point at 3.3×10^{-4} N and its slope was readily determined. For this salt, the slope was found to be 220, the theoretical slope for a 1–1 salt is 77, for a 3–1 salt it is 216. Thus, for this salt, the slope is that of a 3–1 salt within the limit of experimental error. As has been pointed out in earlier papers, the greater slope of these salts might be accounted for on the basis of ion-pair formation. However, in view of the fact that similar salts having ions containing chains of 14 carbon atoms, or less, exhibit a normal slope, it is highly improbable that ion-pairs are formed.

It seems more probable that in the case of ions having chains of 16 or more carbon atoms, association of the chains occurs at concentrations below the critical. In this connection, it is important to note that association is markedly dependent on the size of the substituent alkyl groups on the ion head. Thus, the slope of hexadecyltributylammonium bromate is that of a 3–1 salt. Evidently, the van der Waals interaction between the ions is increased due to the presence of the butyl groups.

On the basis of the evidence presently available, we may conclude that if the chains on the ions are of sufficient length, association occurs at concentrations below the critical. The size of the substituent groups on the head of long chain quaternary ammonium ions likewise affects the tendency for such ions to associate. It should not be concluded, however, the the multiple ions in a given case all have the same degree of complexity. Rather, we should expect multiple ions of different degrees of complexity to exist in equilibrium with one another and probably with simple ions. With different salts, the mean value of the association number will differ and may approximate that of a 2–1 or a 3–1 salt, for example. If an equilibrium exists, we should expect it to shift as concentration decreases. Unfortunately, the critical concentrations of these salts are so low and the observable conductance differences are so small that it is difficult, it not impossible, to demonstrate any shift of equilibrium.

d. Ion Conductances.—Values for the conductance of the long chain ions have been derived from the Λ_0 values of Table II. They are based on Daggett's value of 55.66 for the conductance of the bromate ion and are collected in Table III.

TABLE III

ION CONDUCTANCES

Ion	No. C atoms	Λ_0^+
Octd·Me_3N^+	21	19.9
Octd·Et_3N^+	24	18.0
Octd·Pr_3N^+	27	17.3
Hexd·Bu_3N^+	28	16.9

The conductance decrease with increasing number of carbon atoms in the cation is very much less for long chain ions than it is for symmetrical quaternary ammonium ions as Bair has shown. Thus, the conductance of the tetraamylammonium ion, with 20 carbon atoms, is 17.13, while that of the octadecyltripropylammonium ion, with 27 carbon atoms, is 17.3. The ratio of conductances of the octadecyltrimethyl and tripropylammonium is 1.15; for the tetramethyl and the tetrapropylammonium ions, the ratio is 1.92. It is true that in the first instance above only 6 carbon atoms were added while, in the second, 8 were added. However, in going from the tetramethyl- to the tetraethylammonium ion, where only 4 carbon atoms are added, the conductance ratio is 1.38.

The addition of carbon atoms to the alkyl groups on the head of a long chain ion decreases the conductance far less than a similar addition to the substituent groups of symmetrical ions.

PROVIDENCE, R. I. RECEIVED NOVEMBER 27, 1950

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

The Rates of Decomposition of Acetyl Peroxide in Acetic Acid and Carbon Tetrachloride

BY SIDNEY D. ROSS AND MORTON A. FINEMAN

The rate of decomposition of a commercial 25% solution of acetyl peroxide in dimethyl phthalate has been studied in acetic acid and carbon tetrachloride. It is shown that the presence of dimethyl phthalate does not appreciably affect the decomposition in these solvents. In acetic acid the decomposition is unimolecular and there is no evidence of either induced decomposition or inhibition. In carbon tetrachloride, individual runs are first-order, but the rate is a function of the initial peroxide concentration. The decomposition is subject to inhibition but not to acid catalysis. It is not possible to decide mathematically between the two rate equations. $-dP/dt = k_1P + k_2P^{3/2}$ (1) and $-dP/dt = k_1P + k_2P^2$ (2). There are, nevertheless, reasons for preferring the first rate equation.

