

Chemical Consequences of Through Space 2p–3d Overlap in the Alkaline Cleavage of Benzyltriarylphosphonium Chlorides

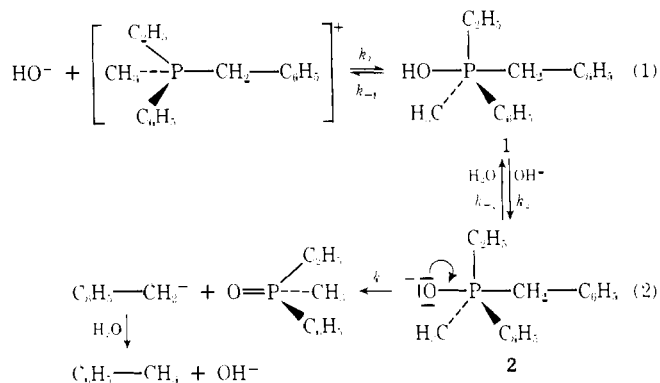
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Abstract: To account for the accelerated rates observed in the quaternization of tertiary phosphines (and arsines) containing *o*-methoxyphenyl groups, McEwen et al. have invoked the concept of anchimeric acceleration involving overlap of a pair of 2p electrons on the methoxy oxygen with a vacant 3d (or 4d) orbital of phosphorus (or arsenic). If such overlap is effective in stabilizing the transition state of an S_N2 reaction, it should be even more effective in stabilizing the phosphonium ion produced in such a reaction. To test this hypothesis, we have determined the rates of alkaline cleavage of a series of benzyltriarylphosphonium chlorides in 50% v/v aqueous dioxane at 10.1 °C. The relative rates of cleavage of the meta- and para-substituted onium salts we have examined give a reasonable Taft correlation ($\rho^\circ = +4.05$, $r = 0.970$ for five salts); however, salts containing *o*-methoxy groups react much more slowly than salts containing *p*-methoxy groups. For example, benzylbis(*o*-methoxyphenyl)phenylphosphonium chloride reacts only 2.6×10^{-3} times as fast as benzylbis(*p*-methoxyphenyl)phenylphosphonium chloride. We ascribe such pronounced rate reductions primarily to stabilization of the *o*-methoxyphenylphosphonium ions by the 2p–3d orbital overlap described above.

The principal thrust of this work has been a study of the kinetics of the alkaline cleavage of a variety of benzyltriarylphosphonium chlorides in 50% v/v 1,4-dioxane–water containing 0.400 M potassium chloride (to maintain a constant ionic strength). The third-order rate constants^{1,2} are summarized in Table I. High values of correlation coefficients (generally in the range of 0.985–0.9996, based on six to eight data points) were obtained in all cases (with the exception of those reactions which were either so fast or so slow that they were difficult to measure). In addition, excellent agreement was obtained in duplicate runs on the same compound (again with the exception of those reactions which were either extremely rapid or extremely slow).

The mechanism of the alkaline cleavage of quaternary phosphonium salts is reasonably well established, and generally it consists of the following steps:^{3–6} (1) rapid, reversible attack by hydroxide ion at a face of the phosphonium tetrahedron to give a hydroxyphosphorane (**1**) in which the hydroxyl group now occupies an apical position in the resulting trigonal bipyramid; (2) rapid, reversible removal of a proton from the hydroxyphosphorane (**1**) to generate its conjugate base, a phosphoranyl anion (**2**), which also has trigonal bipyramidal geometry; (3) irreversible, rate-determining expulsion of a carbanion (which is probably protonated as it is being formed⁶) from an apical position in the trigonal bipyramid to generate a tertiary phosphine oxide. These steps are illustrated below for the alkaline cleavage of methylethylphenylbenzylphosphonium ion (without indicating that expulsion of the carbanion and its protonation by water are probably concerted, rather than separate, steps).



On the basis of this mechanism, it is anticipated that the presence of an electron-withdrawing substituent will cause acceleration of the rate of reaction by increasing the magnitude of K_1 and K_2 , the equilibrium constants for the two first steps of the reaction. Moreover, the presence of an electron-withdrawing substituent in the leaving group should increase the magnitude of k_3 . Previous workers, notably Hoffmann,⁷ McEwen and his colleagues,^{3–5,8,9} and Allen and his co-workers,^{10–14} have documented these statements for a number of different systems. Allen's work is especially notable in that, in certain cases, he was able to determine the relative importance of K_1K_2 , on the one hand, and of k_3 , on the other.

Examination of our own data confirms both the theoretical predictions and the experimental results of earlier workers, namely, that the presence of electron-withdrawing groups, such as *m*-Cl, *p*-Cl, and *m*-CH₃O, causes acceleration of the rate of alkaline cleavage of benzyltriarylphosphonium salts, while the presence of electron-donating groups (such as *p*-CH₃O and *o*-CH₃O) has the opposite effect. In fact, in the case of the meta- and para-substituted phosphonium salts in reactions carried out at 10.1 °C, a least-squares analysis of a plot of the logarithm of the relative rates ($\log k_{\text{rel}}$) vs. the sum of the σ values for the groups bonded to phosphorus ($\Sigma\sigma$) leads to a reasonably satisfactory Hammett correlation (correlation coefficient = 0.936 for five data points) with a slope (Hammett ρ value) of +3.19.

