and 2-dimethylaminostilbene have been reported to inhibit growth of Walker carcinoma of the rat,[3] and several styryl compounds have been reported to be germicides[4] or to inhibit aerobic glycolysis.[5] The method of Phillips[6] was employed in preparing the compounds listed.

The *p*-dialkylaminostyrylquinolinium salts were deep purple or green crystalline solids which formed purple solutions in water, while the other salts ranged from yellow to red in color and formed yellow or orange solutions. The solubilities in hot water were of the order of 0.01–0.5%. In most instances the color was destroyed or weakened by dilute nitric acid so that determination of the ionic halogen content by Volhard analyses was satisfactory.

Samples have been submitted to interested groups for screening against tumors in mice and for testing as plant growth control substances.

Acknowledgments.—This project has been supported, in part, by a research grant from the National Cancer Institute, for which the authors wish to express their gratitude. They are also grateful to Miss Marguerite Close and Miss Betty Gay Walden for carrying out Volhard analyses on samples and to Dr. M. J. Shear and Dr. J. L. Hartwell of the National Cancer Institute for their interest and encouragement.

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

The Kinetics of the Thermal Decomposition of Peresters. I. The Effect of Perbenzoate Concentration on the Decomposition of *t*-Butyl Perbenzoate[1]

BY A. T. BLOMQUIST AND ARTHUR F. FERRIS[2]

The thermal decomposition of *t*-butyl perbenzoate has been studied at several different temperatures and initial peroxide concentrations in *p*-chlorotoluene and at two concentrations at one temperature in chlorobenzene and xylene. The increase in the over-all first order rate constant with increasing initial peroxide concentration is small but real and appears to be caused by free radical attack on undecomposed peroxide, since it was eliminated by acetanilide, a known free radical inhibitor. The method developed by Nozaki and Bartlett for calculating unimolecular rate constants did not give consistent results when applied to perbenzoate data. The energy of activation for the decomposition of *t*-butyl perbenzoate in *p*-chlorotoluene was calculated to be 34.5 kcal./mole.

It has been shown recently that the rate of the thermal decomposition of benzoyl peroxide increases with increasing initial peroxide concentration in a given solvent[3] and varies widely from solvent to solvent.[4] It appears clear that the unimolecular cleavage of the peroxide is accompanied by a higher order reaction, and considerable evidence has been accumulated to indicate that this is a radical induced attack on undecomposed peroxide.[4a,5b] On the other hand, the decomposition of di-*t*-butyl peroxide appears to be a simple unimolecular reaction, proceeding at essentially the same rate in the vapor phase and in widely different solvents, and showing no concentration effect.[6]

In view of the detailed study which has been made of the kinetics of the decomposition of benzoyl peroxide and di-*t*-butyl peroxide it is somewhat surprising that only fragmentary reports have been published[7] on the kinetics of the decomposition of *t*-butyl perbenzoate, which is, in a sense, intermediate between them. This paper presents the results of a study of the effect of initial peroxide concentration on the rate of decomposition of *t*-butyl perbenzoate. The effect of solvent and the effect of strong acid are discussed in a following paper.

Experimental

The decomposition of the perbenzoate was followed by periodically withdrawing samples of reaction mixtures and analyzing them for undecomposed perbenzoate iodometrically.

t-Butyl Perbenzoate.—The *t*-butyl perbenzoate used in the first part of this investigation was prepared by the method of Milas and Surgenor.[8] Distillation from a cold finger type of molecular still at about 70° (0.05 mm.) gave a product which typically showed the following properties: $n^{20}{}_{D}$ 1.4990, $d^{20}{}_{4}$ 1.0427, % active oxygen 8.13 (theoretical 8.24%, hence purity 98.7%). Later in the investigation undistilled perbenzoate freed of low boiling impurities by prolonged vacuum treatment and having a purity of 95.5% was used, and still later commercial perbenzoate from the Lucidol Division of the Novadel-Agene Corporation Buffalo, New York, likewise freed from low boiling impurities and showing a purity of 96.3%. Both of the later samples decomposed at essentially the same rate as the highly purified material in *p*-chlorotoluene under standard test conditions (temperature 119.4°, peroxide concentration 0.065 *M*).

