

reactivity of *p*-phenyltoluene in the bromination reaction is not predicted on a purely polar basis. We believe that the large reactivity is due to a contribution of structure II to the transition state.

There is no doubt that there is a polar effect operative in hydrogen abstraction reactions. In view of the present findings it seems highly doubtful that σ^+ is the appropriate measure of this effect. There must also be radical-stabilizing effects operating in these reactions. The suggestion of Streitwieser and Perrin¹⁷ that a modified form of the Hammett equation, $\rho(\sigma + \lambda\sigma^-)$, be used seems appropriate. Unfortunately,

no suitable values for the radical-stabilizing term, σ^- , are available. Quantitative information on radical stabilization would be extremely valuable. The source of the radical-stabilizing effect is also unknown. It may arise from a changed Coulomb integral for the *para* carbon carrying a substituent or by extension of the π system. This problem is currently under investigation.

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Mechanisms of Substitution Reactions at Phosphorus. XII. A Kinetic Study of the Decomposition of Quaternary Phosphonium Hydroxides

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A series of p-Y-benzyltribenzylphosphonium halides (where Y = p-NO₂, m-NO₂, m-Br, m-Cl, m-F, p-Cl, p-F, H, m-CH₃, p-CH₃, p-t-butyl, and p-CH₃O) has been subjected to reaction with sodium hydroxide in 50% (by volume) aqueous 1,2-dimethoxyethane. The determination of accurate rate and product ratio data revealed several facts: (1) all of the reactions were third order, with a first-order dependence on the concentration of phosphonium cation and a second-order dependence on the concentration of hydroxide ion; (2) the relative ease of elimination of the various benzyl groups paralleled their stability as anions; (3) the relative ease of departure of a given group was definitely influenced by the nature of the nondeparting groups; and (4) the rate data could be correlated with σ^- -values in a suitable adaptation of the Hammett equation.

The decomposition of a quaternary phosphonium hydroxide to give a phosphine oxide and a hydrocarbon is one of the best known nucleophilic displacement reactions at phosphorus. Although recent kinetic³⁻⁵ and stereochemical^{5,6} studies have clarified many of the details of the mechanism of this type of reaction, there are still a number of questions to be answered. Some of these questions arise from the early work of Fenton and Ingold⁷ and of Hey and Ingold.⁸ These workers, in an extension of earlier studies carried out by Mi-

chaelis^{9,10} and by Meisenheimer and Lichtenstadt,¹¹ subjected a series of mixed quaternary phosphonium hydroxides to the decomposition reaction, and, by determining the product ratios of the hydrocarbons produced, they proposed the following sequence for the ease of elimination of various groups: benzyl > phenyl > methyl > β -phenethyl > ethyl > higher alkyl groups.

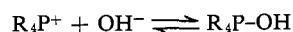
The English workers also investigated the decomposition of quaternary phosphonium alkoxides¹² and compared the ratios of saturated hydrocarbon to olefin produced. They found that, in favorable structural situations, the stronger base, ethoxide ion, produces a greater proportion of olefin than the weaker base, hydroxide ion. From the results of the various competition reactions they came to the following conclusions. (1) Since olefin formation is dependent on base strength, paraffin formation must be similarly dependent. (2) The rate-determining step is therefore the initial formation of the pentacovalent intermediate. (3) The rate of the reaction is probably second order, showing a first-order dependence on the concentration of each of the phosphonium cation and the hydroxide (or alkoxide) ion. (4) An intermediate in which phosphorus is pentacovalent must be postulated, but the loss of a proton from this intermediate before it collapses to give products may not be an essential step in the reaction sequence. (5) The relative ease of elimination of the various groups parallels their anionic stability. (6) The relative ease of elimination of the various groups is independent of the other groups attached to the phosphorus.

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(3) M. Zanger, C. A. VanderWerf, and W. E. McEwen, *J. Am. Chem. Soc.*, **81**, 3805 (1959).
(4) H. Hoffmann, *Ann.*, **634**, 1 (1960).
(5) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **86**, 2378 (1964).
(6) K. F. Kumli, W. E. McEwen, and C. A. VanderWerf, *ibid.*, **81**, 3805 (1959).
(7) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).
(8) L. Hey and C. K. Ingold, *ibid.*, 531 (1933).

