Specific Catalysis of the Peroxidic Cleavage of Benzil. II. Observations on the Mechanism of Peroxyanion Formation

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The catalytic effect on the hydroperoxide cleavage of benzil by borate, carbonate, phosphate, and tungstate has been measured in aqueous t-butyl alcohol solution at 45°. The interesting variation of the catalytic coefficients of borate and carbonate with pH has also been noted and correlated with the rapid equilibrium formation of their several peroxyanion species. Suitable rate equations have been derived which are consistent with the observed rate dependencies. These results together with the failure to obtain catalysis by acetate anion and the lack of correspondence of the catalytic effect with base strength or nucleophilicity of the catalytic anion provide a basis for discussing the mechanism of peroxyanion formation. These results also provide the first proofs by a pure chemical method of the existence of peroxycarbonate anions in essentially aqueous solutions and confirm the same conclusions with regard to peroxyborate anions. Furthermore, in some cases the usual mechanism of oxyanion replacement reactions has been shown to be inapplicable for understanding the formation of peroxyanions from oxyanion interaction with peroxide.

Introduction

In a previous paper[2] we have demonstrated that the cleavage of α-diketones with peroxidic reagents is catalyzed by hydroxide ion and occurs predominantly in the range ca. pH >6.0 through the agency of the peroxidic anion. We have also demonstrated the absence of general base catalysis for the cleavage reaction. These circumstances consequently appeared to be ideal from the point of view of studying specific ion catalysis of peroxidic reactivity, that is to say the ability of specific ions to form peroxyanions of different reactivity from that of the parent peroxide. We have conceived these circumstances also as the basis of a program directed to understanding the nature and mechanism of interaction of oxyanions with peroxides.

Experimental

The methods and equipment used to pursue (spectrophotometrically) the rates of benzil cleavage by peroxidic reagents under all experimental conditions have been described in our previous article.[2] In studying the rate effects of added oxyanions on the cleavage reaction the pH-stat was employed to maintain the selected hydrion concentrations rather than buffers, for obvious reasons. All reactions reported here were carried out in the standard medium, which is composed by diluting 35 volumes of pure t-butyl alcohol to 100 volumes with pure water at 45°, the reaction temperature used throughout. The molar concentrations of additives used were in the range: borate, 0.01 to 0.09; carbonate, 0.01 to 0.11; phosphate, 0.0025 to 0.07; acetate, 0.005 to 0.05; tungstate, 0.01 to 0.02; and borate in reaction with t-BuOOH, 0.01 to 0.045. Each reaction was about 0.0024 M in benzil, while the initial peroxide concentration varied from 50 to 500 times that value.

Under all experimental conditions employed, as well as in the presence of the above additives at concentration levels at least three times as great as the maximum concentrations of these additives employed in our studies, no phase separation could be observed.

The following reagents were used after drying overnight at 105°: Baker and Adamson reagent grade sodium acetate, sodium bicarbonate, and sodium oxalate; Merck reagent potassium phosphate, monobasic; and National Bureau of Standards acidimetric standard potassium acid phthalate. Other reagent grade chemicals used were Baker and Adamson reagent grade 30% hydrogen peroxide, glacial acetic acid, sulfuric acid, hydrochloric acid, boric acid, sodium hydroxide, sodium tetraborate, and potassium permanganate. Merck reagent grade sodium tungstate, Eastman White Label Spectrograde acetone, American Cyanamid guanidine carbonate, and sodium perchlorate, anhydrous reagent, from the G. Frederick Smith Chemical Co. were also used.

Calculations

We have continued here to use the symbols employed in our previous article[2] to denote the various quantities we encountered in the computation of reaction rates. Thus

$$k' = \frac{k_0 K_0 K_1}{K_w K_2} + \frac{k_1 K_0 K_1}{K_w}(\mathrm{OH^{-1}}) \qquad (1)$$

$$k' = k_0' + k_{\mathrm{OH}}(\mathrm{OH^-}) \qquad (2)$$

Results and Discussion

When acetate ion concentration was varied over an approximately 10-fold range at constant pH (8.32) and ionic strength, no significant change in the rate of benzil cleavage by hydrogen peroxide could be observed. However, with a number of other anions such as borate, carbonate, phosphate, and tungstate rate changes were noted which showed some proportionality to concentration of the added anion but did not correlate with its base strength characteristic nor the ionic strength of the medium. Furthermore, the previous work[2] has established that ionic strength dependence of the rate of benzil cleavage only occurs with substituted benzils bearing charged functional
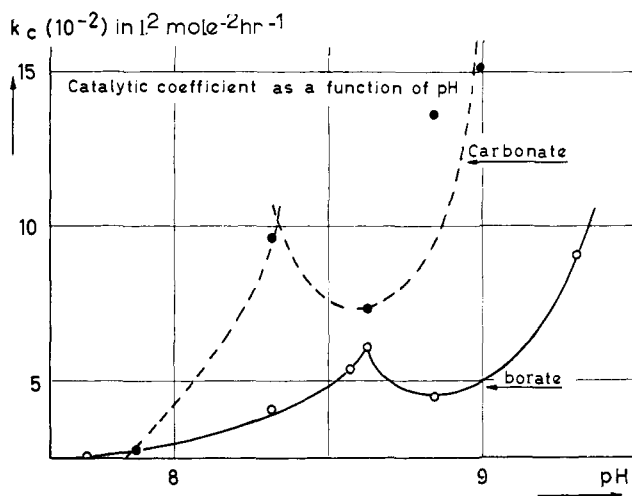
k_c (10^{-2}) in l^2 mole^{-2}hr^{-1}

Figure 1. Benzil cleavage rates with H_2O_2 and added anion at 45°; 35% t-BuOH; 65% H_2O.

groups, such responses being identified as Brønsted primary salt effects.

It was also shown[2] that the rate dependence with respect to (B_z), the benzil concentration, and (OH^-) were not affected by the added oxyanion, and that in general the readily recognizable features of specific ion catalysis were observed. Deviations were noted at high pH values in terms of the common catalytic relationship

$$k' = k_0' + k_{OH}(OH^-) + k_c(C) \qquad (3)$$

Here all parameters have their original[2] significance (eq. 1 and 2) and k_c is the catalytic coefficient of the specific ion present in concentration C, invariant throughout the course of the reaction. These deviations were manifested as negative intercepts when $(k' - k_0' - k_{OH}(OH^-))$ was plotted against C at constant pH. Furthermore, when the computed catalytic coefficient, k_c, was plotted as a function of pH the resulting curve showed no smooth trend that might be expected to indicate the changing concentration of a single catalytic species with pH. Instead we observed an almost discontinuous variation of the k_c with pH as illustrated for carbonate and borate catalysis in Figure 1.

