

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

A Re-examination of the Ionic Decomposition of *t*-Butyl Arylpersulfonates

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The ionic decomposition of *t*-butyl pertosylate in aqueous methanol to acetone and toluenesulfonic acid has been confirmed by infrared and n.m.r. examination. In absolute methanol the products are acetone dimethyl ketal and toluenesulfonic acid. Errors have been discovered in the analytical method previously used,¹ and some of the peculiar kinetic effects previously observed have been carefully reinvestigated using kinetic methods based upon conductivity, base titration, polarography, infrared and nuclear magnetic resonance spectroscopy, and semi-quantitative observation by isolation of unconverted starting material. By these methods of investigation *t*-butyl pertosylate in a series of methanol-water mixtures is found to behave like 9-decalyl perbenzoate, showing no deviation from the Grunwald-Winstein equation nor any abnormal salt effects, such as had been reported by Bartlett and Storey.¹ The following constants have been determined: In absolute methanol $k(4.5^\circ) = 0.000108 \text{ sec.}^{-1}$, $\Delta H^\ddagger = 21.5 \text{ kcal.}$, $\Delta S^\ddagger = 0.9 \text{ e.u.}$; $m = 0.72$ in methanol-water at 4.5° , at 20.19° , $m = 0.59$ in methanol-water, 0.52 in ethanol-water, and about 0.5 in dioxane-water. Identical rates were observed in mixtures of dioxane with ordinary water and with heavy water. The rate constant is an approximately linear function of the lithium chloride concentration with $0.3 M$ lithium chloride producing a 40% rate increase.

Introduction

Two years ago a paper from this Laboratory described the preparation of the very unstable compound, *t*-butyl benzenepersulfonate, and four substitution products carrying methoxy, methyl, chloro and bromo substituents at the *p*-position. It was shown that the effect of substituents on the decomposition rates of these peresters in methanol at 4.5° is the opposite of the effects of the same groups on the decomposition rates of *t*-butyl perbenzoates, and this was correlated with the demonstration that *t*-butyl pertosylate gave quantitative yields of acetone and toluenesulfonic acid as would be expected for a molecular rearrangement of the Criegee type leading to a very rapidly hydrolyzed hemiacetal sulfonate.¹

By a difficultly-controlled iodometric method of analysis, the rate of decomposition of *t*-butyl pertosylate was followed in a series of methanol-water mixed solvents and compared with the behavior in the same media of 9-decalyl perbenzoate, a substrate known to undergo rearrangement by an ionic mechanism.²⁻⁴ A sharp negative deviation of the pertosylate rate from the Grunwald-Winstein equation⁵ at the low-water end of the range, as well as some extraordinary salt effects, have remained inexplicable, and we have returned to this problem to reinvestigate the effects with alternative methods of analysis. In the course of this work we have confirmed the properties and general instability of *t*-butyl benzenepersulfonate and *p*-toluenepersulfonate and the ionic character of its decomposition in methanol and methanol-water solutions. However, we have not been successful in obtaining reproducible rate constants with the iodometric procedure previously employed, and indeed all our new methods agree in showing that the deviation from a linear Grunwald-Winstein plot, reported by Bartlett and Storey, is in error. The behavior of *t*-butyl pertosylate in this respect is in fact very close to that of 9-decalyl perbenzoate.

Experimental

Solvents and Reagents. Methanol.—Reagent grade methanol from the Fisher Scientific Co. was used in all but a

few rate runs. It was shown to contain 0.05% water by Karl Fischer titration.⁶ Where this grade of methanol was not used, careful purification of methanol by the method of Fieser⁷ did not change the kinetics.

Ethanol.—Commercial Solvents Corporation Gold Shield ethanol was used directly. It gave an analysis for 0.215 g. per liter of water.

Dioxane was purified by the method of Fieser.⁸

Acetone was reagent grade from the Fisher Scientific Co. **Standard Sodium Hydroxide.**—A solution of sodium hydroxide in methanol, $0.03 M$, was standardized against potassium acid phthalate-water using phenolphthalein and against carefully purified 3,5-dinitrobenzoic acid using brom thymol blue in methanol.

Lithium chloride, reagent grade, from the Mallinckrodt Chemical Works was used directly in runs 54, 55 and 56 and dried at 150° overnight for runs 65 and 68-78.

All solvent mixtures were made up by weight to accuracies of $0.1-0.3\%$. Separate solvent preparations were made for each run.

***t*-Butyl hydroperoxide** from the Lucidol Corporation was distilled under 25 mm. pressure.

Apparatus.—In general all aliquots and solvent mixtures were prepared using special syringes calibrated to accuracies of $0.01-0.1\%$. A 10-ml. microburet was used for all acid titrations.

Conductivity.—An Industrial Instruments Inc. model RC16B1 conductivity bridge was used along with cells of cell constant approximately unity.