(9) A. Michaelis and H. V. Soden, *Ann.*, **229**, 295 (1885).
(10) A. Michaelis, *ibid.*, **315**, 43 (1901).
(11) J. Meisenheimer and L. Lichtenstadt, *Ber.*, **44**, 356 (1911).
(12) For a fuller discussion of this reaction, see M. Grayson and P. T. Keough, *J. Am. Chem. Soc.*, **82**, 3919 (1960); also C. B. Parisek, W. E. McEwen, and C. A. VanderWerf, *ibid.*, **82**, 5503 (1960).

Our demonstration,^{3,5} subsequently confirmed by Hoffmann,⁴ that the decomposition of a quaternary phosphonium hydroxide is a third-order reaction, showing a first-order dependence on the concentration of phosphonium cation and a second-order dependence on the concentration of hydroxide ion, negates conclusions 2 and 3 of the English chemists. Thus, as pointed out by us in a previous paper,⁵ the following modification of the mechanism originally proposed by the English workers accommodates the kinetic data:

(1) Fast, reversible addition of hydroxide ion to the phosphorus atom of the quaternary phosphonium salt



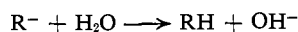
(2) Fast, reversible formation of the conjugate base of the intermediate in which phosphorus is pentavalent



(3) Rate-determining formation of the phosphine oxide and a carbanion



(4) Fast conversion of the carbanion to the appropriate hydrocarbon by the action of water (the solvent)



A detailed discussion of the stereochemistry of the reaction has already been published,⁵ and there is no need for a repetition of the arguments here. However, there are two conceivable variations of the general mechanism cited above which would be consistent with the stereochemical and kinetic data. There could be synchronous attack of the second hydroxide ion and departure of the benzyl anion; *i.e.*, steps 2 and 3 shown above could be a single step. There could also be rapid formation of an unstable intermediate with two hydroxyl groups bonded to phosphorus (tetragonal bipyramidal structure) of the correct geometry to cause inversion of the configuration of the phosphorus atom on the rate-determining departure of toluene and a hydroxide ion.¹³

The present work is concerned mainly with an evaluation of electronic (and possibly steric) effects in the decomposition reactions of quaternary phosphonium hydroxides, particularly in relation to conclusions 5 and 6, cited above, of Ingold, *et al.*

A series of monosubstituted tetrabenzylphosphonium salts, $(C_6H_5CH_2)_3P^+CH_2C_6H_4Y, X^-$, was prepared by the quaternization of tribenzylphosphine with the appropriate benzyl halide. Although the quaternization of tertiary phosphines is often carried out at room temperature or in refluxing ether or benzene, none of these methods was found to be adequate for the preparation of the desired tetrabenzylphosphonium halides.

(13) Insufficient data are available to evaluate completely yet another conceivable mechanism which has been suggested by W. P. Jencks (private communication). This consists of the synchronous reaction



However, the unfavorable energetics of attack by a negative hydroxide ion on a second like species and the fact that the typical plots of the third-order reactions show no serious deviation from linearity, other than that attributable to a build-up of the concentration of phosphine oxide as the reaction progresses,⁴ provide arguments in opposition to this mechanism.

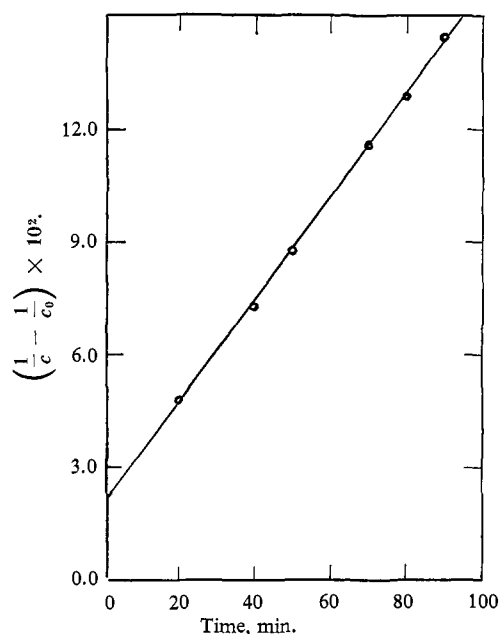


Figure 1. Decomposition of tribenzyl-*p*-chlorobenzylphosphonium hydroxide in water-dioxane at 38.9°, $(OH^-) = 0.00169 N$, $(R_4P^+) = 0.0344 N$, $k_2 = 13.94 l./mole min.$

A satisfactory quaternization reaction was achieved by refluxing the appropriate benzyl halide with tribenzylphosphine in a solution of mixed xylenes.