These results seemed possible of correlation with the idea that the catalytic action occurs through the prior complexing of the oxyanion and peroxide. In fact, several such complexes possessing differing peroxide stoichiometry, charge type, and formation constants which are a direct function of pH may easily be conceived. Consequently, if we make the additional assumption that each complex also possesses a catalytic coefficient in benzil cleavage which is either greater or less than the peroxide from which it was derived, the strongly nonlinear character of the relations displayed in Figure 1 are made understandable.
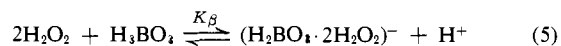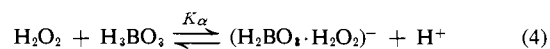
The procedure we followed, therefore, was to make these assumptions the basis for developing a computer program by means of which we could estimate from our data the catalytic activity of each of the most likely peroxyanion complexes. Previous considerations and estimates[3-6] of the formation constants and stoichiometry of several of the peroxyanion complexes we examined in this fashion were extremely helpful. Further

discussion of this aspect of our study is conveniently presented in terms of specific examples.

A. Borate Catalysis. As an operational hypothesis we may assume that the interaction of borate and a hydroperoxide results in the formation of a perborate complex. In this we take cognizance of the reported observations that borate may complex with H_2O_2 to form peroxyborate in solution.[3-6] The catalytic effect of added borate, on the basis of this assumption, must be correlated with the ability of peroxyborate (anion) to compete with hydrogen peroxide (anion) in the cleavage of benzil.

It should be mentioned at this point that both Antikainen[5] and Wilson[6] stress the formation of two different peroxyborate complexes, one with a single mole of H_2O_2 and the other with 2 moles. This implies that two or more catalytic species may be active in our reaction system. Since eq. 3 will yield only a single catalytic coefficient, the linearity observed when the data was plotted according to this equation is incidental, but not inexplicable since the concentration of all species would depend upon the first power of total borate concentration.

Since Antikainen[5] gives equilibrium constants for the following reactions (eq. 4 and 5) (using his notation)

$$H_2O_2 + H_3BO_3 \underset{}{\overset{K_\alpha}{\rightleftharpoons}} (H_2BO_4 \cdot H_2O_2)^- + H^+ \qquad (4)$$

$$2H_2O_2 + H_3BO_4 \underset{}{\overset{K_\beta}{\rightleftharpoons}} (H_2BO_4 \cdot 2H_2O_2)^- + H^+ \qquad (5)$$

it was decided to solve for the concentration of the two complexes as a step toward obtaining true catalytic coefficients. Designating the equilibrium concentration of $(H_2BO_3 \cdot H_2O_2)^-$ (extent of reaction 4) as α and the equilibrium concentration of $(H_2BO_3 \cdot 2H_2O_2)^-$ (extent of reaction 5) as β, an equation can be derived of the form

$$a\alpha^3 + b\alpha^2 + c\alpha + d = 0; \quad \beta = \frac{(H_2O_2)\alpha - \alpha^2}{2\alpha + (K_\alpha/K_\beta)} \qquad (6)$$

This equation was programmed for a digital computer using K_α as 1.59×10^{-8}, K_β as 4.08×10^{-8}, initial concentrations of H_2O_2 and H_3BO_3, and the equilibrium value of (H^+) from pH measurements.[7] Values of α and β were obtained for each experiment.

For simplicity in notation we will designate the quantity $k' - k_0' - k_{OH}(OH^-)$ as k^* (see eq. 3), keeping in mind that k' is the observed rate constant per mole of H_2O_2. Catalysis by the two anionic species should then follow the relationship

$$(H_2O_2)k^* = k_\alpha\alpha + k_\beta\beta \qquad (7)$$

where k_α and k_β are the catalytic coefficients of the respective anions. However, a plot of $(H_2O_2)k^*/\alpha$ vs. β/α was not linear, indicating that eq. 7 is incorrect or incomplete. The next portion of this paper deals

(3) H. Menzel, Z. anorg. allgem. Chem., 164, 1 (1927; Z. physik. Chem. (Frankfurt), 105, 402 (1923).
(4) J. O. Edwards, J. Am. Chem. Soc., 75, 6154 (1953).
(5) P. J. Antikainen, Suomen Kemistilehti, 28B, 150 (1955).
(6) I. R. Wilson, Australian J. Chem., 13, 582 (1960).
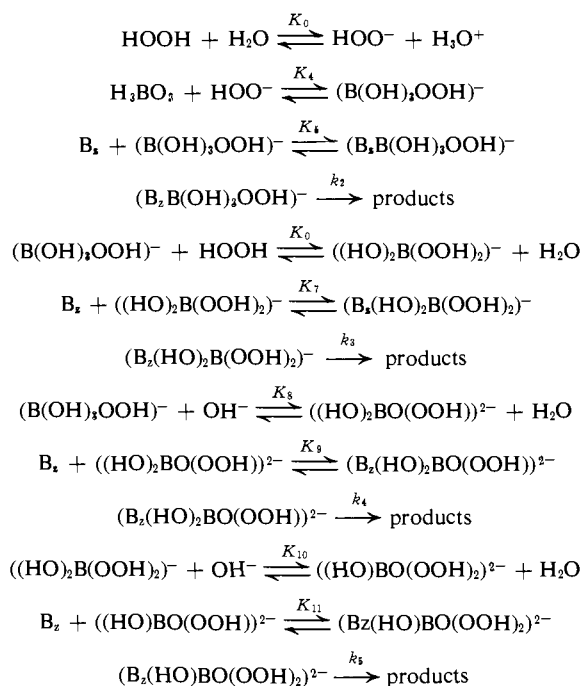(7) For the determination of (H−) and (OH−), our pH meter readings were calibrated against 30 different known concentrations of (OH−) in our solvent system. The meter pH readings were determined to be 0.304 unit higher and pK_w was evaluated as 13.590. Using these data, k_OH in our previous article[2] for the reaction of benzil and HOOH was redetermined as 2.71 × 10^6.

with the derivation of a more exact expression for the observed catalytic effects.