***p*-Chlorotoluene.**—Most of the *p*-chlorotoluene used in this investigation was prepared in the student laboratory of

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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. The Rohm and Haas Company, Philadelphia, Pennsylvania.

[3] (a) D. J. Brown, THIS JOURNAL, **62**, 2657 (1940); (b) S. G. Cohen, *ibid.*, **67**, 17 (1945); (c) P. D. Bartlett and R. Altschul, *ibid.*, **67**, 816 (1945); (d) B. Barnett and W. E. Vaughan, *J. Phys. Chem.*, **51**, 926 (1947).

[4] (a) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946); (b) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947); (c) W. E. Cass, *ibid.*, **68**, 1976 (1946); (d) B. Barnett and W. E. Vaughan, *J. Phys. Chem.*, **51**, 942 (1947).

[5] (a) W. E. Cass, THIS JOURNAL, **69**, 500 (1947); (b) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

[6] J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 88, 1336 (1948).

[7] (a) Shell Development Co., "Di-*t*-Butyl Peroxide," Report No. S-9987, Aug. 15, 1947; (b) J. T. Clarke, Ph.D. Thesis, Massachusetts Institute of Technology, 1948.

[8] N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 642 (1946).

Cornell University from *p*-toluidine and cuprous chloride.[9] It was washed with sulfuric acid and water and dried and distilled before use. A main cut boiling at 161–162° (uncor.) was taken. Later in the investigation commercial *p*-chlorotoluene from the Heyden Chemical Corp. was used after drying and distillation.

Chlorobenzene.—The chlorobenzene used was a mixture of the best grades obtainable from the Eastman Kodak Company and the Paragon Chemical Company. It was purified by treatment with aluminum chloride as recommended by Holmes and Beeman.[10] A main cut boiling at 128.5° was taken in the final distillation.

Xylene.—The xylene used was a mixture of isomers obtained from the General Chemical Company and labeled "Reagent Grade." It was dried and distilled, the main cut boiling at 135.5°.

Analyses.—After considerable experimentation it was found that quantitative reaction between *t*-butyl perbenzoate and sodium iodide in acetic acid could be obtained by allowing the reactants to stand with occasional agitation at least two hours at room temperature under carbon dioxide. When analyzed by this method carefully purified samples of perbenzoate showed active oxygen contents ranging from 7.97 to 8.13% (theoretical, 8.24%), corresponding to purities of 96.7 to 98.7%. Reflux methods gave lower values. Using nitrogen as the inert atmosphere gave higher values except in the presence of acetone, a known inhibitor of atmospheric oxidation.[7] Acetone did not affect the results obtained with a carbon dioxide atmosphere.

Solutions of perbenzoate were analyzed by pipetting 1- to 5-ml. samples into 10 to 15 ml. of glacial acetic acid containing 3% orthophosphoric acid in 250 ml. erlenmeyer flasks, sweeping the flasks with carbon dioxide, adding 1 to 2 g. of sodium iodide, then allowing the flasks to stand for at least two hours under carbon dioxide in a large opaque desiccator containing three sample flasks and a blank. At the end of the standing time 50 ml. of water was added to each flask and the liberated iodine was titrated with thiosulfate, either 0.01 *N* or 0.025 *N*. Blank titers customarily were less than 0.50 ml. of 0.01 *N* thiosulfate, usually varying between 0.10 and 0.20 ml. By way of contrast, sample volumes were chosen to keep sample titers between 10 and 30 ml. wherever possible, although samples taken late in dilute runs showed titers as low as 5 ml. Solutions of known concentration were prepared by weighing samples of perbenzoate from a Lunge pipet into volumetric flasks and making up to volume with various solvents. When these solutions were analyzed, the determined concentrations checked the calculated values (based on the previously determined active oxygen content of the perbenzoate used) within about one part in one hundred at concentrations of the order of 0.2 *M*, and within about three parts in one hundred at concentrations of the order of 0.02 *M*. It was thus demonstrated that the method of analysis was suitable for determining the concentration of *t*-butyl perbenzoate in dilute solutions.

