[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Kinetics of the Thermal Decomposition of Peresters. II. The Effect of Solvent and Strong Acid on the Decomposition of *t*-Butyl Perbenzoate[1]

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In a study of the thermal decomposition of *t*-butyl perbenzoate it has been found that the response to solvents parallels that of benzoyl peroxide closely, the decomposition proceeding at about the same rate in all the aromatic solvents used, and at much faster and widely different rates in the aliphatic solvents. The over-all energy of activation for the decomposition was about 34 kcal./mole in all the aromatic solvents, but decreased with increasing rate in the aliphatic solvents. It is suggested that the variation in the rate of decomposition of peroxides from solvent to solvent is the result of an attack on the peroxide by solvent radicals of varying reactivity arising from chain transfer to the solvent, this induced reaction being superimposed on a unimolecular cleavage which proceeds at essentially the same rate in a large number of solvents. As evidence for this view, it has been shown that a small amount of styrene slows the rate of perbenzoate decomposition in *n*-butyl acetate to approximately the rate observed in aromatic solvents. The rate of perbenzoate decomposition in several solvents is increased by trichloroacetic acid, but not by dichloroacetic, suggesting that a strong acid is necessary to make any part of the decomposition proceed by an ionic path. Surprisingly, the amount by which the rate is increased has been found proportional to the square of the acid concentration. The acid-catalyzed reaction thus appears to be a third order reaction, since it is second order with respect to acid, and first order with respect to perbenzoate.

The preceding paper[3] presented the results of a study of the effect of initial peroxide concentration on the rate of decomposition of *t*-butyl perbenzoate. The present paper discusses the effect of change of solvent, and includes a few observations on the effect of strong acid on this decomposition.

Experimental

The preparation of the *t*-butyl perbenzoate used in these studies, the method of analysis, the method of carrying out the decompositions and the purification of the *p*-chlorotoluene, chlorobenzene and xylene were described in the preceding paper.[3] The other solvents used in this study are described below. (All boiling points are uncorrected.)

The ethylbenzene was the best grade obtainable from the Paragon Chemical Company. It was freed from peroxide by refluxing with sodium as described by Cass,[4] and then was distilled in a slow stream of nitrogen, a main cut boiling at 131.5–132° being taken. A 5-ml. sample of this material showed a titer of 0.75 ml. of 0.01 *N* sodium thiosulfate after treatment with sodium iodide by the standard analytical procedure previously described.[3]

The acetic acid was General Chemical Company Reagent glacial acetic acid. It was used directly from a freshly opened bottle without purification.

The *n*-butyl acetate was material prepared in the student laboratory at Cornell by refluxing a mixture of *n*-butyl alcohol and glacial acetic acid with a little concentrated sulfuric acid.[5] The crude material was washed with aqueous sodium carbonate and water, dried and distilled. A main cut boiling at 122–123.5° was taken.

The methyl benzoate was Eastman Kodak Co. White Label grade, and was dried and distilled, a main cut boiling at 90–91° (20 mm.) was taken.

The *t*-butylbenzene was a mixture of material prepared in the student laboratory by the method of Fieser[6] and of material prepared by Dr. W. Karo by the method of Price.[7] It was dried and distilled before use, a main cut boiling at 169.5–171° being taken.

The di-*n*-butyl ether was Paragon Chemical Company Practical grade, and was contaminated heavily with peroxide, a 5-ml. sample showing a titer of 24.7 ml. of 0.01 *N* thiosulfate in the standard analytical procedure. Treatment with acidified sodium iodide, followed by washing with water, sodium thiosulfate, sodium carbonate and distilled water and drying reduced the titer of a 5-ml. sample to 1.60 ml. of 0.01 *N* thiosulfate. The titer was further reduced to 0.40 ml. by treatment with 80–200 mesh activated alumina as suggested by Dasler and Bauer[8] and distillation under carbon dioxide. In later purifications, the crude ether was allowed to stand over activated alumina for several days and then was passed through a column of the alumina for final purification. This material after distillation showed a titer of 0.70 ml. of 0.01 *N* thiosulfate for a 5-ml. sample.

The *n*-butyl alcohol was General Chemical Company Reagent Grade material. It was dried over activated alumina and distilled, a main cut boiling at 117–118° being taken.