An even better correlation is obtained by use of the Taft equation ($\rho^\circ = +4.05$, $r = 0.970$). This value compares favorably with the ρ value of +4.62 obtained by Hoffmann⁷ for the alkaline cleavage of a series of Y-benzyltriphenylphosphonium bromides (where Y = *m*-Cl, *p*-Br, *p*-Cl, H, *p*-CH₃, or *p*-CH₃O) in 25% isopropyl alcohol in water. It also compares favorably with a ρ value of +3.64 obtained by McEwen and his colleagues⁵ for the alkaline cleavage (in 50% v/v aqueous 1,2-dimethoxyethane) of an extensive series of Y-benzyltriphenylphosphonium salts. The positive sign of these ρ values is, of course, characteristic of reactions which are accelerated by the presence of electron-withdrawing substituents, while the magnitudes of the ρ values indicate that the rate of alkaline cleavage of these phosphonium salts is quite sensitive to such electronic influences.

With regard to our own data, the point which lies farthest from the line obtained by the least-squares treatment is the point for the alkaline cleavage of benzylbis(3-methoxy-

Table I. Kinetic Data for the Decomposition of Phosphonium Hydroxides at 10.1 °C in 50% v/v Dioxane–Water in the Presence of 0.4000 M KCl

phosphonium hydroxide	run	concn, M	$k_3, \text{L}^2 \text{mol}^{-2} \text{s}^{-1}$	k_{rel}	corr coeff	no. of data points
benzylbis(3-chlorophenyl)phenyl	several	$\sim 15.0 \times 10^{-3}$	$\sim 1.7 \times 10^2$	$\sim 1.6 \times 10^3$	0.91–0.99	3–8
benzylbis(4-chlorophenyl)phenyl	1	15.72×10^{-3}	1.30×10^1		0.976	7
	2	15.93×10^{-3}	1.39×10^1		0.995	7
	1 ^a	14.96×10^{-3}	1.18×10^1		0.984	8
	2 ^a	14.96×10^{-3}	1.22×10^1	1.12×10^2	0.993	8
benzylbis(3-methoxyphenyl)phenyl	1 ^a	19.37×10^{-3}	1.86×10^{-1}		0.999	8
	2 ^a	19.37×10^{-3}	1.93×10^{-1}	1.78	0.998	7
benzyltriphenyl	1	19.97×10^{-3}	1.12×10^{-1}	1.00	0.999	8
	2	19.97×10^{-3}	1.02×10^{-1}		0.999	8
benzylbis(4-methoxyphenyl)phenyl	1	20.86×10^{-3}	1.46×10^{-2}	1.39×10^{-1}	0.9991	6
	2	20.86×10^{-3}	1.52×10^{-2}		0.9996	6
benzyl(2-methoxyphenyl)diphenyl	1	19.95×10^{-3}	2.90×10^{-3}	2.69×10^{-2}	0.998	8
	2	19.95×10^{-3}	2.84×10^{-3}		0.999	7
benzyl(2,6-dimethoxyphenyl)diphenyl	1	19.36×10^{-3}	2.71×10^{-4}	2.61×10^{-3}	0.998	8
	2	19.36×10^{-3}	2.87×10^{-4}		0.991	7
benzylbis(2-methoxyphenyl)phenyl	1	19.70×10^{-3}	4.47×10^{-5}	3.6×10^{-4}	0.953	5
	2	19.70×10^{-3}	3.81×10^{-5}		0.965	5
benzyltris(2-methoxyphenyl)phenyl	1	20.39×10^{-3}	$< 3 \times 10^{-5}$	$< 3 \times 10^{-4}$		
	2	20.39×10^{-3}				

^a Prechilled pipets were used.

phenyl)phenylphosphonium chloride. Horner and his colleagues¹⁶ have previously noted an abnormal product distribution in the alkaline cleavage of a 3-methoxyphenyltriphenylphosphonium salt, so there might be a connection between his observation and the slower than anticipated rate that we have observed in the case of our bis(3-methoxyphenyl) compound.

We have also analyzed recent rate data accumulated by McEwen and his colleagues on the rates of quaternization of para-substituted phosphines with benzyl chloride in benzene–methanol (60:40 v/v) at 31.0 °C. In those cases where reasonably accurate values are known, the data give an acceptable correlation with the Hammett equation, as shown in Table II. Here the negative sign of ρ indicates, in agreement with other published studies,^{17,18} that the quaternization reactions are facilitated by the presence of electron-donating substituents, while the magnitude of ρ indicates that such quaternization reactions are only moderately sensitive to such electronic effects. Thus, the quaternization reactions and the alkaline cleavage reactions differ appreciably in their response to electron-withdrawing and -donating substituents, but these differences are exactly what would be expected on the basis of the vastly different mechanisms by which the two reactions proceed.

In order to obtain greater insight into the effect of substituents in the alkaline cleavage of phosphonium salts, we have also examined the ratios of the volatile products produced in one case where electron-withdrawing substituents are present and in one case where electron-donating substituents are present. The results of these investigations, together with earlier data obtained by Pagilagan²¹ on the distribution of products produced in the alkaline cleavage of benzyltriphenylphosphonium chloride, are summarized in Table III. As anticipated, toluene (arising from expulsion of the extensively delocalized benzyl anion) is by far the major product in all three cases. Moreover, the proportion of aryl cleavage increases as the aryl substituent becomes progressively more electron withdrawing, in line with earlier observations^{3,5,7-15} that the ease of departure of a leaving group (in the alkaline cleavage of phosphonium salts) parallels the stability of the corresponding anion.