Our interest in acetyl peroxide was twofold. We were interested in the decomposition characteristics of the acetyl peroxide, which is supplied by the Buffalo Electro-Chemical Company, Inc., as a 25% solution in dimethyl phthalate,[1] since this is the only readily available and easily handled form of this polymerization catalyst. The decomposition of acetyl peroxide was also of interest in connection with an intensive study of the decomposition of lead tetraacetate which is now in progress in these laboratories. The decomposition of lead tetraacetate is characterized by pseudo zero-order kinetics and strong acceleration of the rate of decomposition by both trichloroacetic acid and lead diacetate.[2] The pseudo zero-order kinetics makes Waters[3] suggestion of acetyl peroxide as a possible intermediate in the decomposition of lead tetraacetate an attractive one. Although Kharasch, Friedlander and Urry[4] have recently reported evidence which is contrary to this sugges-

---

[1] This corresponds to a dimethyl phthalate concentration 1.82 times that of the peroxide.

[2] Unpublished results from these laboratories.

[3] W. A. Waters, *Ann. Reports of the Chemical Society, London*, **42**, 143 (1945).

[4] M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.*, **14**, 91 (1949).

tion, we have considered it desirable to determine whether or not the decomposition of acetyl peroxide is subject to acid catalysis.

Comparison of our results with available results in the literature on the decomposition of acetyl peroxide in the absence of dimethyl phthalate makes it apparent that this solvent exerts, at most, a second order influence on the rate of decomposition of this peroxide in the solvents which we have studied. Walker and Wild[5] have determined the rate of decomposition of pure acetyl peroxide in toluene at 80.0 and 87.3°. Using the same initial concentration (0.04 *M*), we have made measurements at 73.2 and 85.5°. At all four temperatures linear first-order plots are obtained. The first-order rate constants are given in Table I. In Fig. 1, log k is plotted against $1/T$ for all of the determined values. The excellent straight line indicates that our results, with dimethyl phthalate present, are in agreement, within experimental error, with results obtained with the pure peroxide in toluene. The activation energy (33.0 kcal.) obtained from all the data is in good agreement with the value of 31.0 kcal. reported by Walker and Wild.

TABLE I

RATES OF DECOMPOSITION OF ACETYL PEROXIDE IN TOLUENE

Temp., °C.	k, min.$^{-1}$ × 10^3
73.2	1.84
80.0[a]	4.57
85.5	10.3
87.3[a]	10.9

[a] Data from Walker and Wild.

More recently Edwards and Mayo[6] have reported the rate of decomposition of acetyl peroxide in carbon tetrachloride. We have studied the rate of decomposition in this solvent in some detail, and, as will be shown later, the decomposition is not a purely first-order reaction, the observed rate being a function of the initial peroxide concentration. However, at a comparable initial peroxide concentration our apparent first-order rate constant at 73.2° is in agreement with a ln k *vs.* $1/T$ plot of the data of Edwards and Mayo at 60 and 100°.

The chief perturbation that might be expected from dimethyl phthalate is that it might act as a retarder or inhibitor for the decomposition. Radicals formed by attack of fragments from the peroxide on the dimethyl phthalate could conceivably be more stabilized by resonance and less effective in inducing decomposition of the peroxide than radicals from solvent molecules. The effect of dimethyl phthalate would then be to limit the maximum rate of decomposition. We measured the rate of decomposition in carbon tetrachloride as a function of the initial acetyl peroxide concentration. In increasing the acetyl peroxide concentration we were increasing the dimethyl phthalate concentration proportionately. Nevertheless, a plot of the apparent first order rate constant *vs.* the square root of the initial peroxide concentration was linear, with the rate increasing with increasing peroxide concentration. In view of this evidence and the agreement between our results and results with the pure peroxide in both toluene and carbon tetrachloride, it seems to us reasonable to conclude that dimethyl phthalate has no appreciable influence on the decomposition of acetyl peroxide in the systems which we have studied.

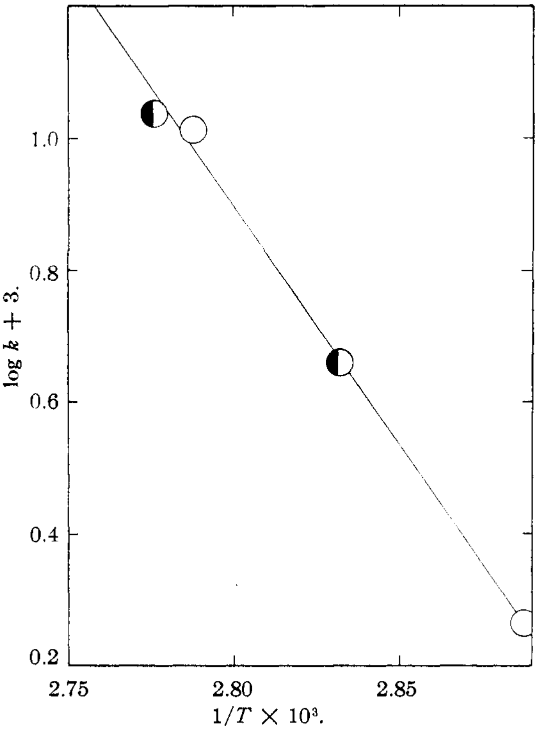


Fig. 1.—Log of rate of decomposition of acetyl peroxide *vs.* $1/T$ in toluene; radii of circles are equivalent to a 5% error in the rate constants: ◐, data of Walker and Wild; ○, data from this research.