Results and Discussion

It was shown previously[3] that the decomposition of *t*-butyl perbenzoate in three aromatic solvents resembled that of benzoyl peroxide rather than that of di-*t*-butyl peroxide, since the over-all first order rate constant showed a small increase with increasing initial peroxide concentration. The data presented in Tables I and II indicates that perbenzoate decomposition likewise resembles that of benzoyl peroxide in showing a marked dependence of rate upon the nature of the solvent in which the perbenzoate is decomposed. In fact, the pattern of response to solvent shown by *t*-butyl perbenzoate is remarkably similar to the pattern shown by benzoyl peroxide, as comparison of the present

TABLE I

DECOMPOSITION OF *t*-BUTYL PERBENZOATE IN AROMATIC SOLVENTS

Initial peroxide concentration 0.065 *M*

Solvent	Over-all first order constant (hr.$^{-1}$) at 110°	at 119.4°	at 130°	Over-all activation energy kcal./mole
Methyl benzoate		0.281		
p-Chlorotoluene	0.123	.364	1.206	34.5
t-Butylbenzene		.372		
Benzene[a]	.126	.375	1.189	34.5
Ethylbenzene		.384		
Xylene[b]		.393	1.228	33.8
Chlorobenzene	.138	.401		33.9
Bromobenzene		.477		

[a] Calculated from data of Shell Development Co., Report No. S-9987, "Di-*t*-Butyl Peroxide," Aug. 15, 1947. Initial perbenzoate concentration was 0.011 *M*. [b] Mixture of isomers.

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[1] Taken from the thesis of A. F. Ferris presented to the Graduate School of Cornell University in September, 1950, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Allied Chemical and Dye Corporation Fellow, 1947-1948.

[3] A. T. Blomquist and A. F. Ferris, THIS JOURNAL, **73**, 3408 (1951).

[4] W. E. Cass, *ibid.*, **68**, 1976 (1946).

[5] R. Adams and J. R. Johnson, "Elementary Laboratory Experiments in Organic Chemistry," 3rd ed., The Macmillan Co., New York, N. Y., 1948, p. 157.

[6] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 180.

[7] C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 17.

[8] W. Dasler and C. D. Bauer, *Ind. Eng. Chem., Anal. Ed.*, **18**, 52 (1946).

TABLE II

DECOMPOSITION OF *t*-BUTYL PERBENZOATE IN ALIPHATIC SOLVENTS

Initial peroxide concentration 0.065 *M*

Solvent	Over-all first order constant (hr.$^{-1}$) 90°	100°	110°	119.4°	Over-all activation energy kcal./mole
n-Butyl acetate			0.380	0.962	29.5
n-Butyl acetate + 0.2 *M* styrene			.130	.397	35.5
Acetic acid		0.138	.412		31.1
Di-*n*-butyl ether		.281	.648		23.7
n-Butyl alcohol	0.334	.974			28.8

data with those of Nozaki and Bartlett[9] indicates. Both peroxides exhibit fairly constant rates of decomposition in most aromatic solvents, and more rapid and widely varying rates in most aliphatic solvents. The parallelism is not quite perfect, failing most notably in the cases of *t*-butylbenzene and *n*-butyl alcohol, but is none the less striking in view of the wide difference in the absolute rates of the two decompositions. (Very roughly, *t*-butyl perbenzoate decomposes as fast at 110° as benzoyl peroxide does at 80°.)

In Figs. 1, 2 and 3 are presented typical first order plots of the decomposition data from aromatic solvents at 119.4° (Fig. 1), and from aliphatic solvents at 110° (Fig. 2) and 100° (Fig. 3). To aid comparisons, one solvent is carried over from Fig. 1 to Fig. 2, and one from Fig. 2 to Fig. 3.