In connection with our results for the *p*-methoxyphenyl substituent, it should be mentioned that Eaborn and his colleagues²² have observed that *p*-methoxyphenyl is a better

Table II. Correlation of Relative Rates of Reaction of Triarylphosphines (with Benzyl Chloride in Benzyl–Methanol (3:2 v/v) at 31.0 °C) with Hammett σ Values

substituents on ring(s) of triphenylphosphine	$10^2 k_2$ L mol ⁻¹ h ⁻¹	k/k_H	log (k/k_H)	$\Sigma \sigma_p^{15}$
tris(4-MeO)	47.8	6.62	+0.821	-0.804
tris(4-Me)	25.8	3.57	+0.552	-0.510
4-MeO-bis(4-Me)	24.3	3.37	+0.528	-0.536
bis(4-MeO)	20.0	2.77	+0.442	-0.608
4-MeO	14.6	2.02	+0.305	-0.268
4-Me	9.44	1.31	+0.117	-0.170
4-MeS	8.66	1.20	+0.0791	0.000
H	7.22	1.00	0.000	0.000
4-F	4.60	0.637	-0.196	+0.062
4-Cl	3.78	0.524	-0.281	+0.227
4-CH ₃ CO ₂ ¹⁷	3.41	0.472	-0.326	+0.31
4-Br	2.10	0.291	-0.536	+0.232
slope = $\rho = -1.081$		y intercept = -0.0607		
corr coeff = 0.968				

Table III. Ratios of Volatile Products Produced in the Alkaline Cleavage of Benzylbis(*p*-Y-phenyl)phenylphosphonium Chlorides (as Determined by GC Analysis of Hydrocarbon Extracts of Aqueous Reaction Mixtures)

	Y =		
	Cl	H	OCH ₃
mol % toluene	87.0	97.3	100.7
mol % Y-benzene	6.75		0.36
mol % benzene	0.092	2.7	0.44

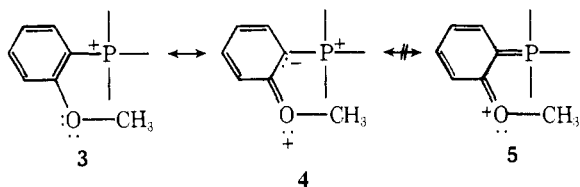
leaving group than phenyl in the base-catalyzed cleavage of aryltrimethylsilanes and -stannanes. Based on these data, together with the observation²³ of a kinetic isotope effect ($k_H/k_D = 1.4-4.6$) for protonation–deuteration of the leaving group, Eaborn and his co-workers proposed the concept of electrophilic participation by a solvent molecule in the formation of anisole. Since it is now known⁶ that electrophilic participation by a solvent molecule also occurs in the last step of the alkaline cleavage of at least some phosphonium salts, one may wonder why this does not cause *p*-methoxyphenyl to be a better leaving group than phenyl in this case as well. The answer to this ap-

parent dilemma lies in the magnitudes of the kinetic isotope effects observed in the tin and silicon cases ($k_H/k_D = 1.4-4.6$) as compared to the phosphorus case ($k_H/k_D \sim 1.2$). In the latter case, the smaller isotope effect indicates that there is only a small degree of carbanionic character in the transition state, with the result that electrophilic participation by a solvent molecule does *not* occur to so great an extent that it inverts the usual order of carbanion stability.

Finally, it should be pointed out that, since the benzyl anion is undoubtedly the major leaving group in all of the reactions that we have studied, the rate-accelerating and -decelerating effects caused by the presence of meta and para substituents must be primarily due to the influence of these substituents on the magnitudes of K_1 and K_2 (rather than on the magnitude of k_3). These influences are obviously quite powerful, as indicated both by the relatively large magnitude of ρ and by the spread of 10^4 in rate constants for our meta- and para-substituted compounds.

We also find some very pronounced rate effects in the ortho-substituted compounds that we have examined (cf. Table I). For example, the introduction of a single *o*-methoxyl group into the benzyltriphenylphosphonium structure reduces the rate of alkaline cleavage to only $1/37$ of its value for the unsubstituted compound. Similarly, benzyl(2,6-dimethoxyphenyl)diphenylphosphonium chloride, in which two *o*-methoxyl groups are bonded to the same aromatic ring, undergoes alkaline cleavage only $1/380$ times as fast as the parent compound. An especially interesting case is that of benzylbis(2-methoxyphenyl)phenylphosphonium chloride, not only because it reacts at only $1/2800$ of the rate of benzyltriphenylphosphonium chloride, but also because of its very slow rate compared to that of the isomeric benzylbis(4-methoxyphenyl)phenylphosphonium chloride. In fact, k_o/k_p for these two compounds is only 2.6×10^{-3} . Finally, benzyltris(2-methoxyphenyl)phosphonium chloride reacts so slowly with hydroxide ion in 50% v/v aqueous dioxane at 10.1 °C that its rate cannot readily be determined. (This is quite the opposite of our experience with benzylbis(3-chlorophenyl)phenylphosphonium chloride where the reaction proceeds so rapidly even at 10.1 °C that it is difficult to follow.) Thus, clearly the *o*-methoxyl group is exerting a profound rate-inhibiting effect on the alkaline cleavage reaction of these compounds.