Experimental

The acetyl peroxide solution was used as received from the Buffalo Electro-Chemical Company, Inc. Absolute ethanol and C.P. glacial acetic acid were used without further purification. Only a single batch of acetic acid was used, and this had a freezing point of 15.8 ± 0.1°. Reagent grades of toluene and carbon tetrachloride were distilled through a Widmer column, and only a constant boiling middle cut was used. *m*-Dinitrobenzene was crystallized from absolute ethanol; m.p. 89–89.5°.

Solutions were prepared by dissolving the requisite volume of the peroxide solution in the appropriate solvent. Aliquots (5–10 ml.) were added to individual tubes, which had been thoroughly cleaned with a solution of chromic acid in sulfuric acid, rinsed with distilled water and dried. Air was removed by three cycles of freezing in Dry Ice–trichloroethylene, evacuating, thawing and flushing with dry nitrogen, before sealing under 150–200 mm. nitrogen pressure. The ampules were placed in a thermostat at the required temperature. Two were removed after 6 minutes, the total contents of each tube were analyzed for peroxide, and the average of the two values obtained was taken as the initial peroxide concentration.

To determine acetyl peroxide in acetic acid we used a modification of the method of Nozaki[7] for benzoyl peroxide. One gram of potassium iodide was dissolved in 1 ml. of water in a bromide–bromate flask. Acetic anhydride (10 ml.) was added and the flask was evacuated. The sample was then added and washed down with acetic anhydride (15 ml.). The evacuated flask was placed in a thermostat at 73.6° for 15 minutes, the vacuum was released, the flask

---

[5] O. J. Walker and G. L. E. Wild, *J. Chem. Soc.*, 1132 (1937).

[6] F. G. Edwards and F. R. Mayo, THIS JOURNAL, **72**, 1265 (1950).

[7] K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

was washed down with a minimum amount of water, and the iodine liberated was titrated with standard sodium thiosulfate solution to a colorless end-point without the use of an indicator. Blank determinations were carried out for every run and the corrections never exceeded 0.40 cc. of 0.1 N sodium thiosulfate solution.

For the determinations in carbon tetrachloride and toluene we used a modification of the method of Liebhafsky and Sharkey.[8] One gram of potassium iodide and one gram of sodium bicarbonate were dissolved in 1 ml. of water in a bromide–bromate flask. The flask was evacuated, and glacial acetic acid (25 ml.) was added. The flask was evacuated again, and the sample and 25 ml. of acetic acid were added. The flask was evacuated once again, placed in a thermostat at 73.6° for 15 minutes and finally titrated to a colorless end-point as above. In these solvents and with this method the blank corrections were never more than 0.10 cc. of 0.1 N sodium thiosulfate solution.

Results and Discussion

The decomposition of acetyl peroxide in acetic acid was studied at 73.2°. In every case the data gave a linear first-order plot. The results of representative runs are presented in Table II, and a typical set of data is given in Table III. Representative first order plots are shown in Fig. 2.