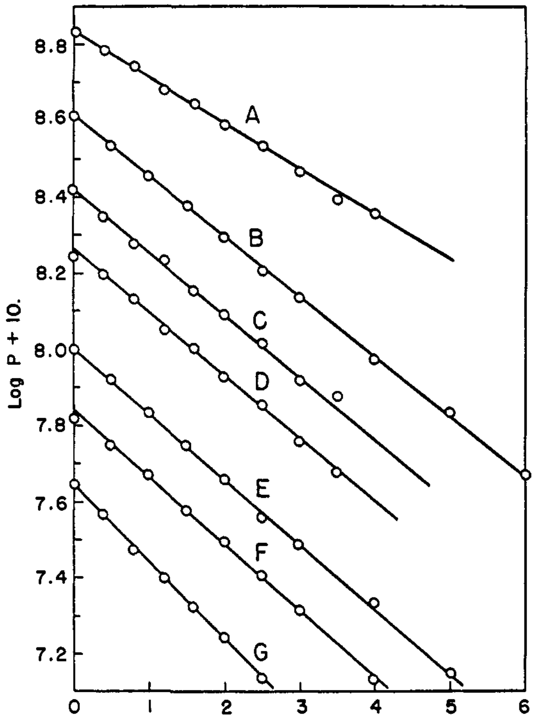

Fig. 1.—Decomposition of *t*-butyl perbenzoate in aromatic solvents at 119.4°. First order plots at initial perbenzoate concentration of 0.065 *M*: A, methyl benzoate; B, *p*-chlorotoluene (ordinate as marked +0.2); C, *t*-butylbenzene (ordinate + 0.4); D, ethylbenzene (ordinate + 0.6); E, xylene (ordinate + 0.8); F, chlorobenzene (ordinate + 1.0); G, bromobenzene (ordinate + 1.2).

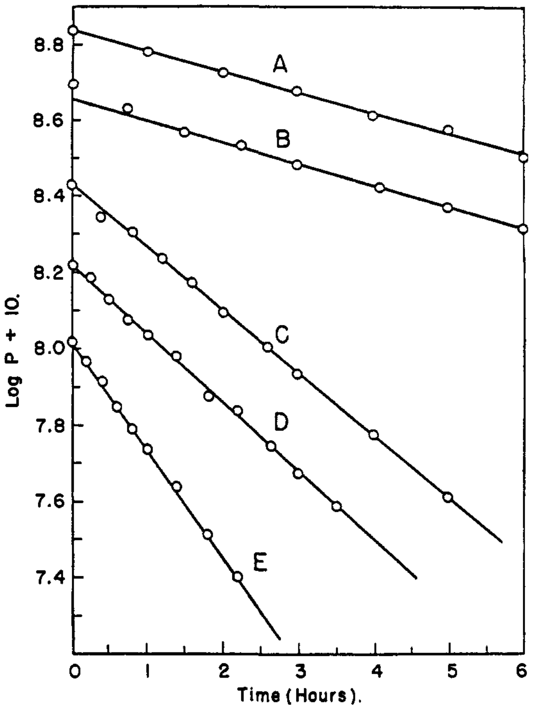

Fig. 2.—Decomposition of *t*-butyl perbenzoate in aliphatic solvents at 110°. First order plots at initial perbenzoate concentration of 0.065 *M*: A, *p*-chlorotoluene; B, *n*-butyl acetate + 0.2 *M* styrene (ordinate as marked + 0.2); C, *n*-butyl acetate (ordinate + 0.4); D, acetic acid (ordinate + 0.6); E, di-*n*-butyl ether (ordinate + 0.8).

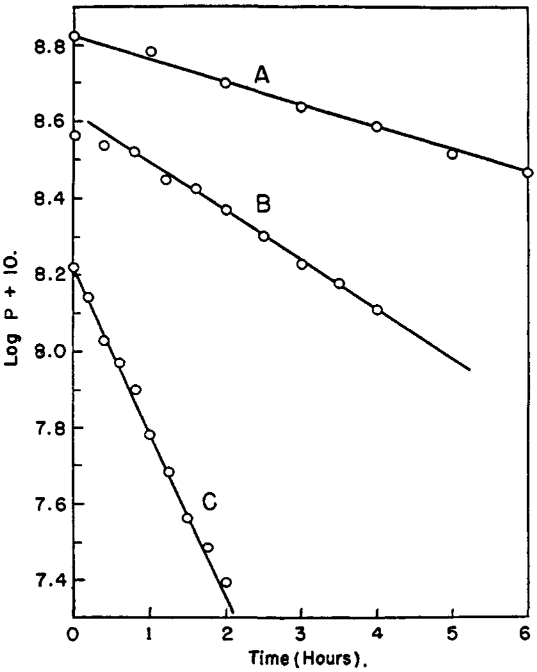

Fig. 3.—Decomposition of *t*-butyl perbenzoate in aliphatic solvents at 100°. First order plots at initial perbenzoate concentration of 0.065 *M*: A, acetic acid; B, di-*n*-butyl ether (ordinate as marked + 0.3); C, *n*-butyl alcohol (ordinate + 0.6).

