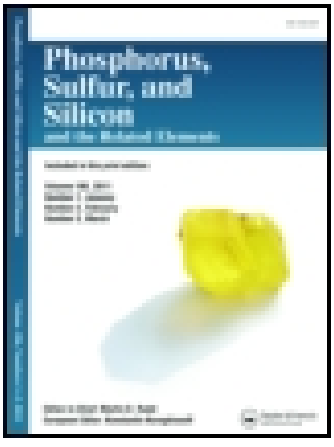

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SOLVOLYSIS OF PHOSPHONIUM COMPOUNDS CONTAINING A THIOPHENOXY GROUP LINKED TO PHOSPHORUS

Gunnar Aksnes [a]
[a] Department of Chemistry , University of Bergen , Allegt. 41, N-5007, Bergen, Norway
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SOLVOLYSIS OF PHOSPHONIUM COMPOUNDS CONTAINING A THIOPHENOXY GROUP LINKED TO PHOSPHORUS

GUNNAR AKSNES

Department of Chemistry, University of Bergen, Allegt. 41, N-5007 Bergen, Norway

Dedicated to Professor John G. Verkade on the occasion of his 60th birthday

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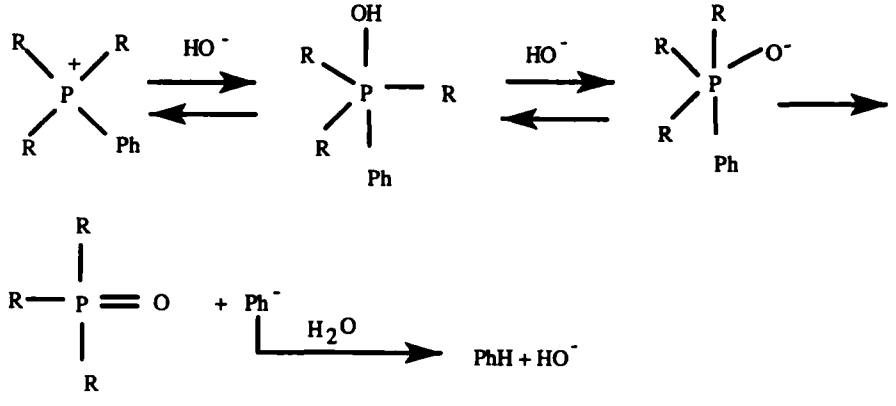
A kinetic study of the solvolysis of six alkylphenyl thiophenoxyphosphonium chlorides in 50% water/methanol is reported. The rates of solvolysis, where thiophenol and phosphine oxides are formed, are little influenced by the substituents linked to phosphorus. The present findings are in sharp contrast to the 10^4 higher rate of the alkaline decomposition of tetraphenyl as compared to trialkylphenyl phosphonium salts, where phenyl is the leaving group. Further, the rate of solvolysis of the cyclic phenyl thiophenoxyphospholanium salt, is nearly identical to the rate of the corresponding dialkylphenyl thiophenoxyphosphonium compound. Calculation of the activation parameters of the solvolysis of thiophenoxyphosphonium compounds shows that the underlying reaction forces, expressed as activation energies and entropies, are strongly influenced by the substituents. The results suggest that the thiophenoxy group is expelled from the pentacovalent, trigonal bipyramidal reaction intermediate, before pseudorotation of the substituents linked to phosphorus takes place.

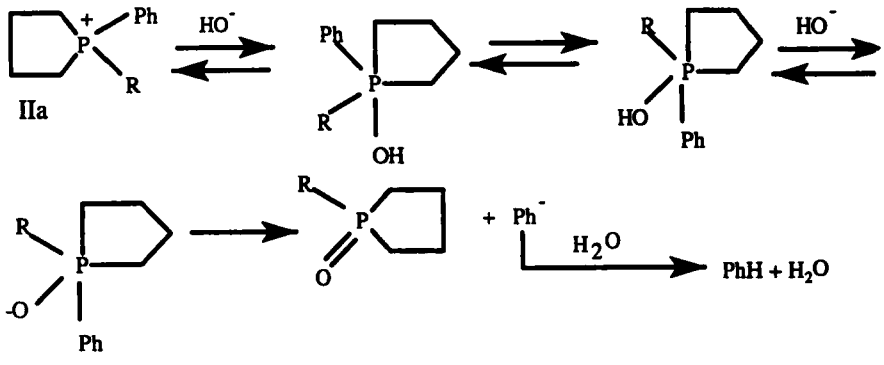
Key words: Alkylphenyl thiophenoxyphosphonium chlorides, solvolysis, activation parameters.