Apparatus.—The decomposition flasks and attachments were essentially the same as those described by Barnett and Vaughan.[3d] Two such flasks were immersed in a glass wool insulated five-gallon oil-bath heated by two immersion heaters, one on continuously and the other controlled by a bimetallic thermoregulator through a time delay relay. With the control apparatus functioning smoothly the temperature of the bath could be held to within ±0.1° of the desired temperature. The thermometer used was an M.C.A.R.-3 three inch immersion type, graduated in fifths of a degree from 70 to 160°. It was calibrated against a platinum resistance thermometer calibrated by the National Bureau of Standards. We are indebted to Dr. E. R. VanArtsdalen for the use of this thermometer.

Rate Measurements.—The decomposition flasks were preheated in the bath to the operating temperature and swept with nitrogen. The solutions were then added and the stirrers set in motion. When the solutions had warmed to bath temperature (15–20 minutes) the "zero time" sample was withdrawn, emptied into a test tube, and quickly cooled in ice-water. Other samples were withdrawn at suitable intervals and treated in the same manner. Most reactions were followed to 50–60% decomposition, some to 80–90%. When all the samples for a given run had been taken, they were allowed to warm to room temperature and samples were pipetted from them for analysis. First order plots were prepared from the concentrations calculated from the analytical data, and first order rate constants were calculated from two experimental points which fell exactly on what was judged to be the best straight line which could be drawn for each set of data.

Results and Discussion

The results of a study of the effect of initial perbenzoate concentration on the rate of its decomposition in *p*-chlorotoluene, chlorobenzene and xylene are presented in Table I. The *p*-chlorotoluene data are shown in Fig. 1, which contains plots of over-all first order constant *vs.* initial peroxide concentration for three temperatures. Figure 2 contains simple first order plots of typical runs at 119.4° with initial perbenzoate concentrations varying over a tenfold range from 0.02 to 0.2 *M*.

TABLE I

DECOMPOSITION OF *t*-BUTYL PERBENZOATE VARIATION IN FIRST ORDER CONSTANT WITH CONCENTRATION

Temp., °C.	Approx. initial perbenz. concn. (*M*)	No. expts. avgd.	First order constant (hr.$^{-1}$) Range	Average
		p-Chlorotoluene		
110.0	0.02	2	0.116–0.118	0.117
	.065	2	.121– .124	.123
	.2	3	.124– .127	.125
119.4	.02	3	.347– .356	.353
	.065	3	.357– .371	.364
	.125	3	.371– .376	.374
	.2	3	.377– .384	.381
130.0	.02	2	1.06 –1.14	1.10
	.065	2	1.20 –1.21	1.21
	.2	2	1.18 –1.25	1.22
		Chlorobenzene		
119.4	.065	4	0.391–0.407	0.401
	.2	3	.412– .423	.417
		Xylene		
119.4	.065	4	.383– .399	.393
	.2	3	.399– .414	.405

It will be noted that the first order rate constant increases steadily with increasing initial peroxide concentration, the increase being somewhat smaller in magnitude than the similar increase found with benzoyl peroxide.[3] In preliminary runs at higher concentration it was observed that the decomposition of *t*-butyl perbenzoate was exothermic, and it was thought that the concentration effect might be accounted for as a temperature effect. However, when this was checked with a 0.2 *M* solution of perbenzoate in *p*-chlorotoluene, using a thermometer in the reactor which had been calibrated against the bath thermometer with pure solvent in the reactor, it was found that the maximum temperature rise in the reactor was 0.25°, and that this dropped off to 0.15° by the time one-third of the perbenzoate had decomposed, and to 0.05° by the time half had decomposed. From the energy of activation for the decomposition in *p*-chlorotoluene (see last paragraph) the temperature rise necessary to account for the observed difference in rate between a 0.2 *M* solution and a 0.02 *M* one was calculated to be

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[9] R. Adams and J. R. Johnson, "Elementary Laboratory Experiments in Organic Chemistry," 3rd ed., Macmillan, N. Y., 1948, p. 264.

[10] H. N. Holmes and N. Beeman, *Ind. Eng. Chem.*, **26**, 172 (1934).