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[9] (a) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 686 (1946); (b) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

In all solvents, even in the aliphatic ones in which the decomposition was the most rapid, the plots of log P *vs.* time were strictly linear to high percentages of total decomposition (at least 80% in most cases).

As indicated in Tables I and II, decomposition data were obtained at two temperatures in a number of solvents to permit calculation of over-all energies of activation. Since the first order constants from which the energies were calculated were obtained by applying the simple first order rate expression, $-\mathrm{d}P/\mathrm{d}t = kP$, to the experimental data, the energies represent a summation of the energy of the unimolecular decomposition and the energies of any radical induced decomposition, either by peroxide fragments or by solvent fragments, which may have taken place as part of the reactions under study. However, since the combined contribution of radical induced reactions of both types has been shown to be small in the case of perbenzoate decomposition in aromatic solvents,[3] it follows that in all the dilute solutions (0.065 M) used in this work decomposition induced by peroxide fragments should have been of minor importance. It follows also that decomposition induced by solvent fragments should have made a small contribution at best in the aromatic solvents. It was thus to be expected that the activation energies for perbenzoate decomposition would be about the same in all the aromatic solvents used, and this was found to be the case (Table I). The average value, about 34 kcal./mole, is probably a fairly close approximation to the true energy of the unimolecular decomposition. It is noteworthy that this value is roughly intermediate between the value determined in similar solvents for the decomposition of benzoyl peroxide, variously reported between 28 and 33 kcal./mole[4,9,10] and that for the decomposition of di-*t*-butyl peroxide, about 38 kcal./mole.[11]

An excellent indication of the relative contribution of decomposition induced by solvent fragments in aliphatic solvents is provided by the over-all energies themselves. As noted previously, in aliphatic solvents the energies (Table II) were not all the same, and in all cases were smaller than the energies in aromatic solvents by significant amounts. The same type of decrease in the energy of activation in aliphatic solvents was noted with benzoyl peroxide decomposition by Nozaki and Bartlett[9a] and Cass.[4] Since, as has been pointed out by Bartlett,[12] the previous work on the initiation of vinyl polymerization by *t*-butyl perbenzoate[13] indicates that perbenzoate decomposition proceeds by a free radical mechanism similar to that observed in the decomposition of benzoyl peroxide and di-*t*-butyl peroxide, it seems unlikely that solvents not differing greatly in polarity could exert a strong enough influence directly on the unimolecular cleavage to produce the observed changes in the energy of activation. A far more likely interpretation is that the unimolecular cleavage is accompanied by some other reaction of lower activation energy, presumably an attack by solvent fragment radicals. That this is not inconsistent with over-all first order kinetics has been pointed out by Leffler.[14] Data suggesting that the above interpretation is not unreasonable were obtained when a small amount of styrene, a known free radical inhibitor, was added to the *n*-butyl acetate in which perbenzoate was decomposed. The rate constants were depressed well into the aromatic solvent range (Table II) and the energy of activation for the decomposition, which again should have been a fair approximation of the energy of the simple unimolecular cleavage, was 35.5 kcal./mole, a reasonable check with the average value of 34 obtained in aromatic solvents. Similar results with free radical inhibitors were obtained by Swain, Stockmayer and Clarke[15] in their study of benzoyl peroxide decomposition in dioxane.

It thus appears that in aliphatic solvents chain transfer to the solvent leads to new radicals which are more reactive toward undecomposed peroxide than the radicals which they replace, with the result that the decomposition is greatly accelerated and the over-all energy of activation reduced. It may well be that the variation in the rate of decomposition of both benzoyl peroxide and *t*-butyl perbenzoate from solvent to solvent is in most cases the result of attack on the peroxide by solvent radicals of varying reactivity, this induced reaction being superimposed on a unimolecular cleavage which proceeds at essentially the same rate in most solvents at a given temperature. Certain highly halogenated solvents appear to be a notable exception to this general principle.[16]

Effect of Strong Acid

It has been shown by Leffler[14] that the decomposition of the unsymmetrical peroxide, *p*-methoxy-