The alkaline decomposition of aliphatic and aromatic phosphonium cations is generally assumed to proceed through pentacovalent phosphorus intermediates. The third order kinetics correspond with rate determining P—C splitting of a phosphorane anion, with the leaving group in an axial position[1–3] (Scheme 1).

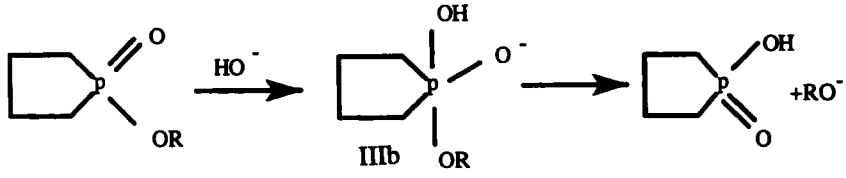
According to the conformational preferences regarding the positioning of ligands



Scheme 1



Scheme 2



Scheme 3

in a trigonal bipyramidal framework, the following rules have been found to influence the formation of product isomers, and the reaction rates[4]:

1. The most electronegative ligands preferentially occupy axial sites.
2. Four- and five-membered cyclic systems preferentially span axial-equatorial positions.
3. Steric effects are minimized by locating bulky groups in equatorial positions.
4. The axial bonds are weaker, and the leaving group is therefore preferentially lost from one of these positions.

Phenyl substituted phosphonium compounds containing a five-membered phospholane ring (**IIa**), decompose 10^3 times faster than corresponding six-membered ring analogues.[3,5] According to the preference rule 2 prior, this means that the five-membered phospholane ring spans axial-equatorial positions, with the incoming hydroxyl group occupying the second axial position. An X-ray study of a phospholane compound at our institute[6] showed that the C—P—C angle in the ring was approximately 95°, indicating that the axial-equatorial placement of the ring in trigonal bipyramids is practically without ring strain. Pseudo-rotation of the substituents, bringing the leaving phenyl group into the weaker axial bonding position, and the hydroxyl group into equatorial position, where deprotonation is easier, is assumed to take place prior to the rate determining expulsion of the phenyl group (Scheme 2).

On the other hand, the rates of the alkaline hydrolysis of phosphinic esters, containing five- and six-membered rings, are of comparable magnitude.[7] During formation of the bipyramidal intermediate, two strong electronegative groups (OR and

OH), preferring axial positions, are present, which forces the five-membered ring to accept equatorial placement. Presumably the OR group is expelled from the pentacovalent intermediate (**IIIb**) before pseudo-rotation takes place. The kinetics of the hydrolysis is accordingly of second order (Scheme 3).

The energy barrier of the rate determining P—C splitting in the alkaline decomposition of alkyl phenyl phosphonium cations (Scheme 1) is assumed to be so high that the preceding steps reach equilibrium. The observed, overall rate constant, includes therefore the equilibrium constants of the preceding steps, resulting in third order kinetics, first order in the concentration of phosphonium ions, and second order in hydroxyl ions.

When a better leaving group than phenyl is linked to phosphorus in the phosphonium cation, as the *p*-nitrobenzyl group, the kinetics of the alkaline decomposition are no longer of third order.[8] The displacement of the *p*-nitrobenzyl group is, however, not strictly comparable to the displacement of phenyl, due to accompanying ylid formation.

In the present work we have studied the rates of displacement of the weakly bonded thiophenoxy group in various alkylphenyl thiophenoxyphosphonium salts. The decompositions in water/methanol constitute clean solvolytic reactions, where thiophenol and phosphine oxides are the only reaction products.