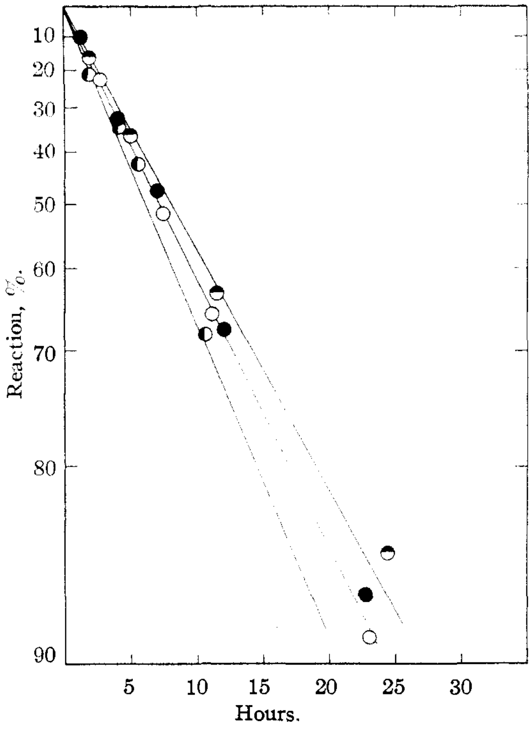


Fig. 2.—Decomposition of acetyl peroxide in acetic acid at 73.2°: ○, 0.487 M acetyl peroxide; ●, 0.252 M acetyl peroxide; ◐, 0.0866 M acetyl peroxide with 0.203 M *m*-dinitrobenzene; ⊖, 0.100 M acetyl peroxide with 0.100 M trichloroacetic acid.

TABLE II

DECOMPOSITION OF ACETYL PEROXIDE IN ACETIC ACID AT 73.2°

Initial peroxide concn., M	k_1, min.$^{-1}$ $\times 10^3$	Remarks
0.0502	1.57	Standard run
.252	1.54	Standard run
.487	1.60	Standard run
.102	1.65	In erlenmeyer under air
.0515	1.75	Tubes filled with air
.100	1.45	0.100 M trichloroacetic acid
.0866	1.76	0.203 M *m*-dinitrobenzene

TABLE III

DECOMPOSITION OF 0.0502 M ACETYL PEROXIDE IN ACETIC ACID AT 73.2°

Hours	Decomposition, %
1.00	7.90
3.00	22.6
7.25	46.7
11.5	63.7
14.3	73.2
25.0	90.1

In acetic acid the decomposition of acetyl peroxide conforms to the first-order rate law over the whole course of the reaction. Measurements beyond 90% decomposition show no deviation from first-order dependency, and a ten-fold variation in the initial peroxide concentration changes the rate constant by only 2%, which is less than our experimental error. In the presence of air or oxygen the rate was increased 3–10%. Bartlett and Leffler[9] observed a similar acceleration due to oxygen in the case of bis-phenylacetyl peroxide. Also, 0.203 M *m*-dinitrobenzene, which, as we shall see later, can inhibit the induced decomposition of acetyl peroxide, accelerated the decomposition rate by 10%. On the other hand, trichloroacetic acid caused a small decrease in the rate. Although the specific effects involved in these latter experiments are not clear, it is clear that, in acetic acid, the decomposition is not subject either to inhibition or acid catalysis. We conclude, therefore, that the decomposition of acetyl peroxide in acetic acid is first-order and free from any measurable amount of induced decomposition.

The results of representative runs in carbon tetrachloride at 73.2° are summarized in Table IV, and data for two individual runs are shown in Tables V and VI. As can be seen from Fig. 3 individual runs give excellent first-order plots. However, in this solvent the decomposition is not adequately described by a first-order formulation, since the apparent first-order constant is a function of the initial peroxide concentration. A tenfold increase in the initial peroxide concentration increases the unimolecular rate constant by 30%.

TABLE IV

DECOMPOSITION OF ACETYL PEROXIDE IN CARBON TETRACHLORIDE AT 73.2°

Run	Initial peroxide concn., M	Apparent first-order rate constant, min.$^{-1}$ $\times 10^3$	Remarks
11	0.0492	1.17	
13	.116	1.22	
14	.318	1.43	
15	.525	1.52	
16	.314	1.41	0.150 trichloroacetic acid added
17	.309	1.33	0.30 trichloroacetic acid added
18	.310	1.16	0.297 *m*-dinitrobenzene added

---

[8] H. A. Liebhafsky and W. H. Sharkey, THIS JOURNAL, 63, 1432 (1941).

[9] P. D. Bartlett and J. E. Leffler, *ibid.*, 72, 3030 (1950).

TABLE V

DECOMPOSITION OF 0.0492 M ACETYL PEROXIDE IN CARBON TETRACHLORIDE AT 73.2°

Hours	Decomposition, %
2.50	15.7
6.00	34.7
12.0	56.6
23.6	79.8
31.5	89.4

TABLE VI

DECOMPOSITION OF 0.314 M ACETYL PEROXIDE IN CARBON TETRACHLORIDE IN THE PRESENCE OF 0.150 M TRICHLOROACETIC ACID AT 73.2°

Hours	Decomposition, %
2.00	16.4
6.00	40.1
11.5	62.9
24.0	86.8
26.0	88.7

Similar dependence of the rate on the initial peroxide concentration has been observed in the case of benzoyl peroxide[9a,b,c] where the deviations from first-order kinetics are attributed to a reaction of higher order which accompanies the unimolecular decomposition. It has been shown[9a,b] that this reaction of higher order is a chain reaction which is subject to both induction and inhibition. However, the exact order of this reaction is still subject to some uncertainty. Nozaki and Bartlett[9a] find that their data can be satisfactorily accommodated by simultaneous first and three-halves-order reactions while Barnett and Vaughan[9c] obtain a satisfactory fit with simultaneous first and second-order reactions.