Temperature control baths were constant to $\pm 0.01^\circ$ except for the 4.5° bath, which was within $\pm 0.05^\circ$.

Polarography.^{9a}—The potential across the cell was set and the current measured using the circuit described by Kolthoff and Lingane^{9b} with the exception that the current was measured as IR drop across a $100-200\text{-ohm}$ resistor using a 10-millivolt Leeds and Northrup Speedomax type G recorder model S60000, which made a direct record of current versus time.

The cell assembly and operation were exactly those described by Kolthoff and Coetzee.¹⁰ The all-glass cell was 24 mm. in diameter and about 15 cm. long so the heat exchange with the bath was rapid.

Infrared.—A Perkin-Elmer model 21 infrared spectrophotometer was used for all the present work.

Nuclear Magnetic Resonance.—A Varian High Resolution model V4300B spectrometer operating at 40 mc. was em-

(4) H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).

(5) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

(6) J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 94.

(7) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., p. 289.

(8) Reference 7, p. 284.

(9) (a) The assistance of Dr. D. H. Geske in applying the polarograph to this problem is gratefully acknowledged. (b) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1952, p. 298.

(10) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 870 (1957).

(1) P. D. Bartlett and B. T. Storey, *J. Am. Chem. Soc.*, **80**, 4954 (1958).

(2) R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948).

(3) P. D. Bartlett and J. L. Kice, *J. Am. Chem. Soc.*, **75**, 5591 (1953).

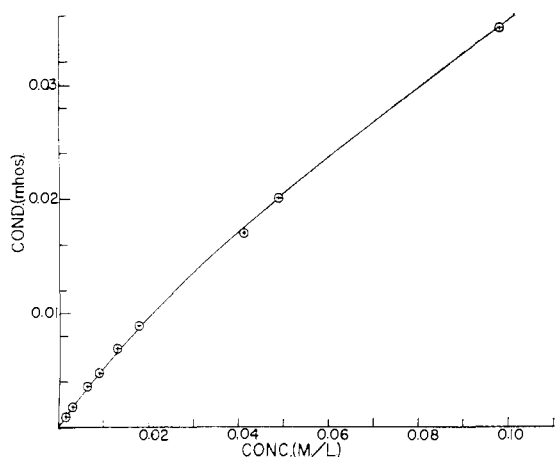


Fig. 1.—Calibration curve for conductivity method, using successive dilutions of a solution of *t*-butyl pertosylate after complete reaction in methanol at 4.6°.

ployed. All data are reported as $\tau = 10^{-8}$ using hexamethyldisiloxane as an internal standard.

***t*-Butyl Pertosylate.**—This perester was prepared several times by the method previously described.¹ The perester melted at 38.0–38.9° to a clear liquid, which in the course of about 30 seconds decomposed to a red tar. If carefully freed of acid and carefully dried before recrystallization, the crystalline perester was stable at room temperature for 1–2 hours after which time it decomposed violently. The infrared spectrum was identical with that previously reported.¹ The nuclear magnetic resonance spectrum showed sharp peaks at $\tau = 8.93$ and 7.70 and two doublets, $\tau = 2.27$, 2.45, 2.67 and 2.85, with relative areas of 9:3:2:2. The n.m.r. spectrum of ethyl tosylate was the same but with the 8.93 peak replaced by the expected quartet at 6.13 and triplet at 8.83. As previously, we were unable to obtain satisfactory carbon–hydrogen analyses, but the sulfur analysis checked that calculated and the acid titers of the rearranged products were always within $\pm 0.5\%$ of the theoretical.

Anal. Calcd. for $C_{11}H_{16}O_4S$: S, 13.1. Found: S, 13.27.

The pertosylate used in all kinetic runs was tested for chloride ion with hot ethanolic silver nitrate. In the preparation if insufficient reaction time is allowed, some of the sulfonyl chloride appears in the product. If, on the other hand, the pyridine solution of the sulfonyl chloride is not cooled to -25° before adding *t*-butyl hydroperoxide, the reaction proceeds so fast that the temperature rises to 70–80° and all product is decomposed.

***t*-Butyl benzenepersulfonate** was also prepared according to the previous method.¹

Products of Decomposition in Absolute Methanol.—The infrared spectrum of *t*-butyl pertosylate showed a strong peak at 6.27 μ , which rapidly disappeared at room temperature and was replaced by a very broad absorption from 5–7 μ . No peak appeared in the ketone region. However, in methanol containing 2.44 volume per cent. (5.44 mole per cent.) water the 6.27 μ peak was replaced by a strong peak at 5.84 μ (acetone) and much less of the general absorption developed. The solutions above were also observed with nuclear magnetic resonance using hexamethyldisiloxane as internal standard. The peak at $\tau = 8.93$ (hydrogen of the *t*-butyl group) disappeared rapidly at 21° and was replaced by a peak at 8.73 (ketal) in absolute methanol and at 7.73 (acetone) in 2.44 volume per cent. aqueous methanol. A small broad peak also appeared at 8.73 as the reaction progressed in the latter solvent, indicating that a mixture of acetone and the dimethyl ketal is obtained in this solvent.