TABLE III

EFFECT OF ACID ON THE RATE OF DECOMPOSITION OF *t*-BUTYL PERBENZOATE

Initial perbenzoate concentration 0.065 M

Acid	Acid concn., M.	Temp., °C.	Over-all first order constant, k_t, (hr.$^{-1}$)	Acid catalysis constants (k_a) 1st order hr.$^{-1}$/(m./l.)	Acid catalysis constants (k_a) 2nd order hr.$^{-1}$/(m./l.)^2
In *p*-chlorotoluene					
None	....	119.4	0.364	...	...
Trichloroacetic	0.0673	119.4	.429	0.966	14.34
Trichloroacetic	.1343	119.4	.598	1.742	12.97
Dichloroacetic	.0725	119.4	.367	...	...
None	....	110.0	.123	...	...
Trichloroacetic	.1343	110.0	.211	.655	4.88
In acetic acid					
None	....	110.0	.412	...	...
Trichloroacetic	.0682	110.0	.439	.396	5.80
In *n*-butyl acetate					
None	....	110.0	.380	...	...
Trichloroacetic	.0676	110.0	.409	.429	6.34

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[10] B. Barnett and W. E. Vaughan, *J. Phys. Chem.*, **51**, 926 (1947).

[11] J. H. Raley, F. F. Rust and W. E. Vaughan, This Journal, **70**, 1336 (1948).

[12] P. D. Bartlett, *Record Chem. Progress* (*Kresge-Hooker Sci. Lib.*), **11**, 47 (1950).

[13] (a) N. A. Milas and D. M. Surgenor, This Journal, **68**, 642 (1946); (b) R. P. Perry and K. P. Seltzer, *Modern Plastics*, **26**, No. 3, Nov., 1947, p. 134.

[14] J. E. Leffler, This Journal, **72**, 67 (1950).

[15] C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

[16] G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

p′-nitrobenzoyl peroxide, is much more sensitive to acid catalysis than the decomposition of benzoyl peroxide, and it was expected that acid would likewise exert a marked effect on the decomposition of the unsymmetrical *t*-butyl perbenzoate. That this expectation was not realized is shown by the over-all first order constants reported in Table III, which contains data from three solvents with and without trichloroacetic acid and from one solvent with and without dichloroacetic acid. Typical first order plots for the decomposition in *p*-chlorotoluene in the presence of trichloroacetic and dichloroacetic acids are presented in Fig. 4. Since dichloroacetic acid was without effect on the first order constant in *p*-chlorotoluene, it appears safe to assume that all weaker acids would likewise be without effect. Hence *t*-butyl perbenzoate resembles benzoyl peroxide and differs from *p*-methoxy-*p*′-nitrobenzoyl peroxide in that only strong acid increases the rate of its decomposition. Percentagewise, the effect of strong acid was considerable in *p*-chlorotoluene and small in acetic acid and *n*-butyl acetate.

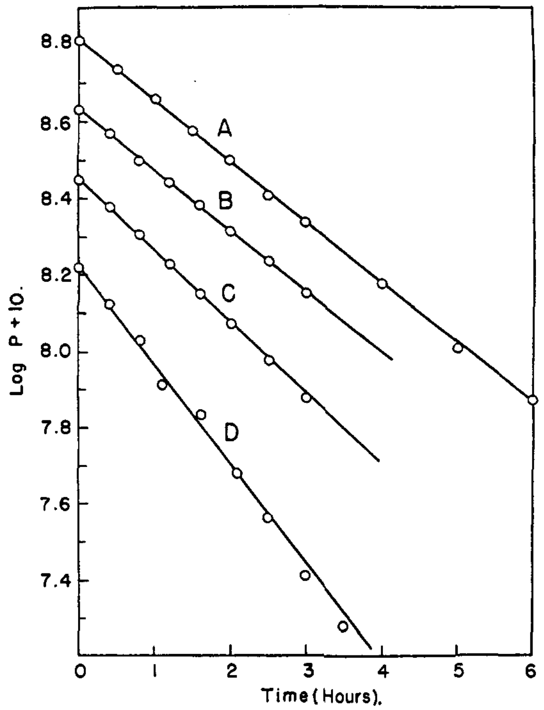

Fig. 4.—Effect of acid on the rate of decomposition of *t*-butyl perbenzoate in *p*-chlorotoluene at 119.4°. First order plots at initial perbenzoate concentration of 0.065 *M*: A, no acid; B, 0.0725 *M* dichloroacetic (ordinate as marked + 0.2); C, 0.0673 *M* trichloroacetic (ordinate + 0.4); D, 0.1343 *M* trichloroacetic (ordinate + 0.6).