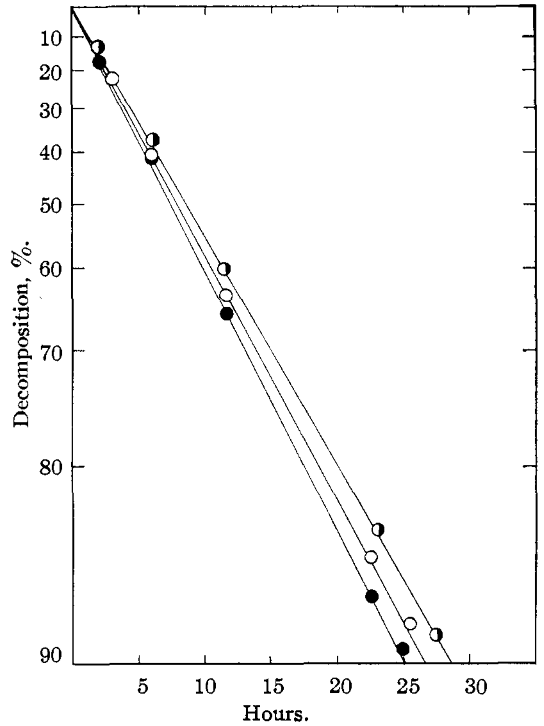


Fig. 3.—Decomposition of acetyl peroxide in carbon tetrachloride at 73.2°: ○, 0.318 M acetyl peroxide; ●, 0.525 M acetyl peroxide; ◑, 0.309 M acetyl peroxide with 0.30 M trichloroacetic acid.

Using the first four runs of Table IV we have tried to choose between these two kinetic formulations. The simultaneous first and three-halves order case was fitted by the method of Nozaki and Bartlett.[9a] Figure 4 shows plots of $1/\sqrt{P_1}$

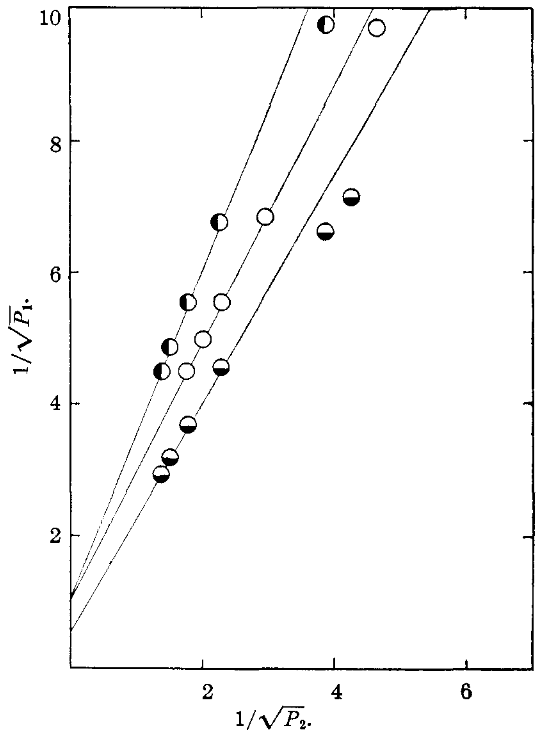


Fig. 4.—Plot of $1/\sqrt{P_2}$ vs. $1/\sqrt{P_1}$ for the decomposition of acetyl peroxide in carbon tetrachloride at 73.2°: ○, run 14 (2)...run 11 (1); ⊖, run 15 (2)...run 13 (1); ◐, run 15 (2)...run 11 (1).