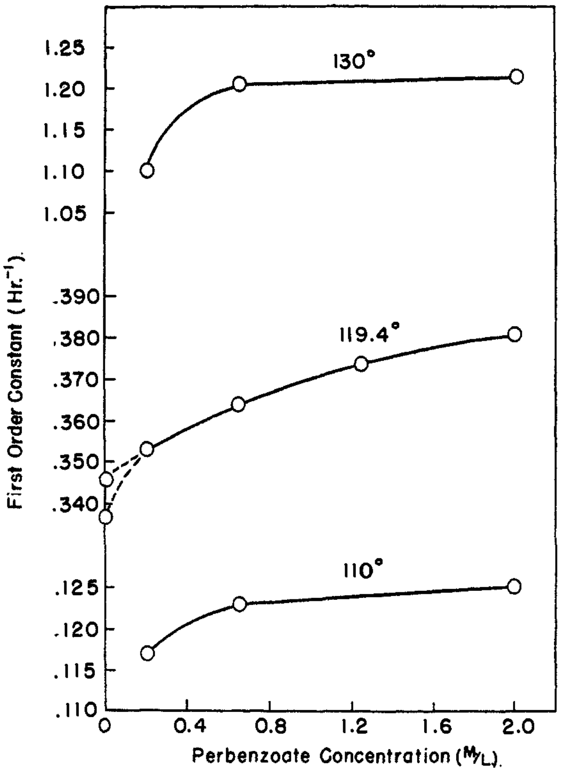

Fig. 1.—Effect of concentration on the thermal decomposition of *t*-butyl perbenzoate in *p*-chlorotoluene. Points on zero concentration axis: Lower—average value of unimolecular rate constant calculated by the method of Nozaki and Bartlett. Upper—rate constant determined at 0.2 *M* perbenzoate concentration in the presence of 0.2 *M* acetanilide.

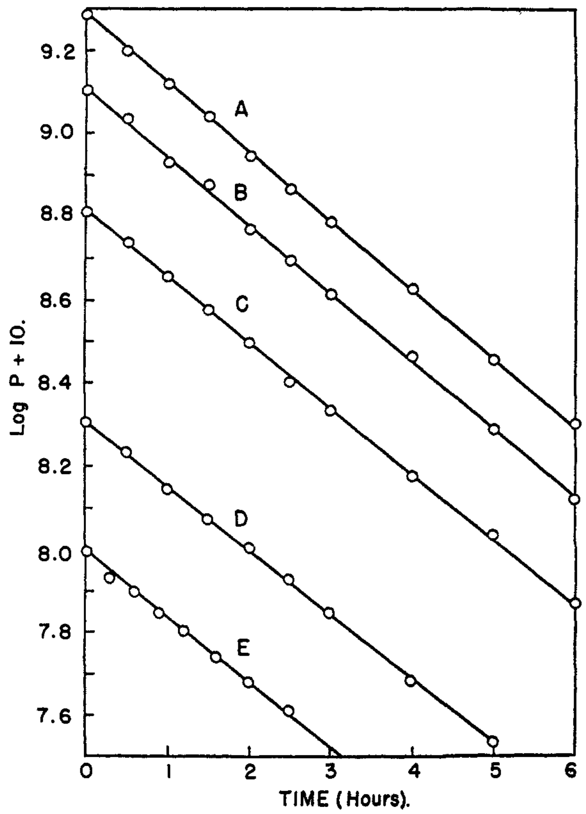

Fig. 2.—Effect of concentration on the thermal decomposition of *t*-butyl perbenzoate in *p*-chlorotoluene at 119.4°. Typical first order plots at various concentrations: A, 0.2 *M*; B, 0.125 *M*; C, 0.065 *M*; D, 0.02 *M*; E, 0.2 *M* + 0.2 *M* acetanilide (ordinate as marked +1.3).

about 0.7°. It thus appears that the concentration effect is largely a real one, and not an artifact resulting from the exothermic nature of the decomposition reaction.

On the basis of their postulation that the complicating reaction in the decomposition of benzoyl peroxide is a radical attack on undecomposed peroxide, Nozaki and Bartlett[4a] represented the over-all kinetics as the sum of a first and a three-halves order reaction