1. Kinetic Assumptions and Derivation of a Rate Equation. It seems evident that complex formation (and the reverse reaction of hydrolysis) between borate and hydroperoxide must occur very rapidly or we would have observed more serious deviations when plotting our data according to eq. 3. This assumption is supported by Edwards[4] who reported no delay in the attainment of equilibrium in the pH measurements by which the complex formation was detected.

In addition to the kinetic steps for the HOOH and HOO^- cleavage reactions that occur concomitantly (and which lead to eq. 1; see ref. 2), we propose that the following rate equations and equilibrium conditions are attained in the presence of certain oxyanions[8] capable of exhibiting the properties of specific ion catalysis in benzil cleavage. We use H_3BO_3 and its anions merely as an illustration. Other oxyacids and anions may be substituted without affecting the form of the deviation.

Since eq. 7 did not fit the experimental data, there may be more than two borate complexes present which contribute toward the observed rate constant. Edwards[4] has concluded that undissociated H_3BO_3 may not interact with H_2O_2, but rather the interaction is confined to the anion $B(OH)_4^-$. Wilson[6] also gives strong support for the view that there is no interaction between boric acid and hydrogen peroxide as such. We therefore will initially consider the possibility of one or more dianions being present in addition to the two monoanions. The notation used is consistent with that in ref. 2.

$$HOOH + H_2O \underset{}{\overset{K_0}{\rightleftharpoons}} HOO^- + H_3O^+$$

$$H_3BO_3 + HOO^- \overset{K_4}{\rightleftharpoons} (B(OH)_3OOH)^-$$

$$B_z + (B(OH)_3OOH)^- \overset{K_5}{\rightleftharpoons} (B_zB(OH)_3OOH)^-$$

$$(B_zB(OH)_3OOH)^- \overset{k_2}{\longrightarrow} products$$

$$(B(OH)_3OOH)^- + HOOH \overset{K_6}{\rightleftharpoons} ((HO)_2B(OOH)_2)^- + H_2O$$

$$B_z + ((HO)_2B(OOH)_2)^- \overset{K_7}{\rightleftharpoons} (B_z(HO)_2B(OOH)_2)^-$$

$$(B_z(HO)_2B(OOH)_2)^- \overset{k_3}{\longrightarrow} products$$

$$(B(OH)_3OOH)^- + OH^- \overset{K_8}{\rightleftharpoons} ((HO)_2BO(OOH))^{2-} + H_2O$$

$$B_z + ((HO)_2BO(OOH))^{2-} \overset{K_9}{\rightleftharpoons} (B_z(HO)_2BO(OOH))^{2-}$$

$$(B_z(HO)_2BO(OOH))^{2-} \overset{k_4}{\longrightarrow} products$$

$$((HO)_2B(OOH)_2)^- + OH^- \overset{K_{10}}{\rightleftharpoons} ((HO)BO(OOH)_2)^{2-} + H_2O$$

$$B_z + ((HO)BO(OOH))^{2-} \overset{K_{11}}{\rightleftharpoons} (Bz(HO)BO(OOH)_2)^{2-}$$

$$(B_z(HO)BO(OOH)_2)^{2-} \overset{k_5}{\longrightarrow} products$$

However, since k' is the observed rate constant per mole of HOOH, it is necessary to determine the equilibrium concentration of HOOH in order to evaluate k'. Neglecting this correction may have contributed to the failure of eq. 7. The expression derived from the above equilibria is represented by eq. 8.

(8) J. O. Edwards, *J. Chem. Educ.*, **31**, 270 (1954).

$$(HOOH)_{eq} = (HOOH)_0\left[1 - \left(\frac{K_0K_4}{(H_3O^+)}\right)(H_3BO_3)(H_2O) + \right.$$

$$\frac{2K_0K_4K_6}{(H_3O)^+}(H_3BO_3)(HOOH) + \frac{K_0K_4K_8}{(H_3O^+)}(H_3BO_3)(OH^-) +$$

$$\left.\frac{2K_0K_4K_6K_{10}}{(H_3O)^+(H_2O)}(H_3BO_3)(HOOH)(OH^-)\right)\right] \quad (8)$$

We divide the observed rate constant by the initial (subscript zero) concentration of HOOH to obtain k' in eq. 2, so we must multiply the right side of eq. 2 by the term in large brackets in eq. 8. Since the first item in the brackets is unity we can still use k^* as defined above. However, it is now convenient to define a new term, the normalized rate constant

$$k^{**} = (H_3O^+)k^*/(H_3BO_3) \quad (9)$$

The final equation, after rearrangement, is

$$k^{**} = k_2K_0K_4K_5(H_2O) + k_4K_0K_4K_8K_9(OH^-) -$$
$$k_0'K_0K_4(H_2O) - k_0'K_0K_4K_8(OH^-) -$$
$$k_{OH}K_0K_4(H_2O)(OH^-) - k_{OH}K_0K_4K_8(OH^-)^2 +$$
$$\left(k_3K_0K_4K_6K_7 + k_5K_0K_4K_6K_{10}K_{11}\frac{(OH^-)}{(H_2O)} - \right.$$
$$2k_0'K_0K_4K_6 - 2k_0'K_0K_4K_6K_{10}\frac{(OH^-)}{(H_2O)} -$$
$$2k_{OH}K_0K_4K_6(OH^-) -$$
$$\left.2k_{OH}K_0K_4K_6K_{10}\frac{(OH^-)}{(H_2O)}\right)(HOOH) \quad (10)$$

This equation states that for a given pH, the variation of k^{**} with HOOH concentration will be linear with both the slope and the intercept (at zero peroxide concentration) defined by equations that are quadratic in hydroxide ion concentration. For simplicity of notation we will call the intercept A and the slope B.

$$A = (k^{**})_{HOOH=0} = k_2K_0K_4K_5(H_2O) -$$
$$k_0' K_0K_4(H_2O) + (k_4K_0K_4K_8K_9 - k_0'K_0K_4K_8 -$$
$$k_{OH}K_0K_4(H_2O))(OH^-) - k_{OH}K_0K_4K_8(OH^-)^2 \quad (11)$$

$$B = \frac{dk^{**}}{d(HOOH)} = k_3K_0K_4K_6K_7 - 2k_0'K_0K_4K_6 +$$
$$\left(\frac{k_5K_0K_4K_6K_{10}K_{11}}{(H_2O)} - \frac{2k_0'K_0K_4K_6K_{10}}{(H_2O)} - \right.$$
$$\left.2k_{HO}K_0K_4K_6\right)(OH^-) - \frac{2k_{OH}K_0K_4K_6K_{10}(OH^-)^2}{(H_2O)} \quad (12)$$

2. Interpretation of the Experimental Data in terms of the Derived Rate Equation. Table I contains the data used to solve for A and B at each pH value investigated. Figure 2 was constructed from these data.