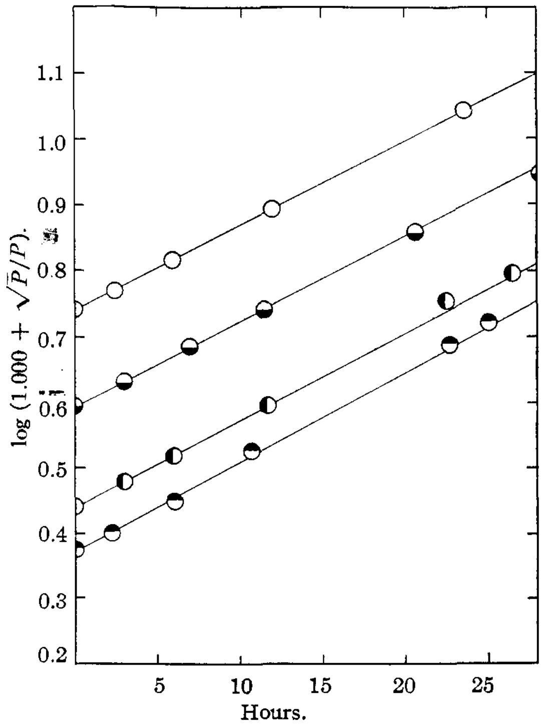


Fig. 5.—Plot of log $(1.000 + \sqrt{P})/(\sqrt{P}$ vs. time for decomposition of acetyl peroxide in carbon tetrachloride at 73.2°: ○, run 11; ⊖, run 13; ◐, run 14; ⊖, run 15.

---

(9) (a) K. Nozaki and P. D. Bartlett, This Journal, 68, 1686 (1946). (b) W. E. Cass, ibid., 68, 1976 (1946). (c) B. Barnett and W. E. Vaughan, J. Phys. Colloid Chem., 51, 926 (1947). Extensive references to other work in this field are available in these three papers.

vs. $1/\sqrt{P_2}$ which result from using three combinations of the four runs.[10] From these plots three values (1.34, 0.70 and 0.93) are obtained for a. Taking the average of these three values for a, we can then get four plots of the function $\ln(a + \sqrt{P}/\sqrt{P})$ *vs.* time (Fig. 5), and, from these plots, we obtained the following four values of k_1, the first order rate constant: 0.99×10^{-3}, 0.92×10^{-3}, 1.01×10^{3} and 1.04×10^{-3} min.$^{-1}$.

The simultaneous first and second-order case was fitted in a similar manner.[11] Again using three combinations of the four runs, and in this case plotting $1/P_1$ *vs.* $1/P_2$ (Fig. 6), we obtained the following three values for α: 3.35, 4.31 and 2.94. Taking the average α we then plotted $\log(1 + \alpha P/P)$ *vs.* time for each run (Fig. 7). These plots gave the following four values of k_1: 0.93×10^{-3}, 0.93×10^{-3}, 1.04×10^{-3} and 1.02×10^{-3} min.$^{-1}$.

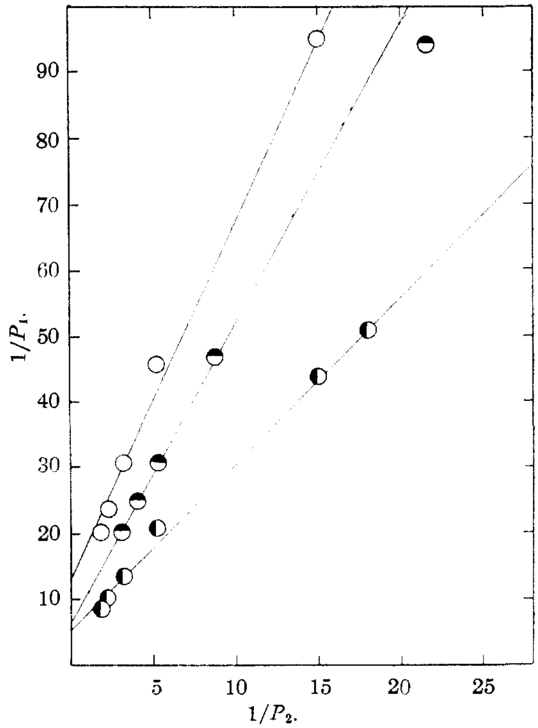


Fig. 6.—Plot of $1/P_1$ *vs.* $1/P_2$ for the decomposition of acetyl peroxide in carbon tetrachloride at 73.2°: ○, run 15 (2)...run 11 (1); ◓, run 14 (2)...run 11 (1); ◐, run 15 (2)...run 13 (1).