Tetrabenzylphosphonium chloride proved to be too poorly soluble in water to permit a successful kinetic study to be undertaken in this solvent. Solubility studies did reveal, however, that water-dimethoxyethane (1:1) was adequate as a solvent. Alcohols were avoided as a cosolvent since the basic species in such media would no longer be unambiguous.¹⁴ Tetrabenzylphosphonium chloride was found to be sufficiently soluble in 1:1 water-dimethoxyethane to give a 0.334 *N* solution. All of the other phosphonium salts were at least this soluble in the same medium, and, accordingly, all the kinetic determinations were carried out at 38.9° with solutions of this normality.

Since we had established previously that the decomposition of methylethylphenylbenzylphosphonium hydroxide was a third-order reaction,^{3,5} we decided to simplify the present studies by maintaining the concentration of phosphonium halide at a 20-fold excess over that of the sodium hydroxide. This meant that the phosphonium salt concentration was essentially constant and that the disappearance of the hydroxide ion was the only variable in the rate expression. The use of an excess of the phosphonium halide also served to suppress the rate-inhibiting effect of one of the products, the phosphine oxide, as previously reported by Hoffmann.⁴ A typical kinetic plot, one for the decomposition of tribenzyl-*p*-chlorobenzylphosphonium hydroxide, is shown in Figure 1. Good pseudo-second-order specific rate constants were obtained for all of the reactions, except for that of the *p*-nitro compound.¹⁵

(14) This did not seem to interfere, however, in kinetic studies carried out by G. Aksnes and J. Songstad, *Acta Chem. Scand.*, 16, 1426 (1962), and by G. Aksnes and L. J. Brudvick, *ibid.*, 17, 1616 (1963).

(15) Aksnes and Songstad¹⁴ have reported that the decomposition of triphenyl-*p*-nitrobenzylphosphonium hydroxide follows second-order kinetics, even though the decompositions of triphenylbenzylphosphonium hydroxide and tetraphenylphosphonium hydroxide follow the normal third-order kinetics. As pointed out by Aksnes and Songstad, the greater departure aptitude of a *p*-nitrobenzyl anion over that of benzyl or phenyl anion accommodates these results.

Table I. Rate and Product Ratio Data for the Decomposition of $Y-C_6H_4CH_2P^+(CH_2C_6H_5)_3, OH^-$

Y	$k_2, l. mole^{-1} min^{-1}$ (at 39.4°)	Mole % toluene	Mole % $Y-C_6H_4CH_3$	Yield, %	k_2^*	k_2^1	k_2^*/k_H^*	k_2^1/k_2^*	k_2^1/k_H^*
<i>p</i> -NO ₂	479 ^a	0.00	100.00	95	...	479 ^a
<i>m</i> -NO ₂	327	1.30	98.70	97	1.42	323	2.14	227	485
<i>m</i> -Br	25.50	23.53	76.47	100	2.00	19.50	3.01	9.75	29.20
<i>m</i> -Cl	22.07	34.52	65.48	98	2.54	14.45	3.82	5.69	21.73
<i>m</i> -F	18.83	41.79	58.21	100	2.62	10.96	3.94	4.18	16.48
<i>p</i> -Cl	13.77	64.79	35.21	94	2.97	4.85	4.47	1.63	7.29
<i>p</i> -F	8.73 ^b	92.83	7.17	88	2.70	0.63	4.06	0.23	0.95
H	2.66	(75.00)	(25.00)	100	0.665	0.665	1.00	1.00	1.00
<i>m</i> -CH ₃	1.82	77.25	22.75	98	0.47	0.42	0.71	0.89	0.63
<i>p</i> -CH ₃	2.01	82.51	17.49	92	0.55	0.35	0.83	0.64	0.53
<i>p</i> - <i>t</i> -Bu	2.06	70.70	29.30	99	0.49	0.60	0.73	1.24	0.90
<i>p</i> -CH ₃ O	1.45	93.17	6.83	82	0.45	0.10	0.68	0.22	0.15

^a Calculated value (see Experimental) based on the assumption that this is also a third-order reaction; however, in view of the results of Aksnes and co-workers,¹⁵ this assumption may be an incorrect one. ^b There was some contamination of this product with the *meta* isomer.

