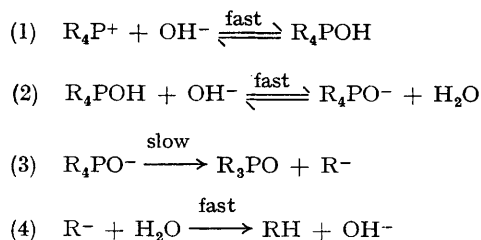# Steric Effects in Phosphonium Salt Formation and in Phosphonium Hydroxide Decomposition Reactions

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IT is reasonably well established[1] that the mechanism of decomposition of quaternary phosphonium hydroxides consists of the following steps:

(1) $\quad R_4P^+ + OH^- \xrightleftharpoons{fast} R_4POH$

(2) $\quad R_4POH + OH^- \xrightleftharpoons{fast} R_4PO^- + H_2O$

(3) $\quad R_4PO^- \xrightarrow{slow} R_3PO + R^-$

(4) $\quad R^- + H_2O \xrightarrow{fast} RH + OH^-$

In view of theoretical calculations carried out by Aksnes and co-workers[2] which led them to conclude that steric effects would prove to be of no major importance in determining the relative rates of decomposition of quaternary phosphonium hydroxides, it seemed of importance to test this conclusion experimentally. Accordingly, the kinetics of reaction of a series of *o*- and *p*-tolylphosphonium chlorides with sodium hydroxide was studied. The results are summarized in Table 1.

of reaction are observed can be attributed to a cancellation of effects. In the first step of the reaction, addition of hydroxide ion to the phosphonium cation to form the intermediate in which the phosphorus atom is quinquecovalent, and in which the geometry of the intermediate is very probably that of a trigonal bipyramid, there is relief of *B*-strain as the bond angles between the groups which eventually form the basal plane increase from 109° to 120°. Thus, the argument can be made that, owing to the greater relief of *B*-strain, the concentration of the intermediate in which phosphorus is quinquecovalent would be greater in the case of the *o*-tolylphosphorus systems than in the case of the *p*-tolylphosphorus systems. Consequently, the concentration of the conjugate base of the *o*-tolylphosphorus quinquecovalent intermediate would also be greater than that of the conjugate base of the *p*-tolylphosphorus quinquecovalent intermediate. However, the rate-determining step is the collapse of the conjugate base to the phosphine oxide and the carbanion. In this step, the phosphorus atom is undergoing change from the less sterically hindered trigonal bipyramidal back to the more crowded tetra-

TABLE 1

Reaction of quaternary phosphonium chlorides with sodium hydroxide in 50% *aqueous dioxan containing* 0·4 N-*sodium chloride at* 31·0°; [R_4P^+] = [OH^-] = 0·017—0·019

Phosphonium chloride				k_3 (l.²mole⁻²min.⁻¹)	k_p/k_o
Triphenylbenzyl	..	..	..	66·55 ± 0·35	
Diphenyl-*p*-tolylbenzyl	..	..	..	25·20 ± 0·20	2·60
Diphenyl-*o*-tolylbenzyl	..	..	..	9·68 ± 0·26	
Phenyldi-(*p*-tolyl)benzyl	..	..	..	3·70 ± 0·03	2·65
Phenyldi-(*o*-tolyl)benzyl	..	..	..	1·40 ± 0·04	
Tris-(*p*-tolyl)benzyl	..	..	..	0·94 ± 0·05	2·18
Tris-(*o*-tolyl)benzyl	..	..	..	0·429 ± 0·003	

It can be seen from the data that there is only a 2·2—2·6-fold difference between the rates of reaction of the *para*-substituted as against the *ortho*-substituted phosphonium salts in each of the related pairs of reactions. These small rate differences cannot be explained adequately in terms of steric effects alone, as steric effects usually produce variations in rate of a much larger magnitude. These results indicate the operation principally of an inductive effect in this reaction.

The fact that no major steric influences on rate

hedral form. The increased steric interaction caused by this change in geometry increases the energy of the transition state. It then follows that whatever rate enhancement through favourable concentration effects is gained from the prior equilibria (steps 1 and 2) for the *o*-tolylphosphorus systems is lost in the rate-determining reaction (step 3).

The role of steric effects in the reaction of triarylphosphines with benzyl chloride in benzene–methanol solution has also been evaluated. The results are summarized in Table 2. The fact

Table 2

Reactions of triarylphosphines with benzyl chloride in benzene–methanol (3:2 *by volume*) *at* 31·0°;
[PhCH$_2$Cl] = [Ar$_3$P] *and* [PhCH$_2$Cl] = 2[Ar$_3$P]

Phosphine				$k_2 \times 10^{-2}$ (l. mole^{-1} hr.$^{-1}$)	Rel. rate
Triphenylphosphine	..	..	..	..	7·22 ± 0·12	1·0
Tri-*p*-tolylphosphine	..	..	..	..	32·80 ± 0·86	4·5
Tri-*o*-tolylphosphine	..	..	..	..	0·333 ± 0·004	0·046

that the rate of reaction of tri-*p*-tolylphosphine with benzyl chloride is greater than that of triphenylphosphine is in agreement with expectations and with the observations of Davies and co-workers[3] that the presence of an electron-donating substituent increases the nucleophilic reactivity of the phosphine. On the other hand, the decidedly lower rate in the case of tri-*o*-tolylphosphine, in spite of the somewhat greater inductive effect of the methyl groups in the *ortho*-position, can be attributed to the steric interference of the methyl groups of the phosphine with the phenyl group and the methylene hydrogen atoms of the benzyl chloride in the transition state for the typical S_N2 reaction.

Satisfactory elemental analyses were obtained for all new compounds. The products of each reaction were isolated and identified. The kinetics of the phosphonium hydroxide decomposition reactions was determined as described previously,[1c] and all of the reactions followed the third-order kinetic law as required by the mechanism. The Mohr method of chloride analysis was used to follow the rate of reaction of the triarylphosphines with benzyl chloride. In some experiments the concentration of benzyl chloride equalled that of triarylphosphine and in other experiments the concentration of benzyl chloride was twice that of the phosphine. All of these reactions followed the second-order kinetic law.

(*Received, August 25th,* 1966; *Com.* 628.)

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