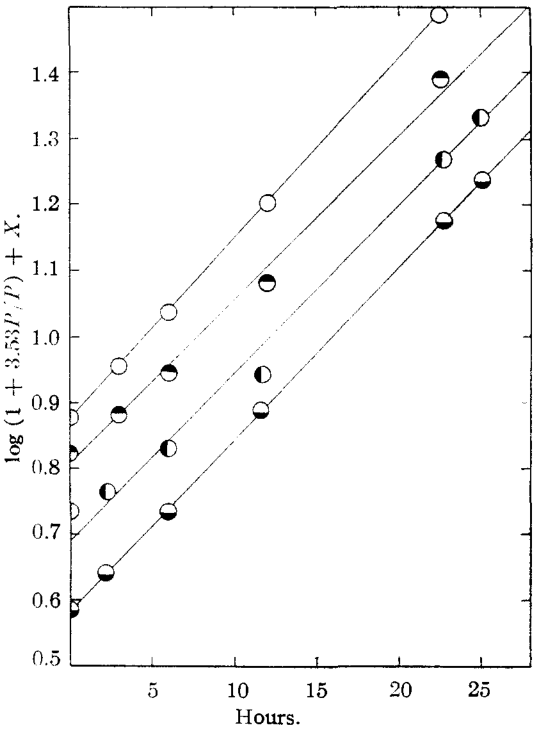


Fig. 7.—Plot of $\log(1 + 3.53P)/P$ *vs.* time for the decomposition of acetyl peroxide in carbon tetrachloride at 73.2°: ○, run 11, $x = 0.5$; ◓, run 14, $x = 0$; ◐, run 15, $x = 0$; ◒, run 13, $x = 0.5$.

Either choice of order for the induced step, thus, affords a respectable fit to the data. A choice between the alternatives, if one is possible, must be made on some other basis. In addition to the mechanism proposed by Nozaki and Bartlett,[9a] it is possible to write other mechanisms which lead to three-halves or second-order induced decomposition by differentiating between radicals from the peroxide and radicals from the solvent.[12] These are presented in Table VII where S refers to a radical from the solvent and R a radical from the peroxide.

TABLE VII

Induced step	Termination step	Induced rate
S + P	2 S	$k_i P^{3/2}$
R + P	2 S	$k_i P^2$
R + P	S + R	$k_i P^2$

None of the mechanisms in Table VIII is completely consistent with the products formed in carbon tetrachloride.[5] The best description of the reaction which we can write is probably that given by the mechanism proposed by benzoyl peroxide by Nozaki and Bartlett.[9a] This mechanism makes no distinction between solvent radicals and peroxide radicals, and it can accommodate the products formed in the reaction. From the products formed we know that there is *some* termination by the combination of two peroxide radicals as well as by combination of two solvent radicals. It is also possible that there may be *some* induced de-

---

[10] The notation of Nozaki and Bartlett[9a] is used throughout this discussion.

[11] For this case

$$-\mathrm{d}P/\mathrm{d}t = k_1 P + k_i P^2 \qquad (1)$$

Defining α as k_i/k_1, we obtain the integrated form of (1)

$$\log\left(\frac{1 + \alpha P}{P}\right) - \log\left(\frac{1 + \alpha P_0}{P_0}\right) = \frac{k_1 t}{2.303} \qquad (2)$$

By using pairs of runs as before, equation (3) can be used to obtain α.

$$\frac{1}{P_1} = C\frac{1}{P_2} + \alpha(C - 1) \text{ where } C = \left(\frac{1 + \alpha P_1^0}{1 + \alpha P_2^0}\right)\left(\frac{P_2^0}{P_1^0}\right) \qquad (3)$$

where the subscripts 1 and 2 refer to peroxide concentrations in separate runs at the same time.

[12] It is possible to write plausible reaction schemes which result in half or second-order induced decompositions, but these do not fit our data. Countless other mechanisms are, of course, possible. We have, however, limited ourselves to those which assign specific and unique functions to the peroxide and solvent radicals and result in either a second or three-halves order induced decomposition reaction.

composition by radicals from the peroxide in spite of the absence of induced decomposition in acetic acid.[13] Thus, the three-halves-order induced decomposition step is more consistent with the present state of our knowledge about the decomposition of acetyl peroxide in carbon tetrachloride.

[13] The absence of induced decomposition in acetic acid may be due to the ineffectiveness of radicals from the peroxide in inducing the decomposition of acetyl peroxide, or, alternatively, the radicals from the peroxide may react very rapidly with acetic acid to form other radicals which do not induce the decomposition.