The values of A and B obtained from the intercepts and slopes of Figure 2 by least-squares calculations are listed in Table II. These are plotted (in turn) *vs.* (OH^-) in Figure 3.

Figure 3 shows two curves which may be fitted by quadratic equations. However, eq. 11 and 12 both show negative coefficients for the $(OH^-)^2$ term, and none of the constants in these terms can be negative. Therefore, the upwards curvature observed must have a different explanation, and we can assume that the coefficient of each $(OH^-)^2$ is zero, or at least in-
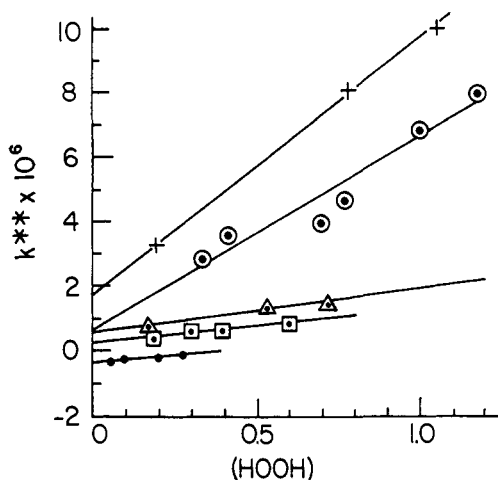
Figure 2. Dependence of normalized rate constant on (HOOH) for added borate (pH: +, 7.42; ⊙, 8.02; △, 8.30; ▣, 8.55; and ●, 9.01).

significant in the pH range studied. On the basis of this assumption, we have drawn straight lines through the linear portion of each curve and extrapolated to zero hydroxyl ion concentration.

Table I. Variation of Normalized Rate Constant with HOOH for Added Borate[a]

$k^{**} \times 10^6$	$(HOOH)_0$	$k^{**} \times 10^6$	$(HOOH)_0$	(H_3BO_3)
——pH 7.42——		————pH 8.02————		
3.25	0.194	2.85	0.339	0.0800
8.09	0.784	3.59	0.412	0.0880
9.97	1.057	3.92	0.701	0.0200
		4.65	0.770	0.0040
——pH 8.30——		6.83	1.002	0.0120
0.75	0.170	7.93	1.185	0.0100
1.33	0.533			
1.43	0.720			
		——pH 8.55——		
		0.405	0.187	
——pH 9.01——		0.663	0.300	
−0.313	0.0549	0.626	0.398	
−0.271	0.0947	0.862	0.602	
−0.206	0.201			
−0.120	0.271			

[a] 35% t-BuOH, 45°; k^{**} in l. mole^{-1} hr.$^{-1}$; 0.0800 M in H_3BO_3 except at pH 8.02.

Table II. Variation of A and B for Added Borate with (OH$^-$)[a]

pH	$A \times 10^6$	$B \times 10^6$	$(OH^-) \times 10^6$
7.42	1.77	7.87	0.670
8.02	0.675	5.83	2.67
8.30	0.570	1.20	5.08
8.55	0.271	0.988	9.04
9.01	−0.359	0.844	26.1

[a] A in l. mole^{-1} hr.$^{-1}$; B in l.^{2} mole^{-2} hr.$^{-1}$.

Examination of the coefficients for the (OH$^-$)^2 terms in eq. 11 and 12 reveals that their zero (or insignificant) value can be attributed only to K_8 and K_{10} since all the other multiplying coefficients have significant magnitudes. Therefore, we can disregard two other terms in each equation also containing one of these constants.
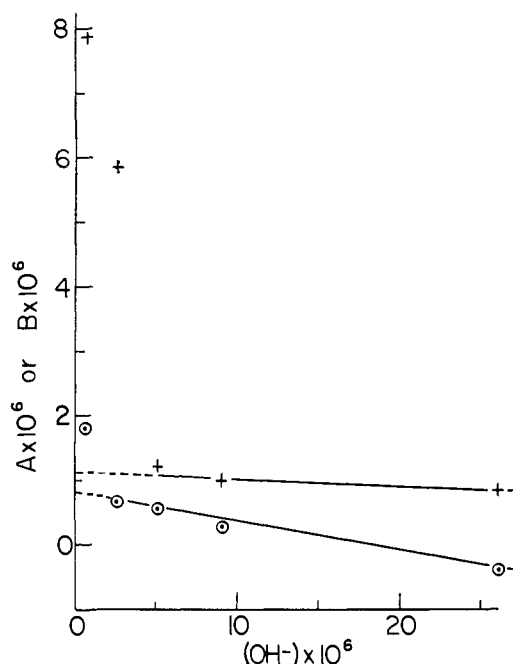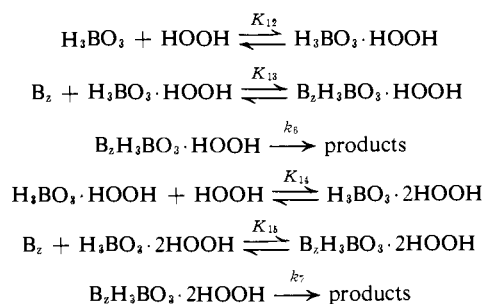

Figure 3. Graph of A or B vs. (OH$^-$); ⊙, dependence of A, intercept at (HOOH) = 0, on (OH$^-$); +, dependence of B, d(k^{**})/d(HOOH), on (OH$^-$) for added borate.

This leaves a single term expressing the slope of each line in Figure 3. For the plot of A vs. (OH$^-$), the slope is $-k_{OH}K_0K_4(H_2O)$ and has a numerical value of −0.0458 from least-squares calculations on the four points. Antikainen's[5] K_α is equivalent to our $K_0K_4 \cdot (H_2O)$ and has the value 1.59×10^{-8}. Multiplying by $-k_{OH}$ we calculate a slope of −0.0431. Similarly, for the graph of B vs. (OH$^-$) we observe a slope of −0.0084, while the value calculated using Antikainen's K_β of 4.08×10^{-8} as $K_0K_4K_6(H_2O)$ is −0.0062. This agreement may be somewhat fortuitous because of the difference in solvent systems, but it does justify the use of linear relationships over the pH range studied.