Here the decomposition, carried out under the stated conditions, was too rapid to follow kinetically. A summary of the kinetic results is provided in Table I.

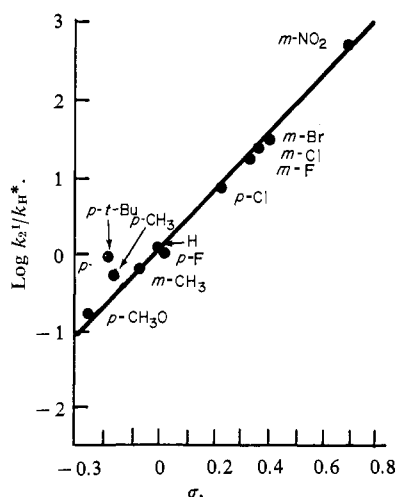


Figure 2. Correlation of rate data with σ -values in an adaptation of the Hammett equation.

Product ratios were also determined for the decomposition of each of the phosphonium hydroxides. In these studies, the phosphonium halide was treated with excess sodium hydroxide, and the ratio of the toluenes produced was measured by vapor phase chromatography. With the exception of the *p*-nitro compound, all of the salts on decomposition yielded mixtures of toluene and the appropriate *meta*- or *para*-substituted toluene. *p*-Nitrobenzyltribenzylphosphonium hydroxide gave only *p*-nitrotoluene, with no detectable amount of toluene being produced. As also found by other workers who studied the decomposition of aryltriphenylphosphonium hydroxides¹⁶ and triphenyl-*p*-Y-benzylphosphonium hydroxides,⁴ the relative ease of elimination of a particular group paralleled its anionic stability. The data are summarized in Table I.

In order to evaluate the effect of the nondeparting groups on the relative rate of displacement of the leaving group, we made use of rate and product ratio data to calculate partial rate factors, as shown in the following equations:

(16) L. Horner, H. Hoffmann, H. G. Wippel, and G. Hassel, *Chem. Ber.*, 91, 52 (1958).

k_2 = specific rate constant for the pseudo-second-order reaction = $3k_2^* + k_2^1$

k_2^* = partial rate factor for departure of a benzyl anion in $Y-C_6H_4CH_2P^+(CH_2C_6H_5)_3, OH^-$ = $[k_2 (\text{mole \% toluene})]/3$

k_2^1 = partial rate factor for departure of the *meta*- or *para*-substituted benzyl anion in $Y-C_6H_4CH_2P^+(CH_2C_6H_5)_3, OH^-$ = $k_2 (\text{mole \% } Y-C_6H_4CH_3)$

k_H^* = partial rate factor for departure of a single benzyl anion in $(C_6H_5CH_2)_4P^+OH^-$ = $k_2/4$

Then, for evaluation in suitable adaptations of the Hammett equation, the following ratios of partial rate factors were calculated: k_2^*/k_H^* , k_2^1/k_2^* , and k_2^1/k_H^* . The partial rate factors and the indicated ratios are presented in Table I. It is of interest that only a plot of $\log k_2^1/k_H^*$ vs. σ was linear, with $\rho = 3.64$, as shown in Figure 2. The plots of $\log k_2^*/k_H^*$ vs. σ , of $\log k_2^1/k_2^*$ vs. σ , and of $\log k_2/k_2^0$ vs. σ were unsatisfactory. In this regard, it should be mentioned that, for the series *m*- or *p*- $Y-C_6H_4CH_2P^+(C_6H_5)_3, OH^-$ ($Y = p-OCH_3, p-CH_3, H, p-Cl, p-Br, m-Cl$), Hoffmann⁴ found a plot of $\log k_3^0$ (the specific rate constant for the third-order reaction extrapolated to zero concentration of the phosphonium salt) vs. σ to be linear with $\rho = 4.62$. When account is taken of the different structures in the two series of compounds, it is evident that Hoffmann's use of the Hammett equation is essentially the same as ours in our plot of $\log k_2^1/k_H^*$ vs. σ . The differences in the ρ -values for the two plots merely reflect the different electronic effects of the stationary groups in the two series.