Kinetic Methods. 1. **Conductivity.**—Up to about 0.03 *M* the conductivity of methanol and methanol–water solutions of *p*-toluenesulfonic acid was directly proportional to the acid concentration. For solutions within this concentration range the solvent being used was equilibrated with the thermostat bath in the conductivity cell. A few mg. of perester was then added and the cell shaken to dissolve the perester. Conductivity readings were started as soon as the perester dissolved. In nearly all cases, the quantity log

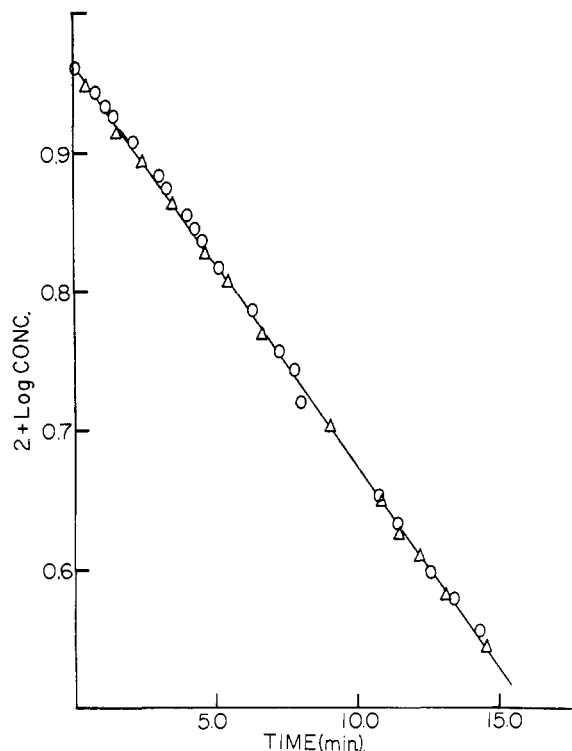


Fig. 2.—A typical duplicate pair of kinetic runs on *t*-butyl pertosylate in methanol at 4.6°; run 41: O, conductivity method; Δ , titration method.

$[(\text{conductivity})_\infty - (\text{conductivity})_t]$ against time was linear to at least 90% reaction. In cases of the highest reaction rates (half-lives of the order of 2 minutes), it was necessary to add the perester in 0.6116 ml. of the organic solvent at the proper temperature to the cell containing 15.00 ml. of the aqueous solvent and to correct for the change in solvent composition. For perester concentrations greater than 0.03 *M*, a calibration curve was prepared by measuring the conductivity of successively diluted infinity solution (Fig. 1). Conductivities were then converted to concentrations of acid by reference to this curve and then acid concentrations plotted against time on a log scale. A typical result is shown in Fig. 2. For these more concentrated solutions, the pertosylate was dissolved by weight in a volumetric flask in the thermostat, brought to volume, and transferred to the glass-stoppered conductivity cell. This operation required 1–2 minutes. The conductivity of toluenesulfonic acid in methanol containing less than 2 mole per cent. of water is extremely sensitive to small changes in the water content (Fig. 3). This kinetic method, therefore, requires great care in keeping the moisture content constant throughout a run in solvents of this type. The method as described is reliable to about $\pm 2\%$ with respect to acid concentrations in anhydrous solvents and about $\pm 1\%$ in aqueous solvents.

2. **Titration Method.**—A 5-ml. syringe was cooled on ice to about 2–3° and rinsed quickly with about 1 ml. of the reaction mixture made up as previously described. An aliquot of reacting solution (3.296 ± 0.001 ml.) was quickly withdrawn and emptied into a 25-ml. flask cooled on a block of Dry Ice. The aliquot was titrated to a stable brom thymol blue end-point with 0.03545 *N* sodium hydroxide in methanol. The acid concentration so determined after 10–12 half-lives always agreed with that expected by initial weight within 0.5%. The temperature of the sample was kept slightly below 0° during the titration by swirling on a block of Dry Ice. When more than 5 ml. of sodium hydroxide was used, the aliquot was emptied into 5.00 ml. of precooled titrant. A typical kinetic plot from a titration run is shown in Fig. 2 and compared with a similar plot from the conductivity method.