$$-\mathrm{d}P/\mathrm{d}t = k_1P + k_iP^{3/2}$$

Since the decomposition of *t*-butyl perbenzoate appeared to resemble closely the decomposition of benzoyl peroxide, an attempt, largely unsuccessful, was made to use their method to evaluate the unimolecular constant, k_1, and the induced reaction constant, k_i, for perbenzoate decomposition. Although the plots of $1/\sqrt{P_1}$ *vs.* $1/\sqrt{P_2}$ were fairly good straight lines (examples in Fig. 3) at all three of the temperatures used, only from the data at 119.4° could even fairly consistent values of the ratio "*a*" (k_1/k_i) be obtained. The use of the average value, 2.4, in plots of $\ln\,[(a + \sqrt{P})/\sqrt{P}]$ *vs.* time (examples in Fig. 4) for runs at several initial peroxide concentrations gave fairly consistent values of k_1 and k_i, the average values being 0.337 hr.$^{-1}$ and 0.140 (m./l.)$^{1/2}$ hr.$^{-1}$, respectively. This value of k_1 has been plotted on the zero concentration axis of Fig. 1.

A study was made also of the effect of free radical inhibitors on the rate of perbenzoate decomposition, both in order to check the assumption that the complicating reaction in perbenzoate decomposition is a radical induced attack on undecomposed perbenzoate, and in the hope that an inhibitor sufficiently effective to permit experimental evaluation of the true unimolecular constant might be found. Of the inhibitors used by Nozaki and Bartlett,[4a] hydroquinone could not be used in *p*-chlorotoluene because it was insufficiently soluble, picric acid gave such deeply colored breakdown products that solutions containing it could not be analyzed, and *m*-dinitrobenzene apparently reacted very rapidly with the perbenzoate, since by the time the solution containing it had warmed to bath temperature about half the perbenzoate had disappeared.

At least one of the inhibitors suggested by the work of Swain, Stockmayer and Clarke[5b] was more

Table II

Effect of Inhibitors

Decomposition of *t*-butyl perbenzoate in *p*-chlorotoluene at 119.4°

Perbenzoate concn., *M*	Inhibitor	Inhibitor concn., *M*	Avg. first order constant, hr.$^{-1}$
0.065	None	. .	0.364
.065	Styrene	0.25	.368
.2	None	. .	.381
.2	Urethan	.2	.378
.2	Styrene	.2	.370
.2	Acetanilide	.2	.346

effective, as shown in Table II. The really effective inhibitor was acetanilide, in the presence of which perbenzoate decomposed more slowly at 0.2 *M* concentration than it did without inhibitor at 0.02 *M* concentration. Thus the constant obtained with acetanilide, 0.346 hr.$^{-1}$, may well represent a close approach to the "pure" unimolecular reaction constant. It, too, is plotted on the zero concentration axis of Fig. 1. For purposes of comparison, a sample first order plot of the data obtained with acetanilide as inhibitor is included with the typical first order plots in Fig. 2.

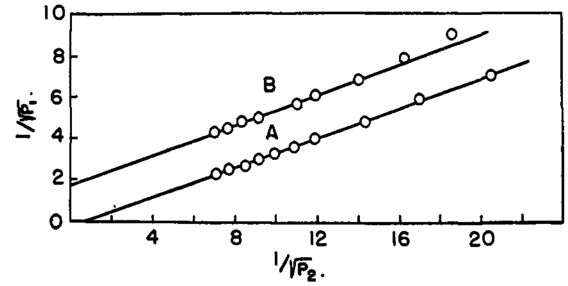

Fig. 3.—Decomposition of *t*-butyl perbenzoate in *p*-chlorotoluene at 119.4°. Plots of $1/\sqrt{P_1}$ *vs.* $1/\sqrt{P_2}$ for runs at 0.2 *M* and 0.02 *M* concentrations. (Line B, ordinate as marked −2.0.)

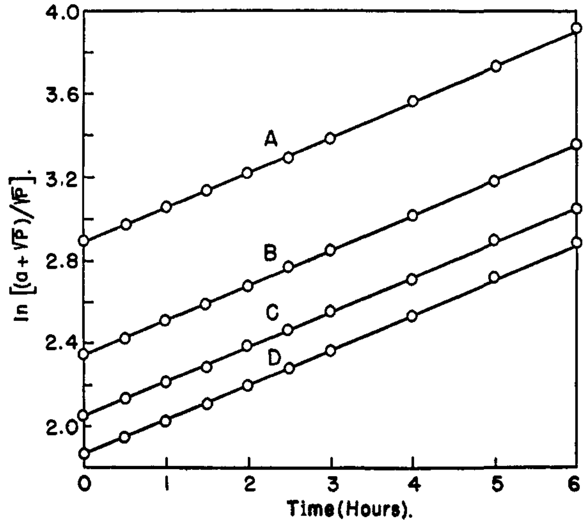

Fig. 4.—Decomposition of *t*-butyl perbenzoate in *p*-chlorotoluene at 119.4°. Plots of $\ln[(a + \sqrt{P})/\sqrt{P}]$ *vs.* time at four perbenzoate concentrations: A, 0.02 *M*; B, 0.065 *M*; C, 0.125 *M*; D, 0.2 *M*.