Both *o*- and *p*-methoxyl groups exhibit electron-donating resonance effects with respect to aromatic rings; e.g., structures such as **4** probably do make a contribution to the resonance



hybrid when an *o*-methoxyl group is present in the phosphonium ion. Moreover, this structure may make a more important contribution in the ortho case than it would in the para case (where there would be greater separation of opposite charges). However, it is unlikely that there is enough difference in the relative importance of the contribution of structure **4** in the ortho case and the contribution of the analogous structure in the para case to account for the rate differences that we have observed. At the same time, there is considerable evidence to indicate that stabilization of such phosphonium ions does *not* involve a significant contribution from $p_\pi-d_\pi$ overlap, as in structures such as **5** above. Allen,¹⁰ for example, has found that benzyltris(2-thienyl)phosphonium ions undergo cleavage 2.5×10^5 times more rapidly than do benzyltriphenylphosphonium ions. Since the thienyl group is a well-known " π excessive" system, it seems clear that $p_\pi-d_\pi$ stabilization of the phos-

phonium ion, if it occurs at all, plays no significant role in determining the overall rate of reaction. Even if $p_\pi-d_\pi$ overlap were to occur, there is no obvious reason why it should be so much more effective in the *o*-methoxyl case than in the *p*-methoxyl case.

Likewise, it seems unlikely that the rate-retarding effect of the *o*-methoxyl groups is due to classical steric hindrance. Pagilagan and McEwen,²⁴ for example, have measured k_o/k_p ratios which are relatively large (0.38–0.46) for the alkaline cleavage of phosphonium salts in which one, two, or three tolyl groups are present. Thus, even the presence of three *o*-methyl groups does not produce a large reduction in the rate of alkaline cleavage of phosphonium salts, and there are at least two lines of evidence which indicate that the effective steric bulk of a methoxyl group ortho to a reaction center is less than that of an *o*-methyl group. Taft,²⁵ for example, in his treatment of the separation of steric and electrical effects for ortho substituents, lists the following in order of increasing steric hindrance: $\text{OCH}_3 < \text{OCH}_2\text{CH}_3 < \text{F} < \text{Cl} < \text{Br} \sim \text{CH}_3 < \text{I} < \text{NO}_2 < \text{C}_6\text{H}_5$. Typical numerical values for his steric parameter, E_s , for ortho substituents are OCH_3 (+0.97), F (+0.49), Cl (+0.18), CH_3 (0.00), and NO_2 (−0.71). Moreover, the van der Waals radius of the methoxyl oxygen is only 1.40 Å, while that of the methyl group is 2.00 Å.²⁶ Thus, since steric effects are not important in the alkaline cleavage of phosphonium salts containing *o*-methyl groups, one would anticipate that steric effects would be relatively unimportant in the *o*-methoxyl cases as well.

Thus, it would seem that neither the electron-donating resonance effect of the *o*-methoxyl group nor the bulkiness of such groups can adequately account for the rate-inhibiting effects that we have observed. Having failed to find a suitable explanation among the classical effects that are invoked by physical organic chemists, we now turn to a line of evidence which suggests that there may be a nonclassical explanation for these phenomena.

McEwen and his co-workers²⁸⁻³⁰ have invoked the concept of anchimeric acceleration by means of *o*-MeO-4 participation at phosphorus (or arsenic) to account for the accelerated rates that are observed in the quaternization of phosphines (and arsines) when *o*-methoxyl groups are present in those compounds. More specifically, they visualize such participation as involving overlap between a pair of 2p electrons on oxygen and a vacant 3d (or 4d) orbital of phosphorus (or arsenic). The effect of this overlap is to disperse the developing positive charge on phosphorus, and also to lower the energy needed to reach the transition state, thus giving rise to the observed increase in rate.

If such overlap occurs when there is only a fractional positive charge on the phosphorus (or arsenic), it is even more likely to occur in the fully developed onium ion. In support of this concept, McEwen and his colleagues²⁸⁻³⁰ have noted that, whenever an *o*-methoxy group is present in such an onium salt, there is a corresponding upfield shift in the ¹H NMR spectrum of the hydrogens in the methylene group directly bonded to the group 5A atom. Schulz³¹ has suggested that these effects may be due to the field effect of the *o*-methoxyl oxygen (rather than an overlap effect); however, more recently Wood, Wikholm, and McEwen³² have carried out an X-ray diffraction study on benzyl(2-methoxyphenyl)diphenylphosphonium bromide in which they discovered that the P–O distance was substantially shorter than the sum of van der Waals radii of phosphorus and oxygen. Moreover, a study of the bond angles calculated from the diffraction data indicate that the methoxyl oxygen is actually leaning toward the phosphorus. Thus, this structural determination provides strong evidence for a weak bonding interaction between the positively charged phosphorus and the oxygen of the neighboring methoxyl group.

Based on the weight of all this evidence, there can be little

doubt that the pronounced rate reductions that we have observed in the alkaline cleavage of phosphonium salts containing *o*-methoxyl groups are principally due to stabilization of such phosphonium ions by the 2p–3d orbital overlap described above. This will reduce the magnitude of at least K_1 and lead to an overall reduction in rate.