3. **Polarographic Method.**—The half-wave potential of *t*-butyl pertosylate in methanol was about 0.0 volt relative to the calomel electrode. The potential used in the kinetic

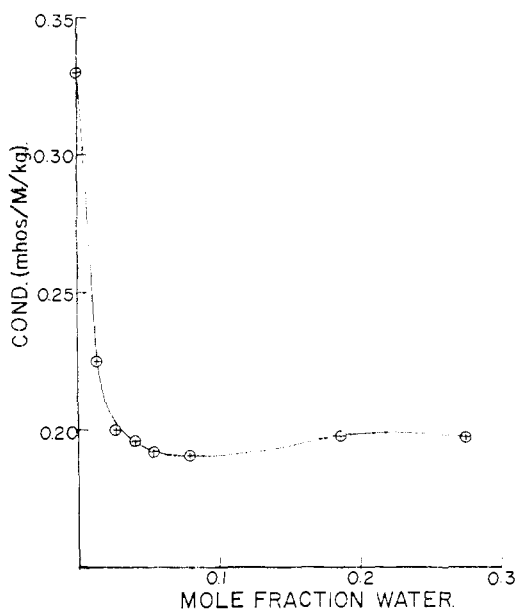


Fig. 3.—Effect of water on the conductivity of toluene-sulfonic acid in methanol at 4.5°.

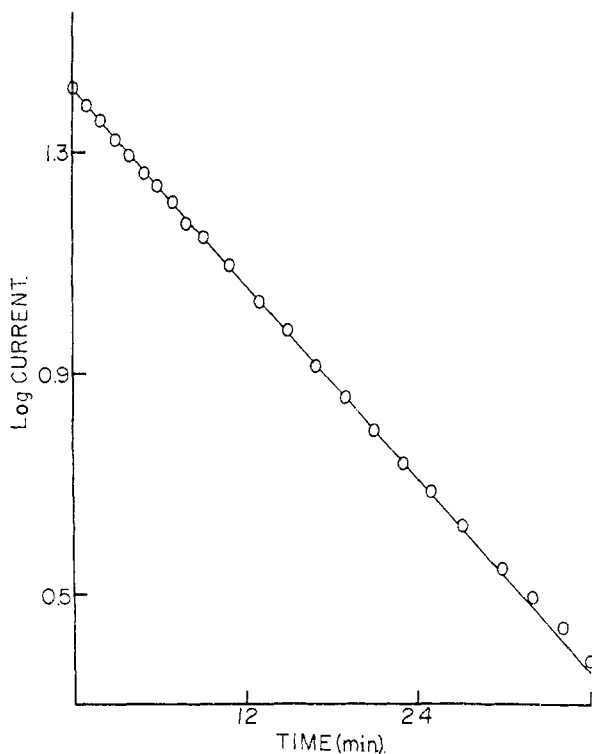


Fig. 4.—Reaction of *t*-butyl pertosylate in methanol containing 0.1414 *M* lithium chloride followed polarographically, at 20.19°; run 76.

runs was -0.4 to -0.5 volt. In some of the runs the resistance R_2^9 was very large (about 10000 ohms), and the cell potential rose to about -0.7 volt during the run. That this rise did not affect the kinetics is shown by the linear first-order plots of all runs over 95% of total reaction and by comparing these runs with those using $R_2 = 100$ ohms, in which case no potential drift occurred. All runs were made in duplicate or triplicate.

The lithium chloride solution, which was prepared by diluting a 1.00 *M* solution in absolute methanol, was placed in the cell in a 20.19° bath. Nitrogen was bubbled through

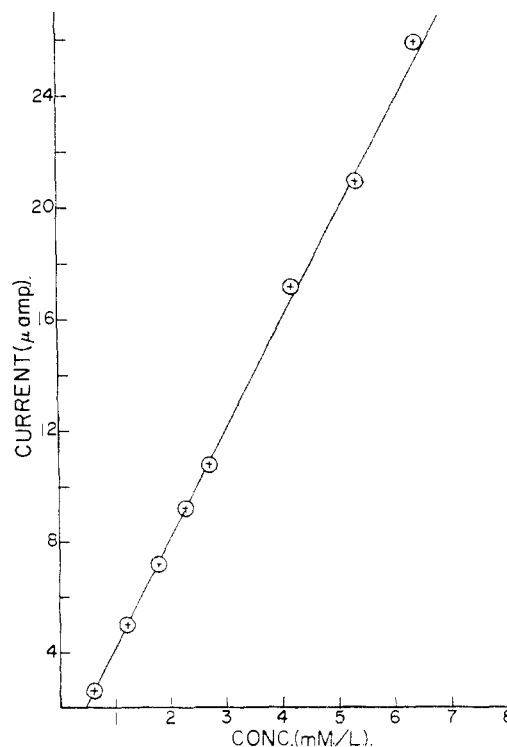


Fig. 5.—Calibration of the polarographic method for *t*-butyl pertosylate in 0.500 *M* lithium chloride solution in absolute methanol at 0.0°; cell potential -0.45 v. versus the calomel electrode.

the solution for about 1 hour. The dropping mercury electrode was inserted and a small amount of *t*-butyl pertosylate added. Bubbling was continued until the pertosylate dissolved. After the nitrogen flow was switched to pass over the solution, recording of the potential drop across R_2 was begun. The run was continued until a constant background current was obtained (usually less than 1 microampere). The recorder was not damped, and therefore large current fluctuations were obtained with the successive mercury drops. The current was taken as the midpoint of these swings. The plots of $\log [(current)_t - \text{residual current}]$ versus time were always at least as linear as that in Fig. 4.