From the data given in Table I, two qualitative generalizations can be offered. (1) An examination of k_2^* (the partial rate factor for departure of a benzyl anion in $Y-C_6H_4CH_2P^+(CH_2C_6H_5)_3, OH^-$) shows that it is not constant in the several compounds which bear substituted benzyl groups. This means that, contrary to the findings of Ingold and co-workers,^{7,8} the relative ease of elimination of a given group is not independent of the stationary groups bonded to the phosphorus atom. (2) A comparison of k_2^*/k_H^* with k_2^1/k_H^* reveals that the magnitude of the effect of a substituent is greatest on the group to which it is directly bonded. This, of course, is the expected result. Substituents with positive σ -values would be expected to facilitate and substituents with negative σ -values to retard the departure of the substituted benzyl group.

In terms of the four-step mechanism of decomposition of a quaternary phosphonium hydroxide cited above, the presence of an electron-withdrawing substituent would be expected to accelerate the reaction for three reasons: (1) the concentration of the adduct of the phosphonium cation with hydroxide ion would be greater with such a substituent present than in the unsubstituted case; (2) the concentration of the conjugate base of the intermediate in which phosphorus is pentavalent would likewise be greater; and (3) the rate of departure of the negatively substituted benzyl anion (the major reaction path) would be greater than the rate of departure of a benzyl anion in the case of the decomposition of tetrabenzylphosphonium hydroxide. A similar line of reasoning leads to the conclusion that the presence of an electron-donating substituent would inhibit the reaction at each of the first three stages.

One additional point is worthy of comment regarding the relative rates of decomposition of the various quaternary phosphonium hydroxides. It was observed that the rate of decomposition of methylethylphenylbenzylphosphonium hydroxide was very much slower than that of any tetrabenzylphosphonium hydroxide investigated by us. The former compound was too unreactive to undergo decomposition at a convenient rate at 38.9°, the temperature at which all of the tetrabenzylphosphonium hydroxides underwent reaction readily. In fact, a temperature of 99.4° was required to bring about decomposition of methylethylphenylbenzylphosphonium hydroxide at a convenient rate.^{3,5} It seems to us that the rate difference is too great to be rationalized either on the basis of the statistical effect (there being four acceptable leaving groups in the tetrabenzylphosphonium case as compared to but one in the case of the methylethylphenylbenzylphosphonium cation) or on the basis of the difference in inductive effects of the groups bonded to phosphorus in the various compounds. Rather, we are inclined to believe that the large rate difference is attributable to a steric effect. We tentatively suggest that there is greater relief of B-strain when the tetrahedral tetrabenzylphosphonium cation is converted, by the addition of hydroxide ion, to the trigonal bipyramidal intermediate in which phosphorus is pentavalent than when the methylethylphenylbenzylphosphonium cation, having smaller groups bonded to phosphorus, is similarly converted. Thus, in the tetrabenzylphosphonium case the concentration of the unstable intermediate in which phosphorus has the sp³d configuration is greater, and, accordingly, the rate of decomposition is greater. Experiments are being carried out to test this hypothesis.

Experimental¹⁷

Preparation of the Tetrabenzylphosphonium Halides. A 2-l. three-necked flask was equipped with a mechanical stirrer. A piece of 9-mm. glass tubing having a 90° bend was attached to one neck of the flask through a rubber sleeve adapter in such a manner that the tube could be lowered or raised. The other end of the glass tube was equipped with a rubber sleeve which could be closed by use of a screw clamp. To the third neck of the flask was attached a Y-tube fitted with a Friedrichs condenser (which, in turn, was fitted with a

(17) Analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

drying tube) and an equilibrating dropping funnel having a nitrogen inlet. The whole apparatus was continually flushed with dry, oxygen-free nitrogen, and ice-cold water was circulated through the condenser.

