶ was used to evaluate the acid dissociation constants of H_3PO_3 . Potentiometric titration, used to determine the acid dissociation constants of $\text{CH}_3\text{CO}_3\text{H}$ and $\text{ClCH}_2\text{CO}_3\text{H}$, could not be used since an equimolar mixture of peroxomonophosphoric and phosphoric acids is obtained on acid hydrolysis of peroxodiphosphate, according to the equation



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Polyoxomethylene Small-Ring Hydrocarbons: Tetramethylenecyclobutane and Dihydropolyoxomethylene¹

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Tetramethylenecyclobutane (I), a cross-conjugated hydrocarbon of theoretical interest, has been synthesized by two independent routes. Although non-isolable, it is stable in dilute solutions to both acid and base and has been characterized by spectral analysis as well as by chemical evidence. By classical standards compound I cannot be considered aromatic although it is indefinitely stable in dilute solution at -78° in the absence of oxygen. Its marked sensitivity to oxygen and tendency to polymerize may be rationalized in theoretical terms. In relation to our work with I, the synthesis of dihydropolyoxomethylene (XII) has also been achieved.

A variety of small carbocyclic systems possessing one or more double bonds exocyclic to the ring have been synthesized during the past decade. In the cyclobutane series, representative examples having one, two and three exomethylene groups have been reported.³ The present study was initiated in order to determine whether tetramethylenecyclobutane which, like cyclo-

butadiene, possesses four such sp^2 -hybridized carbon atoms in the ring would be capable of even precarious independent existence.⁴ We were encouraged in this endeavor by earlier predictions based on simple Hückel-MO calculations which indicated that in contrast to cyclobutadiene a singlet ground state, as well as a substantial delocalization energy (1.67 β), might be anticipated for I.⁵ In order to translate the calculated

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A substituted tetramethylenecyclobutane structure was also considered for a $\text{C}_{20}\text{H}_{28}$ hydrocarbon formed when ascaridole is heated in *p*-cymene, although no experimental evidence other than molecular weight and carbon-