As a final note it should be pointed out that the attraction between the positive phosphorus and the *o*-methoxyl oxygen does cause the methoxyl group to partially shield that face of the phosphonium tetrahedron which is opposite the benzyl group from attack by the incoming hydroxide ion. Thus, the rate reductions caused by *o*-methoxyl groups may have a steric component, but one caused by the 2p–3d overlap.³³

The primary emphasis of this study has been on structure–reactivity relationships rather than on synthesis; nonetheless, four new quaternary phosphonium salts [benzylbis(4-chlorophenyl)phenylphosphonium chloride, benzylbis(3-chlorophenyl)phenylphosphonium chloride, benzylbis(3-methoxyphenyl)phenylphosphonium chloride, and benzyl(2,6-dimethoxyphenyl)diphenylphosphonium chloride] were prepared and characterized for the first time.

Experimental Section

Procedure for Kinetics. 1. General. Kinetics runs were carried out in a Precision Scientific constant-temperature bath using distilled water as the bath liquid. The water was covered with small pieces of polystyrene foam, both to serve as insulation and to cut down on evaporation. The bath temperature was recorded by means of a Fisher 15-000B thermometer. The cooling necessary to achieve a temperature of 10.1 °C was provided by a Lauda Model 1C-6 cooling unit. Elapsed time was followed by means of a Precision Scientific timer.

2. Preparation of 50% v/v Dioxane–Water Containing 0.400 M KCl. A class A 50-mL volumetric pipet was used to add three 50-mL portions of 0.8000 M aqueous KCl to a 500-mL volumetric flask. The same pipet (after having been washed and dried) was used to add three 50-mL portions of dioxane (redistilled from sodium benzophenone ketyl under an inert atmosphere) to the same volumetric flask. The heat of mixing was slightly positive, so the solution was cooled to room temperature in a water bath prior to subsequent use.

3. Preparation of the Phosphonium Salt Solution. The 50% v/v aqueous dioxane (containing 0.400 M KCl) was poured into a plastic squeeze bottle and used to transfer an accurately weighed sample of phosphonium salt (usually approximately 2 mmol) quantitatively to a 250-mL volumetric flask. A 100-mL volumetric pipet was used to transfer a 100-mL aliquot of this solution to a 250-mL Erlenmeyer flask fitted with a 24/40 standard taper joint. The flask was stoppered with a S 24/40 stopper bearing a Teflon sleeve and was placed in the constant-temperature bath at least 2 h prior to the beginning of a kinetic run.

4. Addition of Base to the Phosphonium Salt Solution. A quantity of Fisher 1.000 (± 0.0005) N aqueous sodium hydroxide exactly equivalent to the weighed quantity of phosphonium salt was dispensed from a class A 5-mL microburet into an 18-mL vial. The vial was closed immediately with a tight-fitting cap and placed in the temperature bath at least 2 h prior to the beginning of a kinetics run.

Mixing of the base and phosphonium salt solutions was accomplished with the aid of a 9-in. disposable capillary pipet and a rubber pipet filler. The base solution was withdrawn from the vial by means of the capillary pipet, from which it was added directly to the phosphonium salt solution. (This point was taken as $t = 0.0$ min.) The stoppered Erlenmeyer flask was shaken vigorously 20 times to mix the two solutions, and then some of the mixed solution was withdrawn by means of the capillary pipet and used to rinse the vial which had originally held the base solution. The rinse was then transferred back to the Erlenmeyer flask, and the stoppered flask was shaken vigorously another 20 times. This rinsing procedure was repeated two more times.

5. Sampling Procedure. The solutions which were used to quench aliquots of the reaction mixture at intervals during the kinetics runs were prepared by adding 5-mL aliquots of Fisher 0.100 10–0.099 95 N hydrochloric acid from a volumetric pipet to a 100-mL beaker. Volumetric pipets (10 mL) were used to transfer aliquots of the reaction mixture from the reaction flask to beakers containing the hydrochloric acid solution. The time at which a particular aliquot was

quenched was taken to be the average of the time at which the aliquot started to flow into the quenching solution and the time at which the aliquot ceased to flow into the quenching solution. In the case of some of the faster reactions, Bunnett's suggestion³⁴ of using prechilled pipets was followed. These pipets were chilled in circulating ice–water, wiped dry, rinsed with ice-cold acetone, wiped, and then dried internally by covering the tip with a Kim-wipe and applying house vacuum to the opposite end.

6. Titration Procedure. The above mixtures were diluted to 80 mL (to minimize drifting during the subsequent pH titration) and back-titrated with Fisher 0.100 ($\pm 0.000 05$) N aqueous sodium hydroxide dispensed from a class A 5-mL microburet. pH changes were followed by means of a Corning Model 12 Research pH meter, and, as a general rule, the base solution was added in 0.040-mL increments in the vicinity of the end point.