NORTH ADAMS, MASS. RECEIVED SEPTEMBER 25, 1950

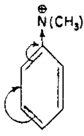
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Electrical Effect of the Trimethylammonium [$-N(CH_3)_3^{\oplus}$] Group

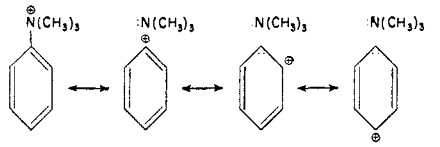
BY JOHN D. ROBERTS, ROBERT A. CLEMENT AND JOHN J. DRYSDALE

A study has been made of the reactivities of a series of anilines and benzoic acids substituted in the meta- and para-positions with trimethylammonium [$-N(CH_3)_3^{\oplus}$] groups. The experimental results offer no support for preferential relay of the inductive effect of a substituent group to the ortho- and para-positions of a benzene ring as postulated by Robinson, Ingold and others. The strong meta-orienting influence of the $-N(CH_3)_3^{\oplus}$ in electrophilic aromatic substitution reactions seems best accounted for by the approach of Pfeiffer and Wizinger.

One of the features of the English electronic theory is the postulation of a preferential relay of the inductive effect of a substituent group to the ortho- and para-positions of the benzene ring. This effect seems to have been evoked originally to explain the very strong meta-orienting influence of the $-N(CH_3)_3^{\oplus}$ group in electrophilic aromatic substitution reactions[1] and has been given some justification by quantum-mechanical calculations.[2] The customary English designation of the electrical influence of the $-\overset{\oplus}{N}(CH_3)_3$ group is represented by I while the counterpart in the resonance interpretation is obtained by consideration of resonance structures such as II. Regardless of symbolism, the effect is presumed to result with induction by the trimethylammonium group of centers of higher positive charge at the ortho- and para-positions than at the meta-positions. In the present investigation, the reactivities of some meta- and para-$N(CH_3)_3^{\oplus}$-substituted benzoic acids and anilines were determined since little experimental evidence for the postulated charge distribution has been obtained except for the strong meta-directing influence of $-NH_3^{\oplus}$ and $-N(CH_3)_3^{\oplus}$ groups.

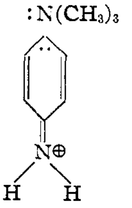


I

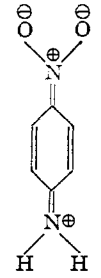


II

The reactions and procedures have been described previously in detail.[3] The experimental results and corresponding σ-constants[4] for the $-N(CH_3)_3^{\oplus}$ group are summarized in Table I. The σ-constants show somewhat larger variations, particularly for the meta-position, than are ordinarily observed.[4] However, the fact that $\sigma_{meta} - \sigma_{para}$ is roughly constant from reaction to reaction makes it likely that the variations are due to solvation effects or the like which alter the influence of the meta- and para-substituents on the reactive center to about the same degree. Solvation effects can reasonably be expected to be quite important when the reactions being compared involve entities ranging from dipolar ions to doubly-charged positive ions. Irrespective of the absolute values of the σ-constants of the $-N(CH_3)_3^{\oplus}$ group, there can be no question that the $\sigma_{meta} - \sigma_{para}$ figures offer no support for the charge distribution previously postulated.[1,2] Indeed, the $-N(CH_3)_3^{\oplus}$ group seems to have a considerably greater electron-attracting influence at the meta-position than at the para-position. This fact alone does not rule out a powerful "alternating" inductive effect[1] since such an effect could be masked by a more powerful direct coulombic influence. However, the relatively small difference in $\sigma_{meta} - \sigma_{para}$ for reactivities of benzoic acids and anilines appears to rule out the possibility that resonance interactions of type III are important in p-aminophenyltrimethylammonium compounds in the manner that forms such as IV are important in p-nitroaniline and similar compounds.[3b] This conclusion is in agreement with an earlier suggestion[3b] that resonance similar to III is not significant for the trifluoromethyl ($-CF_3$) group. The unimportance of III strongly implies that resonance such as II is likewise unimportant since it is difficult to believe that II could contribute significantly and not lead to III when a p-amino group is present



III



IV

---

[1] (a) J. Allan, A. E. Oxford, R. Robinson and J. C. Smith, *J. Chem. Soc.*, 401 (1926); (b) C. K. Ingold *Chem. Revs.*. **15**, 225 (1934); (c) *cf.* A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1949, p. 71.

[2] (a) E. Hückel, *Z. Physik*, **72**, 310 (1931); (b) G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2086 (1935).

[3] (a) J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949); (b) J. D. Roberts, R. L. Webb and E. A. McElhill. *ibid.*, **72**, 408 (1950).

[4] L. P. Hammett, "Physical Organic Chemistry." McGraw-Hill Book Co., Inc., New York, N. Y.. 1940. Chap. VII.