In order to show that current was linear with concentration of perester, a 0.03913 *M* solution of *t*-butyl pertosylate was made at 0° in 0.500 *M* lithium chloride. Aliquots (five of 0.6116 ml. and three of 2.019 ml.) of this solution were added to 35.00 ml. of 0.500 *M* lithium chloride solution in the cell. The cell was swept with nitrogen for about 30 seconds after each addition, and the potential drop across a 100-ohm resistor was recorded on the Speedomax recorder as a function of elapsed time. The concentration was corrected slightly for time using a value of k_1 for decomposition of 7.2×10^{-8} sec.⁻¹, which was determined conductimetrically and corrected for salt concentration. The largest correction was 24%. The resulting plot of current versus concentration is shown in Fig. 5.

4. **Infrared Method.**—The spectrum of *t*-butyl pertosylate in methanol determined against pure solvent showed a strong peak at 6.27 μ , which rapidly disappeared at room temperature, being replaced by a broad, diffuse band from 5 to 7 μ . By repeatedly scanning from 5.5–6.5 μ and recording the times when the 6.27 μ peak was reached, the absorption could be obtained as a function of time at 25°. Because the reaction was very fast, a small amount of perester was placed in a 1-ml. syringe and the solvent drawn into the syringe, then shaken, and immediately emptied into the calcium fluoride cell. Using the base line technique,¹¹ $\log (I_B/I)$ was plotted against time as shown in Fig. 6. The diffuseness of the final absorption made the rate meas-

(11) H. H. Nielsen and R. A. Oetjen, "Physical Methods in Chemical Analysis," Academic Press, Inc., New York, N. Y., 1950, p. 397.

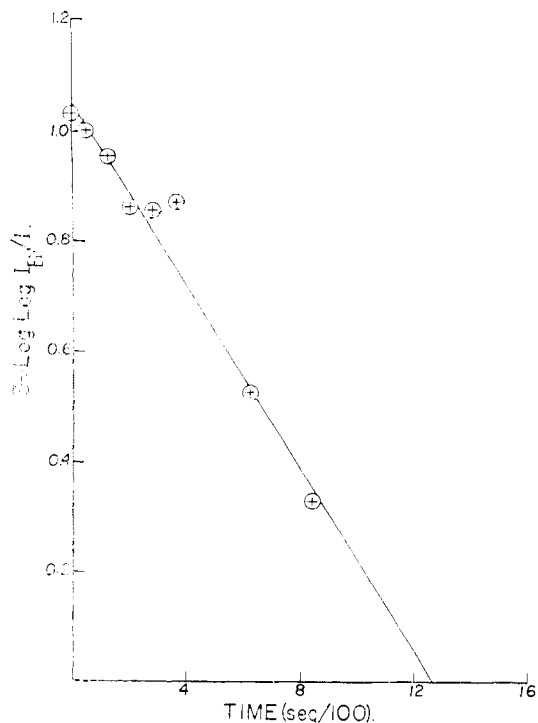


Fig. 6.—Reaction of *t*-butyl pertosylate in 5.44 mole per cent. aqueous methanol, at 25°, followed by infrared absorption at 6.27 μ , run 44A.

urements by this method only semi-quantitative. Duplicate rate constants differed by as much as a factor of 2.

Addition of a small amount of water after completion of a run caused the rapid appearance of an acetone peak at 5.84 μ .

5. Nuclear Magnetic Resonance.—A mixture of solvent, pertosylate and hexamethyldisiloxane was sealed in an n.m.r. tube at 0° and shaken to dissolve the perester. The tube was quickly warmed to probe temperature and scanned repeatedly without stopping the recorder. The *t*-butyl hydrogen peak at $\tau = 8.93$ was very sharp. Therefore, log (peak height) was plotted against time to obtain Fig. 7. The temperature was $21.5 \pm 0.1^\circ$.

6. Recovery of Perester.—Methanol containing 5.34 mole per cent. (2.44 volume per cent.) of water was equilibrated in a 4.0° bath. A sample of *t*-butyl pertosylate, 0.3889 g., was dissolved in this solvent to make 10.00 ml. of solution at 4.0°. From the time the pertosylate dissolved, the reaction proceeded for 105 minutes. The entire solution was emptied quickly into ice-water and the precipitated perester was extracted quickly with two 5-ml. portions of carbon tetrachloride. These were combined and dried over sodium sulfate, then an infrared scan was taken on the extract. This scan was identical to that of starting material as determined in this work and in that of reference 1. A comparison with a standard solution in carbon tetrachloride indicated a concentration of 12.1 mg. per ml. or a total yield of 0.121 g. (31% recovery).