About 200 ml. of anhydrous ether and 12.2 g. (0.50 g.-atom) of magnesium turnings were introduced into the flask. The preparation of the Grignard reagent was carried out by the slow addition of a solution of 63.3 g. (0.50 mole) of benzyl chloride in 100 ml. of anhydrous ether. After the addition had been completed and the exothermic reaction had ceased, the mixture was refluxed on the steam bath for 30 min. To the cooled mixture a solution containing 22.0 g. (0.16 mole) of phosphorus trichloride in 100 ml. of anhydrous ether was added dropwise over a period of 2 hr. After the mixture had been permitted to stir for an additional hour, it was hydrolyzed by the dropwise addition first of 150 ml. of ice-cold water and then 200 ml. of a saturated ammonium chloride solution. Stirring was stopped and the layers were allowed to separate.¹³

The vertical portion of the glass tube was lowered to a point just above the interface of the two layers. The horizontal portion of the glass tube was connected through the sleeve to glass tubing inserted through a stopper into a narrow-necked fritted disk filter funnel charged with anhydrous calcium chloride. The funnel, in turn, was fitted into a 1-l. two-necked flask which had previously been charged with the appropriate benzyl halide (0.16 mole) dissolved in 100 ml. of xylene and maintained under a nitrogen atmosphere. The second neck was connected to a trap designed to prevent air from entering the system. The screw clamp on the rubber sleeve connecting the main reaction flask to the flask containing the benzyl halide was opened, and, by application of nitrogen pressure, the ether solution was forced through the filter funnel into the second flask. When the ether solution of tribenzylphosphine had been transferred, the two-necked flask was disconnected from the rest of the apparatus and quickly connected to the nitrogen supply. Heating was started to drive off the ether. When the solution began to reflux, the air trap was removed and eventually replaced by a condenser after all the ether had been removed. An additional 100 ml. of xylene was added, and, as the temperature of the solution was increased, the phosphonium salt precipitated. The mixture was heated under reflux for 2 hr. and cooled, and the phosphonium salt was collected by filtration. The phosphonium halide was recrystallized several times from water until a constant melting point was observed. The yields, melting points, and analytical data for the salts are given in Table II.

Kinetic Procedure. 1,2-Dimethoxyethane was purified by being washed with saturated sodium hydroxide solution, dried over anhydrous calcium chloride, and distilled from sodium. The pure 1,2-dimethoxyethane was then diluted with an equal volume of carbonate-free distilled water.

An accurately prepared 0.0347 *N* solution of the quaternary phosphonium halide in 50% (by volume) water-1,2-dimethoxyethane was equilibrated in a con-

(18) A large amount of solid material usually collects at the interface, but, if the layers are left undisturbed for a time, the top ether layer can usually be withdrawn without disturbing the settled solid.

Table II. Yields, Melting Points, and Analytical Data for $Y-C_6H_4CH_2P^+(CH_2C_6H_5)_3X^-$

Y	X ⁻	M.p., °C.	Yield, %	Calculated		Analyses, %										
				C	H	P	Cl	Br	N	Found						
				C	H	P	Cl	Br	N	C	H	P	Cl	Br	N	
<i>p</i> -NO ₂ ^a	Cl ⁻	240-241	13
<i>m</i> -NO ₂	Br ⁻	191-192	50	64.62	5.23	5.95	...	15.36	2.69	64.66	5.32	5.70	...	15.19	2.69	
<i>m</i> -Br	Br ⁻	180-181	88	60.67	4.91	5.59	...	28.83	...	60.89	4.95	5.64	...	28.99	...	
<i>m</i> -Cl	Br ⁻	178-179	68	65.96	5.34	6.08	6.95	15.67	...	66.02	5.55	5.89	7.01	15.65	...	
<i>m</i> -F	Cl ⁻	224-225	44	74.91	6.06	6.90	7.90	74.47	6.15	7.12	8.01	
<i>p</i> -Cl	Cl ⁻	229-230	52	72.96	6.03	6.67	15.16	72.26	5.85	6.66	15.24	
<i>p</i> -F	Cl ⁻	228.5-229.5	35	74.91	6.06	6.90	7.90	74.63	5.96	7.20	7.95	
H ^b	Cl ⁻	228-229	58	
<i>m</i> -CH ₃	Br ⁻	181.5-182.0	85	71.16	6.18	6.33	...	16.33	...	70.97	6.39	6.30	...	16.31	...	
<i>p</i> -CH ₃	Cl ⁻	227-228	45	78.42	6.61	7.09	7.75	78.27	6.80	6.96	7.97	
<i>p-t</i> -Bu	Br ⁻	211.0-211.5	76	72.30	6.83	5.83	...	15.04	...	72.51	7.01	5.74	...	15.17	...	
<i>p</i> -CH ₂ O	Cl ⁻	184-185	68	75.41	6.41	6.92	7.47	75.56	6.56	6.72	7.69	