The deviation in the low pH region of the curves in Figure 3 may be due to catalysis by un-ionized complexes not considered in the derivation of eq. 10, or it may result, at least in part, from experimental factors such as the inability to achieve very constant borate concentration at pH 8.02, not having adequate pH stat regulation for pH 7.42, etc. We use the following equations to consider the first possibility.

$$H_3BO_3 + HOOH \overset{K_{12}}{\rightleftharpoons} H_3BO_3 \cdot HOOH$$

$$B_z + H_3BO_3 \cdot HOOH \overset{K_{13}}{\rightleftharpoons} B_zH_3BO_3 \cdot HOOH$$

$$B_zH_3BO_3 \cdot HOOH \overset{k_6}{\longrightarrow} products$$

$$H_3BO_3 \cdot HOOH + HOOH \overset{K_{14}}{\rightleftharpoons} H_3BO_3 \cdot 2HOOH$$

$$B_z + H_3BO_3 \cdot 2HOOH \overset{K_{15}}{\rightleftharpoons} B_zH_3BO_3 \cdot 2HOOH$$

$$B_zH_3BO_3 \cdot 2HOOH \overset{k_7}{\longrightarrow} products$$

After correcting to the equilibrium concentration of HOOH, eliminating all terms containing K_8 or K_{10}, and rearranging we obtain a working equation

$$\frac{k' - (k_0' + k_{OH}(OH^-))}{(H_3BO_3)} = k_6K_{12}K_{13} - k_0'K_{12} +$$

(9) P. von Rysselberghe, P. Delahay, A. H. Gropp, J. M. McGee, and R. D. Williams, *J. Phys. Colloid Chem.*, **54**, 754 (1950).
(10) J. R. Partington and A. H. Fathallah, *J. Chem. Soc.*, 1934 (1950).

$$\frac{k_2 K_0 K_4 K_8 (H_2O)(OH^-)}{K_w} - \frac{k_0' K_0 K_4 (H_2O)(OH^-)}{K_w} -$$

$$k_{OH} K_{12}(OH^-) - \frac{k_{OH} K_0 K_4 (H_2O)(OH^-)^2}{K_w} +$$

$$\left(k_7 K_{12} K_{14} K_{15} - 2k_0' K_{12} K_{14} + \frac{k_3 K_0 K_4 K_6 K_7 (OH^-)}{K_w} - \right.$$

$$2k_{OH} K_{12} K_{14}(OH^-) - \frac{2k_0' K_0 K_4 K_6 (OH^-)}{K_w} -$$

$$\left. \frac{2k_{OH} K_0 K_4 K_6 (OH^-)^2}{K_w} \right)(HOOH)_0 \quad (13)$$

This expression has the same form as eq. 10, and is treated similarly. The intercepts and slopes from linear plots *vs.* $(HOOH)_0$ can be corrected for the known dependence on $(OH^-)^2$. Table III lists the values, A' being the intercept *plus* $k_{OH} K_0 K_4 (H_2O) \cdot (OH^-)^2 / K_w$ and B' the slope *plus* $2k_{OH} K_0 K_4 K_6 (OH^-)^2 / K_w$.

Table III. Dependence of A' and B' on (OH^-) for Added Borate[a]

pH	A'	B'	$(OH^-) \times 10^6$
5.20	2	14	0.0040
7.42	37	(163)	0.670
8.02	83	(607)	2.67
8.30	159	245	5.08
8.55	240	375	9.04
9.01	848	1076	26.1

[a] A' in l. mole^{-1} hr.$^{-1}$; B' in l.^{2} mole^{-2} hr.$^{-1}$.

The data at pH 5.20 are included because we are interested in the low pH region, but they are not weighted equally with the other data in the least-squares calculations because they are derived from only two experiments. The calculated slopes for A' and B' *vs.* (OH^-) are 31.3×10^6 and 41.5×10^6, respectively. (Essentially identical values can be calculated from the extrapolated intercepts of Figure 3.) The intercept calculated from the A' data is 0.7, and the standard deviation for the six points is 7%. For the B' values, the intercept is 7.7. However, only four points can be used, the standard deviation being 3%. Thus, we cannot decide with any degree of confidence as to whether the values of 0.7 for $(k_6 K_{12} K_{13} - k_0' K_{12})$ and 7.7 for $(k_7 K_{12} K_{14} K_{15} - 2k_0' K_{12} K_{14})$ are significant enough to verify the existence of un-ionized complex, especially since this treatment does not completely correct for the deviation of B values in Figure 3.

B. Carbonate Catalysis. Experiments similar to those with borate were carried out using carbonate. The results show that the effects of added carbonate on the rate of cleavage of benzil follow the same pattern as those of added borate. This is best perceived by examination of Table IV and Figure 4.

The data obtained from Figure 4, again designating the intercepts as A and the slopes as B, are listed in Table V and plotted in Figure 5 as functions of (OH^-).

Figure 5 shows that the equations derived using added borate as an example are equally appropriate for analyzing data with carbonate as the additive. Once again the linearity observed implies a zero coefficient for the $(OH^-)^2$ terms, indicating no catalytic dianions. The only significant difference is that the

deviations noted at low pH in the case of borate are not apparent here.

Table IV. Variation of Normalized Rate Constant with $(HOOH)$ for Added Carbonate[a]

| $k^{**} \times 10^6$	$(HOOH)_0$	$k^{**} \times 10^6$	$(HOOH)_0$	(H_2CO_4)
pH 7.48		pH 8.33		
1.96	0.211	0.939	0.148	
3.26	0.500	1.35	0.353	0.0193
3.71	0.625	1.75	0.545	
5.23	0.900			
6.36	1.203	pH 8.55		
		0.585	0.222	0.048
pH 8.02		0.700	0.395	0.0146
1.52	0.230	0.932	0.636	0.0450
1.68	0.311	pH 8.70		
2.38	0.490	0.502	0.066	0.112
3.00	0.651	0.458	0.115	0.112
4.73	1.110	0.329	0.213	0.112

[a] 35% *t*-BuOH, 45°; k^{**} in units of l. mole^{-1} hr.$^{-1}$; 0.0375 *M* H_2CO_3 unless noted otherwise.

Table V. A and B for Added Carbonate as a Function of (OH^-)[a]

pH	$A \times 10^6$	$B \times 10^6$	$(OH^-) \times 10^6$
7.48	0.88	4.60	0.769
8.02	0.70	3.57	2.67
8.33	0.63	2.07	5.45
8.55	0.40	0.82	9.04
8.70	0.56	-1.17	12.8

[a] A in l. mole^{-1} hr.$^{-1}$; B in l.^{2} mole^{-2} hr.$^{-1}$.