Reaction of *t*-Butyl Pertosylate with Lithium Benzyl-oxide.—Redistilled benzyl alcohol was treated with lithium hydride in a little benzene, diluted and filtered to produce a solution which by titration was 0.355 *M* in lithium benzyl-oxide. The concentrated solution had a very slight hydroxyl band in the infrared; 18 ml. of this solution (0.0064 mole) was added to 0.6310 g. (0.0026 mole) of *t*-butyl pertosylate in benzene. After 2 days the gelatinous precipitate which had appeared was filtered off, and the infrared spectrum of the filtrate was determined. A strong absorption at 5.86 μ was observed. The solution was evaporated to an oil which was identified as benzyl benzoate by comparing its infrared spectrum in carbon tetrachloride with an authentic specimen.

Results

Each of the kinetic methods employed has its special characteristics and limitations. The con-

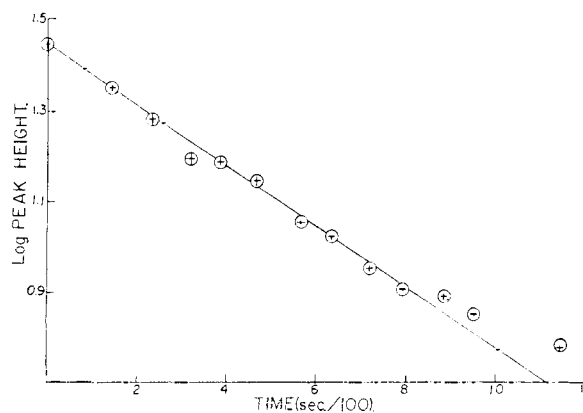


Fig. 7.—Reaction of *t*-butyl pertosylate in methanol at 21.5°, followed by n.m.r. absorption; run 95.

ductivity method is precise and reproducible but responds principally to the production of sulfonic acid during the reaction. It is a suitable measure of the rate of rearrangement only as it can be shown that the rearrangement produces no long-lived intermediate prior to hydrolysis. The same limitation applies to the titration with standard base. After it was established that the conductivity and titration methods gave the same rate constant, the more convenient conductivity method was used rather than titration.

The polarographic method registers the concentration of the reducible peroxidic starting material and hence measures directly its rearrangement irrespective of the rate of its subsequent hydrolysis. This is also a precise method but cannot be operated without electrolyte added to the solution. It is therefore unsuitable for determining all reaction rates at or near zero salt concentration, and a comparison of this method with that of conductivity or titration must be made either in the presence of added salt or by extrapolating a series of measurements to zero salt concentration.

The infrared method is less precise than the other three but again has the advantage of indicating directly the disappearance of starting material.

The two remaining methods, nuclear magnetic resonance and recovery of starting material, were used only in confirmation of the other methods, being best adapted to reactions at relatively high substrate concentration. Table I summarizes the results of these six methods as applied to the reaction of *t*-butyl pertosylate under four sets of conditions—in anhydrous methanol and in methanol containing 2.4 volume per cent. (5.4 mole per cent.) water both at 4.5° and at 20.19°.

Considering only the quantitative methods 1 to 4, the two methods which measure starting material directly appear to give consistently somewhat higher rate constants than those which measure the appearance of acid. This effect is not great enough to cause a characteristic departure from first-order kinetics nor to allow the separation of the reaction into stages. At most, the average *k* by methods 3 and 4 is 21% greater than by methods 1 and 2. Even the greater rate is substantially less than that measured previously¹ by the iodometric method. The latter method appears to have been

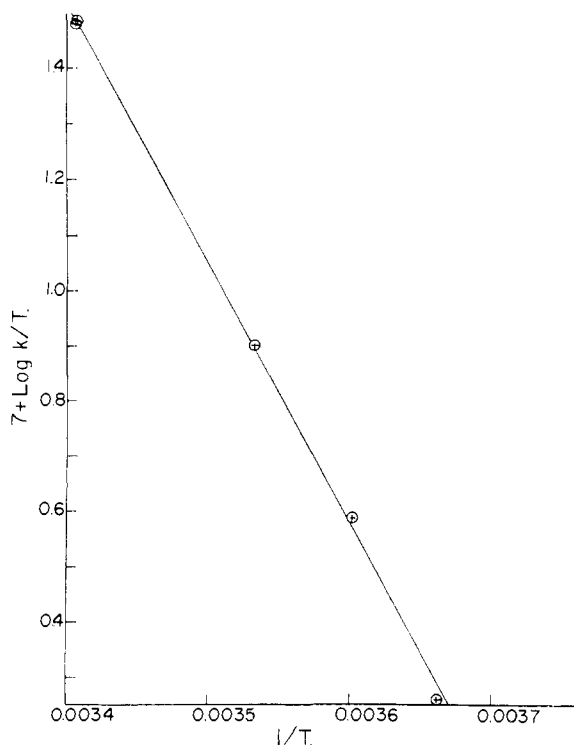


Fig. 8.—Temperature dependence of rate constant of *t*-butyl persulfate in anhydrous methanol, determined conductimetrically.