It therefore appears that the concentration effect in the decomposition of *t*-butyl perbenzoate, like the same type of effect in the decomposition of benzoyl peroxide, is the result of free radical attack on undecomposed peroxide. As pointed out by Nozaki and Bartlett,[4a] speculation as to whether the attacking radical is a fragment of a peroxide molecule or a fragment of a solvent molecule resulting from chain transfer is pointless on the basis of kinetic data alone, since in aromatic solvents like those used in these studies a radical from the solvent would be expected to be about as reactive as a radical from the peroxide, and would lead to the same kinetics. On the other hand, there are at least two cases where this generalization does not hold. When an inhibitor is present, chain transfer to the inhibitor results in a new radical less reactive toward undecomposed peroxide than the one it replaces. This of course is the mechanism of inhibitor action—the more unreactive the radical formed from the inhibitor, the more effective the inhibitor. The opposite situation is encountered when decompositions are carried out in aliphatic solvents, and will be discussed in a following paper.

Another point which was investigated in connection with the study of the variation in the rate of perbenzoate decomposition with concentration was the question of the effect of this variation on energies of activation calculated from the rate constants by the Arrhenius equation. Three plots of log *k* *vs.* $1/T$ were prepared, corresponding to the over-all rate constants determined at initial perbenzoate concentrations of 0.02, 0.065 and 0.2 *M*. As shown in Fig. 5, three practically parallel straight lines were obtained. From the slopes of the lines the energies of activation as determined at each concentration were calculated. The energies found were 34.3 kcal./mole at 0.02 *M*, 34.5 kcal./mole at 0.065 *M*, and 34.8 kcal./mole at 0.2 *M*; average 34.5 kcal./mole. Thus if all the rate constants used to evaluate the energy of activation were determined at about the same initial perbenzoate concentration, the calculated value was the same whatever the concentration.

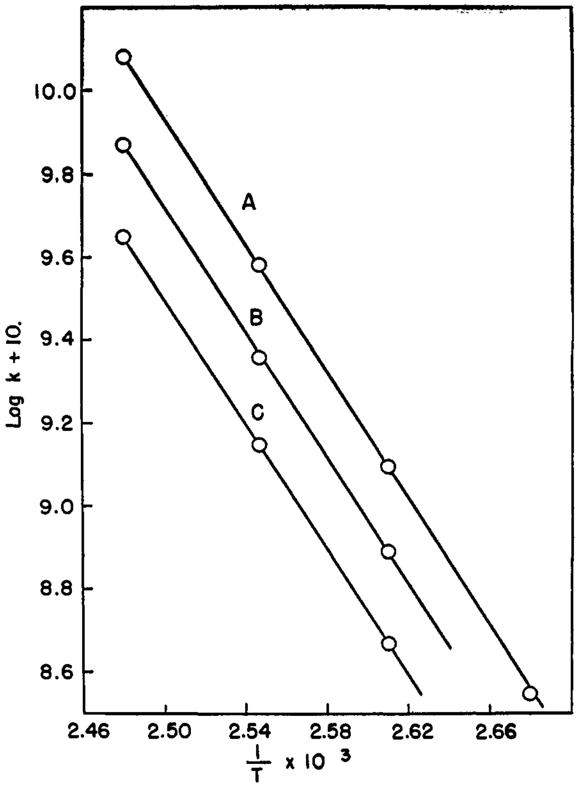

Fig. 5.—Activation energy plots for the decomposition of *t*-butyl perbenzoate in *p*-chlorotoluene. Comparison of data at three concentrations: A, 0.2 *M*; B, 0.065 *M* (ordinate as marked + 0.2); C, 0.02 *M* (ordinate as marked + 0.4).

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