7. Calculations. End points were determined by calculating ($\Delta^2\text{pH}/\Delta \text{mL}^2$),³⁵ and third-order rate constants were determined as described previously.^{3–8}

Synthesis of Benzylbis(4-chlorophenyl)phenylphosphonium Chloride. A magnetically stirred solution of 55.1 g (0.166 mol) of bis(4-chlorophenyl)phenylphosphine³⁶ and 57.5 mL (63.2 g, 0.499 mol) of benzyl chloride (α -chlorotoluene, Eastman reagent grade) in 250 mL of anhydrous benzene was refluxed for 36 h under argon. The resulting white solid was collected by suction filtration, washed with benzene, washed with ether, and dried overnight in a vacuum desiccator. The partially dried material weighed 48.9 g and melted at 239–243.5 °C.

Attempts to purify the phosphonium salt either (1) by recrystallization from chloroform or (2) by dropwise addition of a chloroform solution of the crude product to a large volume of diethyl ether were unsuccessful because, in each case, chloroform formed a low-melting solvate with the phosphonium salt. Drying the solid obtained from each of these treatments for 36 h at 78 °C and 0.5 Torr did not suffice to remove all the chloroform.

The dried phosphonium salt (that which had precipitated out of chloroform–ether) was dissolved in benzene–chloroform. The chloroform was distilled from the magnetically stirred solution through a 16-in. Vigreux column, while additional benzene was added from a dropping funnel to maintain a constant volume. The resulting solid (after being dried overnight at room temperature in a desiccator connected to an oil vacuum pump) weighed 39.6 g and melted at 251.3–253.4 °C. Repetition of this procedure using a Todd column for distillation, followed by drying of the resulting white crystals for 10 h at 0.5 Torr at room temperature, yielded 38.8 g of material melting at 249.0–252.7 °C. Further drying (12 h in a vacuum oven maintained at 110 °C and 0.5 Torr) yielded 38.7 g of material melting at 249.5–253.1 °C. The melt did not resolidify upon cooling, indicating that melting is accompanied by decomposition. This compound is not reported in the literature, but its identity is confirmed by elemental analyses and NMR spectra.

Anal. Calcd for $\text{C}_{25}\text{H}_{20}\text{Cl}_3\text{P}$: C, 65.60; H, 4.40; Cl, 23.23; P, 6.77. Found: C, 65.79; H, 4.80; Cl, 23.42; P, 6.70.

The ^1H NMR spectrum of this compound, which has only limited solubility in CDCl_3 , shows a complex pattern from δ 8.1 to 7.1 and a doublet centered at δ 6.00 (2 H, $^2J_{\text{PCH}} = 15.5$ Hz).

Synthesis of Benzylbis(4-methoxyphenyl)phenylphosphonium Chloride. A magnetically stirred solution of 71.0 g of crude bis(4-methoxyphenyl)phenylphosphine³⁷ (which corresponds to a maximum of 0.220 mol if one assumes that the phosphine is free of solvent and any other impurities) and 63.8 g (0.504 mol) of benzyl chloride in 600 mL of benzene was refluxed for 20 h under argon. During this period, some of the solvent was distilled through a 16-in. Vigreux column to ensure removal of any water, methanol, or ethanol which might be present. The resulting white solid was collected by vacuum filtration (using the rubber dam technique), washed with benzene, washed with ether, and dried overnight in a vacuum desiccator. The partially dried phosphonium salt weighed 64.5 g and melted with decomposition at 199.2–209.8 °C. Recrystallization of the crude material from ethanol–ethyl acetate led to material which began to decompose at 210.5 °C, then began to form a semisolid pool at 214.5 °C, and finally formed a clear liquid melt at 227.0 °C. Chloroform solutions of the recrystallized material were used to spot a 2.5 \times 7.5 cm strip of Eastman Chromagram Sheet No. 6060 (silica gel absorbent with fluorescent indicator). This thin layer chromatography strip was then developed with hexane–benzene (50:20 v/v) to detect any unreacted phosphine.³⁸ No migration occurred; therefore, the phosphine is ab-

sent. Development with diethyl ether-ethyl acetate (50:50 v/v) was then used to detect any phosphine oxide³⁸ that might be present, but the absence of migration ruled out the presence of phosphine oxide. Finally the chromatogram was developed with acetone-concentrated aqueous ammonia (60:6.6 v/v) in order to establish that only one phosphonium salt was present.³⁸ Only one spot with an R_f value of ~ 0.5 resulted, although the spot was slightly spread out. Thus, the TLC evidence indicates that impurities are absent, despite the broad melting (decomposition) range of this compound.

The recrystallized material described immediately above was used for product ratio studies (as discussed later on); however, when an attempt was made to dry a sizable portion of this material further by heating it in a vacuum oven (109 °C, 0.5 Torr), pronounced yellowing of the solid occurred. A quantity of this yellow material was recrystallized from chloroform-ethyl acetate, but vacuum-oven drying at a more moderate temperature (82 °C, 0.5 Torr) again led to discoloration.

Some of the remaining yellow material from the ethanol-ethyl acetate recrystallization was dissolved in refluxing dichloromethane. Diethyl ether was added dropwise until cloudiness appeared, and then the solution was stored in a refrigerator overnight. The white crystals were separated from the yellow mother liquor by vacuum filtration (rubber dam technique), washed with CH_2Cl_2 - Et_2O (1:2 v/v), and dried in a vacuum oven at 49 °C. These crystals begin to melt, with decomposition, at 209.0 °C, form a semisolid pool by 219.2 °C, and form a clear yellow pool by 224 °C. Final drying was accomplished in an Abderhalden drying pistol heated by refluxing acetone and evacuated to 0.05 Torr for 3 days.

Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{O}_2\text{ClP}$: C, 72.24; H, 5.84; Cl, 7.90; P, 6.76. Found: C, 71.66; H, 5.75; Cl, 7.80; P, 6.86. Calcd for hemihydrate: C, 70.82; H, 5.94; Cl, 7.74; P, 6.76. Calcd for monohydrate: C, 69.45; H, 6.04; Cl, 7.60; P, 6.63.

The ^1H NMR spectrum of this compound in deuteriochloroform shows a complex pattern from δ 8.0 to 7.0 (18 H + CHCl_3), a doublet at δ 5.21 (2 H, $^2J_{\text{PCH}} = 14.4$ Hz), and a singlet at δ 3.88 (6 H). Yeh¹⁷ reports a doublet at δ 5.21 ($^2J_{\text{PCH}} = 14$ Hz) and a singlet at δ 3.91.

Synthesis of Benzylbis(3-methoxyphenyl)phenylphosphonium Chloride. A magnetically stirred solution of 30 g of crude bis(3-methoxyphenyl)phenylphosphine and 25 mL of benzyl chloride (Eastman Reagent α -chlorotoluene) in 250 mL of benzene was refluxed for 4 days under nitrogen. The resulting white solid was collected by vacuum filtration and washed with several portions of benzene. After being dried for 48 h in an Abderhalden drying pistol heated by refluxing ethanol and evacuated to 0.05 Torr, this previously unreported compound melted at 228–232 °C with decomposition.

Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{O}_2\text{ClP}$: C, 72.24; H, 5.84; Cl, 7.90; P, 6.90. Found: C, 72.26; H, 5.62; Cl, 7.76; P, 6.87.

The ^1H NMR spectrum of this compound in deuteriochloroform exhibits a complex pattern from δ 8.10 to 7.05 (18 H + CHCl_3), a doublet centered at δ 5.54 (2 H, $^2J_{\text{PCH}} = 14.4$ Hz), and a singlet at δ 3.82 (6 H).

Synthesis of Bis(3-methoxyphenyl)phenylphosphine. The synthesis was modeled after Yeh's procedure for the synthesis of bis(4-methoxyphenyl)phosphine.³⁹ Specifically, a solution of 12.9 mL (17.0 g, 0.095 mol) of redistilled phenylphosphonous dichloride [Eastman Practical dichloro(phenyl)phosphine] in 20 mL of anhydrous reagent-grade tetrahydrofuran (THF) was slowly added (with rapid mechanical stirring) to a solution of Grignard reagent [prepared from 39.27 g (0.2100 mol) of 3-bromoanisole dissolved in 30 mL of anhydrous THF and 4.85 g (0.200 mol) of magnesium covered with 30 mL of anhydrous THF] maintained between -8 and -15 °C. After the addition was complete, the reaction mixture was refluxed for 2 h, and then it was allowed to cool to room temperature. Hydrolysis was accomplished by dropwise addition of 70 mL of saturated aqueous ammonium chloride, followed by 200 mL of water. Workup of the organic layer led to isolation of 30 g of a yellow oil, from which crystals could not be obtained. The crude oil was used in the preparation of the salt described above.

Synthesis of Benzylbis(3-chlorophenyl)phenylphosphonium Chloride. A mechanically stirred solution of 29.7 g of crude bis(3-chlorophenyl)phenylphosphine (which would correspond to 90 mmol if it were free of impurities) and 25 mL of benzyl chloride (reagent grade) in 250 mL of ethyl acetate was refluxed for 48 h under nitrogen. The resulting white solid was collected by vacuum filtration, after which it was washed with two portions of ethyl acetate. Since a relatively small amount of solid was obtained, the original filtrate, as well as the filtrate from the first washing with ethyl acetate, was returned to the

reaction flask for an additional 1 week of reflux (with stirring). The original solid, after 48 h of drying at 0.25 Torr and room temperature, weighed 6.94 g (16.9% yield) and melted (with decomposition) at 279–285 °C. Recrystallization of this material from absolute ethanol-ethyl acetate improved the melting range to 281.5–286.0 °C (with decomposition).

After the additional 1 week of reflux, a second crop of crude material was collected. This amounted to 10.34 g of phosphonium salt melting at 275.3–283.5 °C (with decomposition). Subsequently, a third batch of crude material was collected after an additional 1 month of reflux. The second batch of crude material, when dried for an additional 80 h in an Abderhalden drying pistol heated by refluxing ethanol and evacuated to 0.04 Torr, was used for elemental analysis, NMR spectra, and some kinetics runs.

Anal. Calcd for $\text{C}_{25}\text{H}_{20}\text{Cl}_3\text{P}$: C, 65.60; H, 4.40; Cl, 23.23; P, 6.77. Found: C, 64.45; H, 4.49; Cl, 23.23; P, 6.76.

The ^1H NMR spectrum of this compound in deuteriochloroform exhibits a complex pattern from δ 8.1 to 7.1 (18 H) and a doublet centered at δ 6.00 (2 H, $^2J_{\text{PCH}} = 15.5$ Hz).