high by about 50–80% in anhydrous methanol but by a factor of 8.8 in the media containing 5.4 mole per cent. (2.44 volume per cent.) of water. In resolving this extraordinary disagreement, methods 1 to 5 agree closely in the aqueous medium. Method 6, though not an accurate one for kinetic purposes, is of critical importance since the recovery of starting material sets an upper limit of 2.1×10^{-4} to the rate constant, and this method therefore agrees emphatically with the other five in indicating that the iodometric result was grossly in error. We have not been able to account for this large error, nor have we been able in our recent experiments to bring the iodometric method under sufficient control to obtain any rate constants from it at all.

TABLE I
RATE CONSTANTS FOR DECOMPOSITION OF *t*-BUTYL PERSULFATE AS DETERMINED BY VARIOUS TECHNIQUES

Method	Methanol		Methanol with 2.44 v./v. % water	
	4.5°	20.19°	4.5°	20.19°
Conductivity (1)	1.08	8.94	1.36	12
Titration (2)	1.08		1.36	
Polarography (3)		9.8 ^a		
Infrared (4)		~12 ^b		~13 ^b
N.m.r. (5)		~18 ^c		~14 ^c
Recovery (6)			<2.1	
Iodometry ¹	1.98	14	11.7	

^a Extrapolated to zero salt concentration from 0.141 M LiCl. ^b Corrected from 25°. ^c Corrected from 21°.

Since the conductimetric method was precise and was suited to solutions containing no added electrolyte, this method was adopted for the determina-

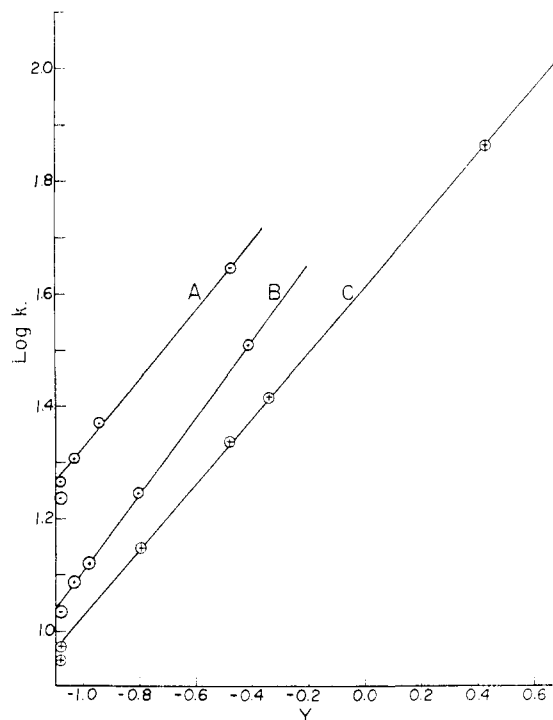


Fig. 9.—Grunwald-Winstein plots for *t*-butyl persulfates in aqueous methanol, superseding that reported in ref. 1: A, *t*-butyl benzenepersulfonate at 4.8°, $\log k + 5$; B, *t*-butyl persulfate at 4.5°, $\log k + 5$; C, *t*-butyl persulfate at 20.19°, $\log k + 4$.

tion of the activation parameters in anhydrous methanol and for the reinvestigation of the rate constants in mixed solvents. Figure 8 shows the plot of $\log(k/T)$ versus $1/T$ which leads to an activation enthalpy $\Delta H^\ddagger = 21.5$ kcal. and an activation entropy $\Delta S^\ddagger = 0.9$ e.u. The rate constant for *t*-butyl benzenepersulfonate in absolute methanol at 4.5° is 1.83×10^{-4} sec.⁻¹, indicating an effect of substitution in the same direction as that previously inferred from the iodometric results.

Reaction Rate in Mixed Solvents.—Figure 9 shows that plots of $\log k_1$ versus the Grunwald-Winstein Y values are linear over the entire measured range for methanol-water mixtures at 4.5° and at 20°. Rates in dioxane-water, ethanol-water and acetone-water mixtures also showed this behavior. A linear plot was also obtained for $\log k_1$ versus Y in the decomposition of *t*-butyl benzenepersulfonate in methanol-water mixtures at 4.8°. All of these results were obtained conductimetrically or titrimetrically, these two methods showing general agreement within experimental error.