Previous evidence for the existence of percarbonic acid and its anions in solution is based on acidity data and polarographic data.[9] The isolation and analysis of solid alkali metal peroxycarbonates has also been reported.[10] Regarding the existence, preparation in solution, and properties of peroxycarbonates it may be stated that the present work represents the first demonstration by a chemical method or reaction criterion. Furthermore, the similarity in behavior to the case of the peroxyborates implies that there are two species present having the possible structures
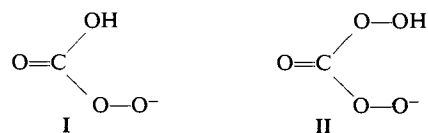
C. Other Additives. A small amount of work was done using other anions as additives. The data for none of these are sufficiently complete for detailed analysis, but we find enough significance to warrant their inclusion in this paper. Table VI contains data for the reaction of benzil and H_2O_2 with added acetate, phosphate, and tungstate, and also for added borate in the reaction of benzil with *t*-BuOOH. The results for added acetate are included in Table VI merely to demonstrate that our earlier statement to the effect that acetate had no catalytic activity was not the

Table VI. Variation of Normalized Rate Constant with Peroxide[a]

$k^{**} \times 10^6$	(Additive)	(HOOH)
——Phosphate, pH 7.42——		
54.1	0.0050	0.651
——pH 8.02——		
3.21	0.0102	0.525
4.28	0.0124	0.552
4.23	0.0148	0.688
6.09	0.0076	0.828
5.39	0.0102	0.893
——pH 8.33——		
−0.34	0.0664	0.789
——Tungstate, pH 7.15——		
9.70	0.0200	0.769
24.5	0.0117	1.276

$k^{**} \times 10^6$	(HOOH)	(Additive)
——Acetate, pH 8.02——		
−0.17	0.461	0.0201
0.68	0.466	0.0299
0.32	0.781	0.0247
0.013	0.788	0.0448
0.33	0.823	0.0049

$k^{**} \times 10^6$	(t-BuOOH)	k'	(Borate)
——Borate with t-BuOOH, pH 8.33——			
...	...	0.184	0
0.0164	0.462	0.225	0.0118
0.0200	0.481	0.277	0.0220
0.0168	0.481	0.335	0.0424

$k_c = 3.80\ \mathrm{l.}^2\ \mathrm{mole}^{-2}\ \mathrm{hr.}^{-1}$

[a] 35% t-BuOH, 45°; k' or k^{**} in l. mole^{-1} hr.$^{-1}$.

fortuitous result of a simpler method of treating the data.

The mean value of k^{**} for added acetate is 0.215 ± 0.204 × 10^6 l. mole^{-1} hr.$^{-1}$. This deviation from zero

Figure 4. Dependence of normalized rate constant on (HOOH) for added carbonate (pH: +, 7.48; ○, 8.02; △, 8.33; □, 8.55; and ●, 8.70).

is within experimental error, being approximately 5% of the values obtained with active additives (borate, carbonate, phosphate) at the same pH and peroxide concentrations.

The k' values are included in Table VI for catalysis by borate in the reaction of t-BuOOH with benzil because this data may be analyzed by eq. 10 or 3. The fact that eq. 3 yields the correct intercept (k_{OH} (OH$^-$) + k_0 = 0.184 for this system) has double significance. It indicates that only a single catalytic species is operative, and that the concentration of t-BuOOH bound up in that species is not sufficient to necessitate the use of a corrective term similar to that for HOOH in eq. 8. The catalytic coefficient obtained corresponds to a k^{**} of 0.0179 × 10^6 l. mol.$^{-1}$ hr.$^{-1}$, about *two orders of magnitude smaller* than with HOOH in the same system.

Since only one catalytic species is detected, it is most logically represented by structure III. Steric considerations no doubt contribute to the fact that no detectable amount of a species containing two t-BuOOH
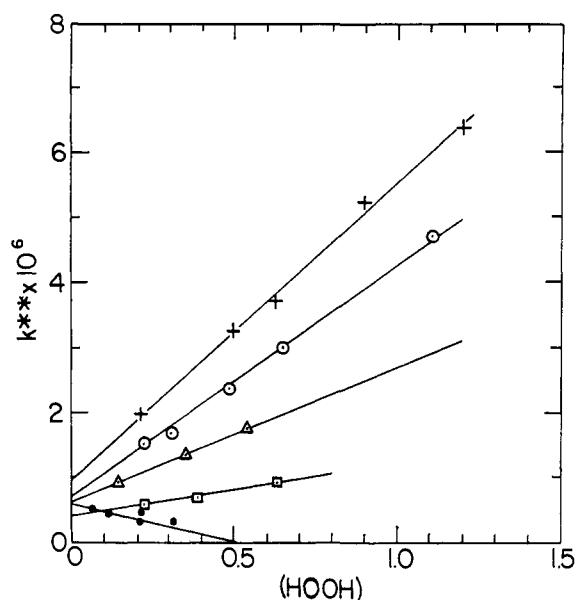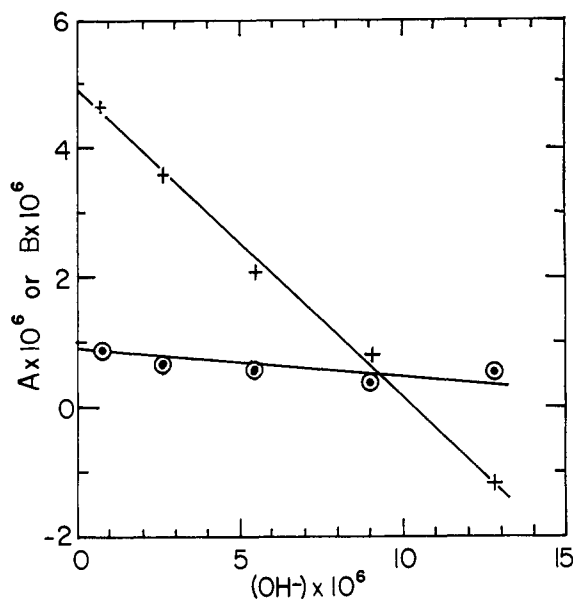

Figure 5. Graph of A or B vs. (OH$^-$); ○, dependence of A, intercept at (HOOH) = 0, on (OH$^-$); +, dependence of B, d(k^{**})/d(HOOH), on (OH$^-$) for added carbonate.

groups is formed. While noting the small catalytic coefficient, we cannot specify whether this is mainly due to low catalytic activity or low equilibrium concentration of the complex anion. The fact that a change in peroxide concentration could not be detected kinetically gives added weight to the latter consideration. This suggests that catalytically effective peroxyanions formed between borate and hydrogen peroxide are preferably represented by structures like IV rather than V.