When an attempt was made to calculate the acid catalysis constants for perbenzoate decomposition from the equations derived by Leffler[14]

$$-\mathrm{d}P/\mathrm{d}t = k_1(\mathrm{P}) + k_a(\mathrm{P})(\mathrm{HA}) = k_t(\mathrm{P})$$

and

$$k_t = k_1 + k_a(\mathrm{HA})$$

the k_a values obtained were not constant (Table III, next to last column). Likewise, a plot of the acid concentration *vs.* the over-all constant, k_t, was not a straight line (Fig. 5, Curve A). However, if the acid concentration was brought into the previous expression as a *squared* term, to give

$$k_t = k_1 + k_a(\mathrm{HA})^2$$

consistent values of the acid catalysis constant were obtained (Table III, last column). Likewise, a plot of the square of the acid concentration against k_t was a good straight line (Fig. 5, Curve B).

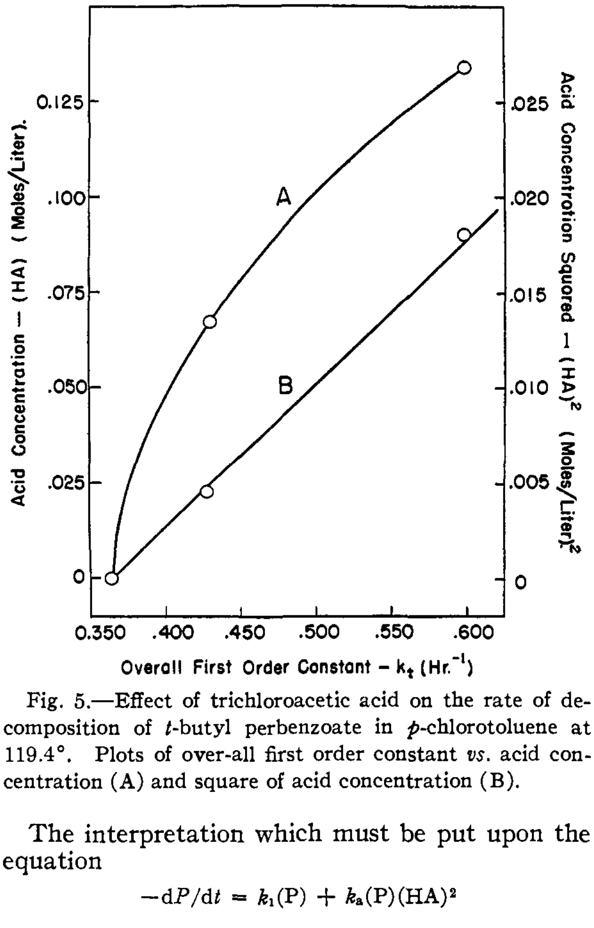

Fig. 5.—Effect of trichloroacetic acid on the rate of decomposition of *t*-butyl perbenzoate in *p*-chlorotoluene at 119.4°. Plots of over-all first order constant *vs.* acid concentration (A) and square of acid concentration (B).

The interpretation which must be put upon the equation

$$-\mathrm{d}P/\mathrm{d}t = k_1(\mathrm{P}) + k_a(\mathrm{P})(\mathrm{HA})^2$$

is somewhat difficult to accept, since it indicates that the acid-catalyzed reaction is that supposedly rare phenomenon, a third order reaction. The reaction appears to involve one molecule of perbenzoate and two of trichloroacetic acid, and hence is first order with respect to perbenzoate and second order with respect to acid. This reaction is not an isolated case, however, since other third order organic reactions have been reported.[17] Although the incompleteness of the present data makes it impossible to do more than speculate as to the mechanism of the acid-catalyzed decomposition of *t*-butyl perbenzoate, it is hoped that the further work which is under way in this Laboratory will permit conclusions to be drawn.

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[17] (a) A. A. Askdown, *ibid.*, **52**, 268 (1930); (b) C. G. Swain, *ibid.*, **70**, 1119 (1948); (c) C. G. Swain and R. W. Eddy, *ibid.*, **70**, 2989 (1948); (d) A. E. Remick, *Record Chem. Progress* (Kresge-Hooker Sci. Lib.), **11**, 55 (1950).