^a Prepared by D. A. Mathewes, M.S. Thesis, University of Kansas, 1955. ^b Reported m.p. 228.5°: E. A. Letts and N. Collie, *J. Chem. Soc.*, **42**, 724 (1882).

stant temperature bath at $38.65 \pm 0.05^\circ$. A 100-ml. aliquot of the solution was introduced into a volumetric flask and allowed to equilibrate in the constant temperature bath for 2 hr. After the addition of 1.00 ml. of 0.168 *N* sodium hydroxide solution, the new solution was shaken for 30 sec. and a 10.00-ml. aliquot withdrawn. This was poured into an excess of a previously prepared standard solution of hydrochloric acid. The excess acid was titrated with standard sodium hydroxide solution with constant stirring to a pH meter reading of 6.0. This value was selected because it was the average value obtained for the equivalence point of acid-base titration conducted in 50% 1,2-dimethoxyethane in the presence of a variety of tetra-benzylphosphonium halides. Similar aliquots were removed at various time intervals and treated similarly.

The plots of $1/c - 1/c_0$ vs. time, where *c* is the normality of the sodium hydroxide used in the decomposition, showed good agreement with pseudo-second-order kinetics. The rate constants were calculated by the method of least squares. At least duplicate determinations were made for each phosphonium salt. The values of the specific rate constants were found to be easily reproducible within $\pm 1.5\%$. The detailed data may be found in the dissertations of Zanger¹⁹ and Axelrad.²⁰

Product Analysis. Precisely 1.000 g. of the quaternary phosphonium halide was placed in a 50-ml. round-bottomed flask containing a magnetic stirrer. Then 10 ml. of 1 *N* sodium hydroxide solution was introduced, and a condenser cooled with ice water was attached to the flask. The reaction mixture was refluxed with stirring for 2 hr. The condenser walls were washed down with 2 ml. of methanol and then with distilled water. The flask was placed in an ice bath and 5.00 ml. of *n*-pentane was added. The flask was stoppered

and the mixture stirred vigorously for 1 hr. To the mixture was added sufficient water to raise the pentane solution into the neck of the flask. The flask was then stoppered and allowed to stand for 3 hr. in the refrigerator. This was sufficient time for the two layers to separate. Samples of the pentane solution were withdrawn with a suitable microdipper and introduced directly into the vapor phase fractometer for analysis.

Compounds which underwent reaction at relatively fast rates were decomposed at 38.65° . In these cases the stoppered reaction flask was agitated for 24-36 hr. in a constant temperature bath. The reaction mixtures were then treated as described above.

The analyses were carried out with a Perkin-Elmer vapor fractometer, Model 154. For the analyses of mixtures of toluene with *m*-xylene, *p*-xylene, *m*-chlorotoluene, *p*-chlorotoluene, *m*-bromotoluene, *p*-methoxytoluene, or *p*-nitrotoluene, a 2-m. "C" column was used under the following conditions: column and detector temperature, 100° ; helium pressure, 25 p.s.i.g.; detector voltage, 8 v.; flow rate, 100 ml./min.; sample size, 1 μ l. For mixtures of toluene with *p-t*-butyltoluene or *m*-nitrotoluene, a 2-m. "C" column was also used, but under the following conditions: column and detector temperature, 150° ; helium pressure, 25 p.s.i.g.; detector voltage, 8 v.; flow rate, 82 ml./min.; sample size, 1 μ l. Finally, for mixtures of toluene with *m*-fluorotoluene or *p*-fluorotoluene, a 2-m. "K" column was used under the following conditions: column and detector temperature, 73° ; helium pressure, 15 p.s.i.g.; detector voltage, 8.0 v.; flow rate, 60 ml./min.; sample size, 1 μ l.

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(19) M. Zanger, Ph.D. Dissertation, University of Kansas, 1959.

(20) G. Axelrad, Ph.D. Dissertation, University of Kansas, 1960.