III   IV   V
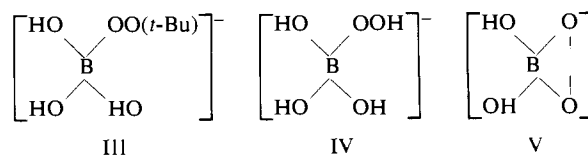
The data for added phosphate is clearly analogous to that for added borate and carbonate. Values of A and B (eq. 11 and 12) at the pH investigated are compared in Table VII.
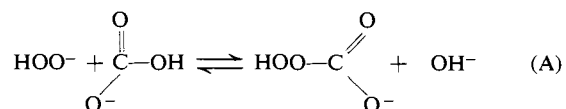
Edwards[8] has suggested that the replacement rates of phosphate with other hydroxylic reagents are still measurable in acid solution. If this was a factor determing the rate of equilibrium establishment in forming the peroxyphosphate anion, we could not have expected adherence to the same kinetic pattern observed by borate and carbonate.

Finally, the two points on Table VI that represent the effect of added tungstate are evidence of a very considerable catalytic influence. It is, perhaps, not surprising that peroxytungstate anions analogous to the peroxyborate and peroxycarbonate are formed very rapidly in almost neutral solution in view of the high replacement rates discussed for the oxyxanion[10] and polarographic studies of the equilibrium established in solutions of H_2O_2, even when weakly acid.[11]

The Mechanism of Peroxyanion Formation. Let us consider first the case of peroxycarbonate as a model. The kinetic data indicate that the carbonate ion in solution with hydrogen peroxide is very rapidly established in equilibrium with the peroxycarbonate species. Under any other circumstances the close fit of the kinetic data to the rate equation could not have been obtained. This is perhaps surprising in view of the report[8] that the rates of ordinary replacement reactions of H_2CO_3 are measurable in alkaline solution. The most probable mechanism suggested[12] involves reversion of the carbonate anion to CO_2 followed by a rate-determining attack of the replacing nucleophile on the CO_2. The high rates of peroxycarbonate formation required by the kinetic interpretation of the catalysis data point up once again that the hydroperoxyanion is an exceedingly powerful nucleophile and is most reactive in this respect toward carbonyl centers. This brings up the question of why acetate anion exhibits no catalysis of the cleavage reaction though the corresponding. peroxyacid is well known. The answer is at least partly provided by the work of Bunton, Lewis and Llewellyn[13] who identified the slow rate of formation and hydrolysis of peracetic acid compared to performic acid and were of the opinion that the results could be explained by assumption of a reaction mechanism of replacement analogous to $A_{AC}2$ carboxyl esterification and hydrolysis. On this basis the slow rates of peroxyacid formation in

(11) I. M. Kolthoff and E. P. Parry, *J. Am. Chem. Soc.*, 73, 5315 (1951).
(12) G. A Mills and H. C. Urey, *ibid.*, 62, 1019 (1940).
(13) C. A. Bunton, T. A. Lewis, and D. R. Llewellyn, *J. Chem. Soc.*, 1226 (1956); see also ref. 52 therein.

acetic acid are due to steric hindrance factors, which are also capable of influencing the reactions of bases and nucleophiles with CO_2.[8]

It seems reasonably certain on the basis of the evidence discussed above that the catalytic influences exerted by various oxyanions on the rate of cleavage of benzils is due to the prior equilibrium formation of the corresponding peroxyanions. Edwards[8] has examined a great deal of data on such equilibria in cases representing a large variety of oxyanions and has generalized them as substitution reactions. From these discussions and others[14,15] we may infer that two different mechanisms (A and B) for peroxyanion formation could conceivably apply. The first, using carbonate as an example, is a displacement reaction on the carbonyl carbon similar to a Walden inversion.[14]

$$HOO^- + \underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{C}} {-}OH \rightleftharpoons HOO{-}C\overset{\nearrow O}{\underset{\searrow O^-}{}} + OH^- \quad (A)$$

The second possibility suggests the occurrence of a prior dissociation catalyzed by acid, followed by reaction of the dissociation product with the displacement reagent, the latter (k_2) being rate determining.

$$HCO_3^- + H^+ \underset{}{\overset{k_1}{\rightleftharpoons}} CO_2 + HOH$$

$$CO_2 + HY^- \overset{k_2}{\longrightarrow} CO_2HY^- \quad (B)$$
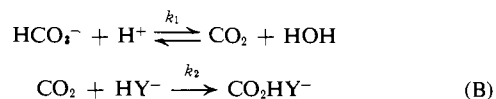
The reaction of carbonates with a variety of bases has been identified as of the latter type where one observes, as expected, acid catalysis corresponding to the prior dissociation step, k_1 (where HY^- is the displacing reagent).[16-19] In fact, it has been pointed out[17-19] that the reaction of carbonates with most nucleophilic agents proceeds rapidly in acid solution but only slowly in basic solution.

The second mechanism (B), however, constitutes a poor fit to the rate law we have observed for peroxyanion formation, and, in fact, the indications are quite strong that we are not dealing here with the usual oxyanion replacement reaction characterized previously.[8,14,15] For example, in studies on the rates of replacement reactions of phosphate by means of heavy oxygen exchange in neutral, acid, and alkaline solution, Winter, Carlton, and Briscol[20] report no measurable action even at 100°; yet our evidence indicates that phosphate is very rapidly equilibrated in alkaline hydrogen peroxide media with its peroxyanion in what is clearly a displacement reaction. We can reject a possible alternative explanation involving nucleophilic displacement by the oxyanion on the oxygen of the peroxide[21] on several grounds. (i) The data in Table VII show that no correspondence exists between the rates and pK_a of the oxyanion acid (concentration of