Synthesis of Bis(3-chlorophenyl)phenylphosphine. The preparation was modeled after the preparation of bis(4-chlorophenyl)phenylphosphine.³⁶ Fractional distillation at 24–25 Torr gave a liquid of bp 271–275 °C, which was used directly in the preparation of the chlorobenzylate.

Preparation of Benzyl(2,6-dimethoxyphenyl)diphenylphosphonium Chloride. A mechanically stirred solution of 22.70 g (70.42 mmol) of 2,6-dimethoxyphenyl diphenylphosphine (research sample, generously supplied by A. B. Janes)⁴⁰ and 26 mL (28.6 g, 226 mmol) of α -chlorotoluene (Eastman Practical) in 250 mL of ethyl acetate was refluxed for 24 h. The resulting white solid was collected by suction filtration and washed with three portions of ethyl acetate. The resulting filter cake was dried in a vacuum oven at room temperature for 48 h, after which it was dissolved in 150 mL of dichloromethane at room temperature. This solution was then added dropwise through Whatman No. 541 filter paper (fast, hardened) to 1500 mL of diethyl ether which was vigorously stirred magnetically. The resulting finely dispersed precipitate was collected by suction filtration and washed with three portions of ether. After being dried at 78 °C and oil pump vacuum, the salt exhibited the following melting behavior: crystals begin to collapse at 173.0 °C, form a light brown semisolid by 173.5 °C, and form a clear melt by 182 °C. Melting was definitely accompanied by decomposition.

Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{O}_2\text{ClP}$: C, 72.24; H, 5.84; Cl, 7.90; P, 6.90. Found: C, 72.21; H, 6.03; Cl, 7.88; P, 6.99.

The ^1H NMR spectrum of this compound in deuteriochloroform exhibited a complex pattern between δ 8.05 and 6.75 (18 H), a doublet centered at δ 4.92 (2 H, $^2J_{\text{PCH}} = 16.2$ Hz), and a singlet at δ 3.70 (6 H).

Other Salts. Benzyltriphenylphosphonium chloride, benzyl(2-methoxyphenyl)diphenylphosphonium chloride, benzyltris(2-methoxyphenyl)phosphonium chloride, and benzylbis(2-methoxyphenyl)phosphonium chloride have been described previously.²⁹

Product Ratio Studies. These were carried out essentially in the same manner as described previously.⁵ The GC analyses were carried out on a Varian Aerograph Model 1200-1 flame ionization gas chromatograph using a 6 ft \times $\frac{1}{8}$ in. o.d. stainless steel column packed with 15% w/w tritolyol phosphate on Chromosorb P of unspecified mesh. Helium was used as the carrier gas, and the chromatograph was connected to a variable speed strip chart recorder having chart speeds as high as 8 in./min. The column oven temperature was 83 °C (isothermal), the injector port temperature was 162 °C, and the detector temperature was 217 °C. The helium flow rate was 32.2 mL/min, the hydrogen flow rate was 33.4 mL/min, and the air flow rate was 321 mL/min. The air flow rate was determined by means of a 100-mL soap-bubble flowmeter fabricated by the University of Massachusetts Glass Shop according to the design of La Hue et al.,⁴¹ while the other flow rates were determined with a 20-mL soap-bubble flowmeter. All flow rates are uncorrected. A sample size of 1 μL was used for all injections. Peak areas were determined by multiplying the peak height by the peak width at half the peak height. A reticle was used to measure the peak widths. Peak area measurements were based on the average of three to five sample injections.

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A Study of Superoxide Reactivity. Reaction of Potassium Superoxide with Alkyl Halides and Tosylates

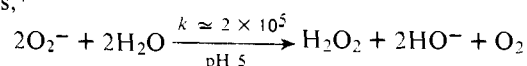
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Abstract: The reaction of superoxide with a representative series of alkyl halides and tosylates in Me_2SO and benzene has been shown to proceed by a pathway involving an initial $\text{S}_{\text{N}}2$ displacement leading to alkylperoxy radicals which, in a subsequent one-electron reduction, are converted to peroxy anions. Processes involving the self-reaction of peroxy radicals play at most a very minor role in product determination. In most instances, the initially isolable principal product is the dialkyl peroxide which, in a subsequent, base-induced reaction(s), is converted into alkoxide. Product studies reveal that a number of factors can influence product ratios, including reactant ratios, the nature of the leaving groups, reaction time, reactant concentration, and workup conditions.

In recent years superoxide (O_2^-), the one-electron reduction product of molecular oxygen, has become the subject of considerable chemical and biological interest and investigation.¹ Much of the current interest about superoxide centers around its production and reactions in biological systems and in particular its role in certain biological oxidations.² There are a number of early (pre-1975) reports describing the chemical reactivity of superoxide;³ however, much of the basic chemistry of superoxide remains ill defined. The work reported here details one avenue of an investigation we have pursued, designed to explore, elucidate, and define the chemical reactivity of superoxide.

Superoxide disproportionates rapidly in aqueous solutions,⁴



complicating the study and interpretation of the reactions of superoxide in protic media. By contrast, superoxide has extended stability in certain aprotic solvents, specifically dimethyl sulfoxide, Me_2SO . For this reason, the studies reported here have been carried out in either dimethyl sulfoxide or benzene. Such studies provide the indirect opportunity to assess the feasibility of superoxide's participation in such reactions when conducted under largely aqueous conditions.