Salt Effects.—The effect of added lithium chloride was determined in two series of experiments in one of which the rate was followed titrimetrically and in the other polarographically. In each case the addition of 0.4 molar lithium chloride caused about a 50% increase in rate over that determined in or extrapolated to solutions free of added electrolyte. These two methods, one measuring disappearance of starting material and the other measuring appearance of acid, agree in indicating that the strange salt effects previously reported from

TABLE II

RATES OF REARRANGEMENT OF *t*-BUTYL PERTOSYLATE IN ABSOLUTE METHANOL

Run	Kinetic method	Temp., °C.	Concn. LiCl, mole/l.	Initial pertosylate concn., mole/l.	$k_1 \times 10^4$ sec. ⁻¹
40	1	4.5	0	0.0992	1.07
41	1	4.6	0	.0988	1.11
41	2	4.6	0	.0988	1.11
45	1	4.5	0	.1018	1.08
54	2	4.8	0.360	.0966	1.55
55	2	4.8	0.177	.1011	1.35
56	2	4.8	0.488	.1005	1.57
62	1	0.0	0	0.498
60	1	9.98	0	2.27
59	1	20.45	0	.0042	8.94
43	4	~25	0	13
44	4	~25	0	25
79	1	20.37	0	9.04
91	1	20.19	0	9.4 ^a
67	5	21.5	0	~20
76	3	20.19	0.1414	11.2
77	3	20.19	.1414	11.0
68	3	20.19	.286	~10 ⁻³	12.9
69	3	20.19	.286	~10 ⁻³	12.5
65	3	23°	.299	17.3
70	3	20.19	.429	13.76
71	3	20.19	.429	13.66
72	3	20.19	.429	13.55
78	3	20.19	.500	14.4
73	3	20.19	.572	14.9
74	3	20.19	.572	14.9

^a Perester concentration in run 91 exceeded region of proportionality between conductance and concentration.

the iodometric titration are as lacking in reality as the non-linear solvent effects.

Within the probable experimental error the value of *m* for *t*-butyl pertosylate at 20° (0.59) is indistinguishable from that for 9-decalyl perbenzoate at 25° (0.57). We conclude that the mechanisms are quite similar—that migration of the methyl group probably accompanies ionization, and there is, of course, no need for the postulation of a reversible step in the ionization which appeared to be necessitated by our earlier abnormal salt and solvent effects.

One property of the rearrangement of 9-decalyl perbenzoate appears to be entirely lacking in *t*-butyl pertosylate, namely the susceptibility to acid catalysis in hydroxylic solvents. There is no autocatalysis observable in any of these experiments, nor is there any isotope effect observable as the aqueous component is changed from H₂O to D₂O. This is consistent with the low basicity of the sulfonate group as compared to the benzoate group

TABLE III

RATES OF REARRANGEMENT OF *t*-BUTYL PERTOSYLATE IN SOLVENT-WATER MIXTURES WITHOUT SALT

Run	Kinetic method	Solvent	Water, % by vol. ^a	Temp., °C.	$k_1 \times 10^4$ sec. ⁻¹
57	1	Methanol	1.24	4.8	1.24
42	1	Methanol	2.06	4.6	1.32
44A	4	Methanol	2.44	~25	20
46	1,2	Methanol	4.09	4.5	1.76
48	1	Methanol	9.07	4.5	3.23
95	5	Methanol	2.46	21.5	15
94	1	Methanol	4.09	20.19	14.1
87	1	Methanol	7.95	20.19	21.7
86	1	Methanol	9.90	20.19	26.1
98	1	Methanol	20.7	20.19	73.0
80	1	Ethanol	0.22	20.37	3.64
89	1	Ethanol	0.22	20.19	3.56
92	1	Ethanol	5.22	20.19	8.39
90	1	Ethanol	10.22	20.19	16.0
83	1	Ethanol	20.22	20.19	40.0
97	1	Ethanol	26.38	20.19	61.1
82	1	Dioxane	20.0	20.19	12.8
93	1	Dioxane-D ₂ O	20 ^c	20.19	13.1
96	1	Dioxane	26.3	20.19	27.0
85	1	Dioxane	40.0	20.19	56 ^b
88	1	Dioxane	40	20.19	81 ^b
84	1	Acetone	30.0	20.19	44.7
64	1	Isopropyl alcohol	(≤2)	26.0	4.70

^a Volume per cent. (*X*) used here refers to *X* volumes of organic solvent plus 100 - *X* volumes water. ^b Inaccurate due to rapid rate and slow dissolution of solid perester. ^c Water was 99.7% D₂O.

TABLE IV

RATES OF DECOMPOSITION OF *t*-BUTYL BENZENE-PERSULFONATE IN AQUEOUS METHANOL AT 4.8° (MEASURED CONDUCTIMETRICALLY)

Run	Mole % water	$k_1 \times 10^4$	Initial concn. of perester, mole/l.
50	0.0	1.83	
51	0.0	1.71 ^a	0.0029
52	5.37	2.35	.0023
53	16.40	4.42	.0032
58	2.70	2.08	.0060

^a During this run the reacting solution was found to be contaminated through a flaw in cell construction.

and with the relative self-sufficiency of the sulfonate ion in solution.

Tables II, III and IV list the results of the series of kinetic experiments performed.

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