(14) E. Abel, *Helv. Chim. Acta*, 33, 785 (1950).
(15) H. Taube, *Chem. Rev.*, 50, 93 (1952).
(16) C. Faurholt, *J. Chem. Phys.*, 21, 400 (1925).
(17) C. Faurholt, *ibid.*, 21, 1 (1925).
(18) A. Jensen, M. B. Jensen, and C. Faurholt, *Acta Chem. Scand.*, 6, 1073 (1952).
(19) A. Jensen, R. Christensen, and C. Faurholt, *ibid.*, 7, 1086 (1952).
(20) E. R. S. Winter, M. Carlton, and H. V. A. Briscol, *J. Chem. Soc.*, 131 (1940).
(21) Mechanisms involving nucleophilic displacement on the peroxy oxygen have been identified by Edwards and summarized at the Peroxide Conference at the Metcalf Chemical Laboratory of Brown University, Providence 12, R. I., June 16, 1960.

nucleophile) nor of the nucleophilicity of the oxyanion which has been correlated with its electrode potential.[22] (ii) Many observations bear out the rule that attack on peroxides by an oxygen function has little likelihood of occurrence; rather peroxides are susceptible to attack only by highly polarizable nucleophiles[23,24] which does not correspond to the order in Table VII.

The most plausible and consistent basis for explaining the rapid equilibration of many oxyanions with their peroxy conjugates in H_2O_2 solution is given by mechanism A, a direct Walden inversion type displacement via HOO^-. The unusual nature of this mechanism with oxyanions is attributable to the phenomenal properties of hydroperoxy anion, HOO^-, as a nucleophile.[25] Thus, while phosphate shows almost no exchange activity toward an ordinarily strong nucleophile like hydroxide ion[21] our results indicate the substitution reaction with hydroperoxy

(22) J. O. Edwards, *J. Am. Chem. Soc.*, 76, 1540 (1954).
(23) G. Levey, D. R. Campbell, J. O. Edwards, and J. Maclachlan, *ibid.*, 79, 1797 (1957).
(24) J. O. Edwards, *ibid.*, 78, 1819 (1956).
(25) See, for examples: (a) W. P. Jencks and J. Carriuolo, *ibid.*, 82, 1778 (1960); (b) K. B. Wiberg, *ibid.*, 77, 2519 (1955); (c) D. L. Ball and J. O. Edwards, *ibid.*, 78, 1125 (1956); (d) H. O. House and R. S. Ro, *ibid.*, 80, 2428 (1958); (e) H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *ibid.*, 81, 108 (1959); (f) R. G. Pearson and D. N. Edgingrow, *ibid.*, 84, 4607 (1962); (g) J. Epstein, M. M. Demek, and D. H. Rosenblatt, *J. Org. Chem.*, 21, 796 (1956).

anion is exceedingly rapid. Again, while the rate of reaction of good nucleophilic agents like amines[26] with carbonate increases only weakly and erratically with the amine basicity,[8] hydrogen peroxide in basic solution appears to give us almost instantaneous conversion to percarbonate; under these conditions acid catalysis appears to be dispensible and, in fact, inhibitive since acid serves to produce uncompensated reduction in the concentration of active nucleophile.

Finally, the extremely rapid reaction of alkaline borate with hydrogen peroxide, documented in the results and discussions above, must be understood on the basis of the great susceptibility of the electrophilic boron (central) atom to nucleophilic attack. Even with hydroxide ion the extremely facile exchange of ligands in the coordination sphere of the $B(OH)_4^-$ ion has received comment. The formation of a diperoxyborate and the corresponding diperoxycarbonate formation can be regarded as indication of the ease of displacement of OH^- by the stronger nucleophile HOO^- accommodating a repetition of the substitution reaction which resulted in their respective monoperoxy species.

(26) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, 75, 141 (1953)

Organic Reactions Under High Pressure. IX. Some Observations on the Decomposition of Diacyl Peroxides[1]

Cheves Walling, Howard N. Moulden, James H. Waters, and Robert C. Neuman[2]

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The rapid decomposition of benzoyl peroxide in acetophenone at high pressures has been shown to be due to adiabatic freezing of solvent, not to a fast induced decomposition as previously reported. However, in a nonfreezing solvent ($CHCl_3$) a small acceleration in rate is observed above 3000 kg./cm.², presumably due to induced decomposition. The products of decomposition at 6700 kg./cm.² are also consistent with an induced decomposition, proceeding, at this pressure, largely through benzoyloxy radicals. The decomposition of trans-4-t-butylcyclohexanecarbonyl peroxide is slightly pressure accelerated, $\Delta V^* = -4$ cc./mole. This result is consistent with a carboxyl inversion reaction to trans-4-t-butylcylohexyl trans-4-t-butylcyclohexanecarbonyl carbonate as the rate-determining step in the chief decomposition path, and this intermediate has been detected on the basis of its infrared spectrum and reactions.

The thermal decomposition of diacyl peroxides[3] may occur by three well recognized paths: homolytic scission

of the O–O bond, induced decomposition via radical chain processes, and rearrangement[4] to give a carbonic anhydride or (perhaps directly) an ester and carbon dioxide. The effect of pressure on the rate of peroxide decomposition provides a useful tool for distinguishing between these paths, because the effect of pressure on each can be predicted rather unequivocally. Homolytic scission as a bond-breaking process converting one molecule into two should plainly be pressure retarded. Induced decomposition involves some sequence of radical displacements or additions and such steps (and the over-all chains) are, in general, pressure accelerated.[5] Rearrangement, if it involves a cyclic transition state as is usually assumed, should also show a small pressure acceleration.[6] This paper describes

(1) Support of this work by grants from the Petroleum Research Fund of the American Chemical Society and from the National Science Foundation is gratefully acknowledged.
(2) National Science Foundation Postdoctoral Fellow, 1962–1963.
(3) For general discussion *cf.* C. Walling, "Free Radicals in Solution,"
John Wiley and Sons, Inc., New York, N. Y., 1957; A. G. Davies, "Organic Peroxides," Butterworth and Co. (Publishers) Ltd., London, 1961.
(4) F. D. Greene, H. P. Stein, C. C. Chu, and F. M. Vane, *J. Am. Chem. Soc.*, 86, 2080 (1964), and references cited therein.
(5) *Cf.*, for example, C. Walling and J. Pellon, *ibid.*, 79, 4776, 4782 (1957).
(6) Cope and Claisen rearrangements, for example, are pressure accelerated: C. Walling and M. Naiman, *ibid.*, 84, 2628 (1962). A possible exception is in rearrangements involving tightly bridged structures where steric requirements require unusual bond stretching: C. Walling and H. Schugar, *ibid.*, 85, 607 (1963).