EXPERIMENTAL

Syntheses

The thiophenoxy phosphonium chlorides used in the present kinetic study were synthesized from the respective phosphines and phenyl sulfenyl chloride. The different alkyl phenyl phosphines, and phenyl sulfenyl chloride were prepared according to descriptions in the literature.[9-13] The reagents were distilled until analytically pure products were obtained.

General Procedure

To a solution of analytically pure phosphine (0.03 M) in 200 ml sodium-dried, freshly distilled ether, was added dropwise, under nitrogen and vigorous stirring. 0.03 M analytically pure phenyl sulfenyl chloride, dissolved in 150 ml sodium-dried ether. When analytically pure reagents and solvent were used, the thiophenoxy phosphonium chloride was obtained in pure, crystalline form, and further purification was unnecessary. The hygroscopic product was filtered under dry nitrogen, directly from the reaction flask onto a glass filter. After washing with dry ether, the purity of the product was confirmed by analysis of chlorine content. Anal. Calc. for $Et_3P^+SPhCl^-$; Cl, 13.4. Found, 13.5; $Et_2PhP^+SPhCl^-$, Cl, 11.7. Found, 11.4; $EtPh_2P^+SPhCl^-$, Cl, 10.6, Found, 10.6; $Ph_3P^+SPhCl^-$, Cl, 9.0. Found, 8.8; $Ph(CH_2)_4P^+SPhCl^-$, Cl, 11.8. Found, 11.4; $Ph(CH_2)_5P^+SPhCl^-$, Cl, 11.3, Found, 11.0. Proton-NMR spectra were also recorded, and found in accordance with the molecular structures. The NMR-spectrum of $Et_3P^+SPhCl^-$ in chloromethane is shown as example in Figure 2.

Kinetic Measurements

The rate of solvolysis of the thiophenoxy phosphonium chlorides was followed by measuring the change in the UV spectra in the region 238–274 nm, in 50% water/methanol mixture, buffered with 0.1 M sodium acetate. In Table I are summarized the data of the six compounds studied: Absorption maxima in UV, concentration of reactants, rates, and activation parameters. Since the reaction rates were pseudo first order, the rates were evaluated using the method of Guggenheim, thus avoiding the use of the original starting concentrations of the hygroscopic, and easily hydrolyzed compounds.

RESULTS AND DISCUSSION

The Guggenheim plot in Figure 1 shows that the rate of solvolysis of thiophenoxy substituted phosphonium compounds exhibits pseudo first order kinetics. At the low concentration of phosphonium chloride used (approximately 10^{-3} M), complete ion-

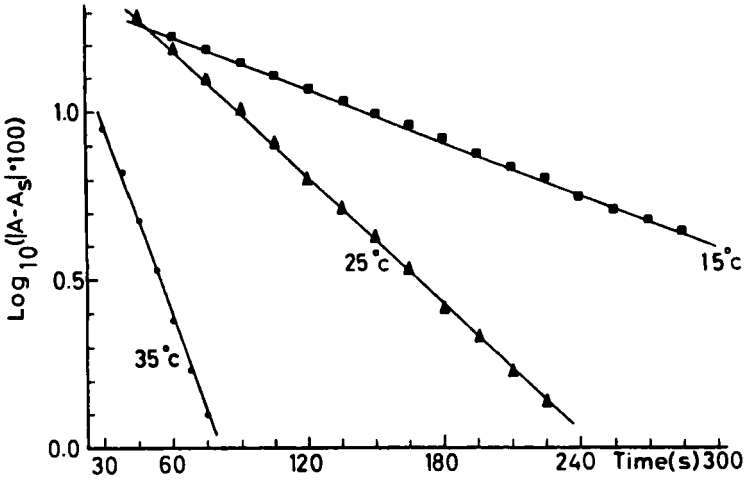


FIGURE 1 Pseudo first order rates of the solvolysis of triethyl thiophenoxyphosphonium chloride in 50% water/methanol, at 15, 25, and 35°C.

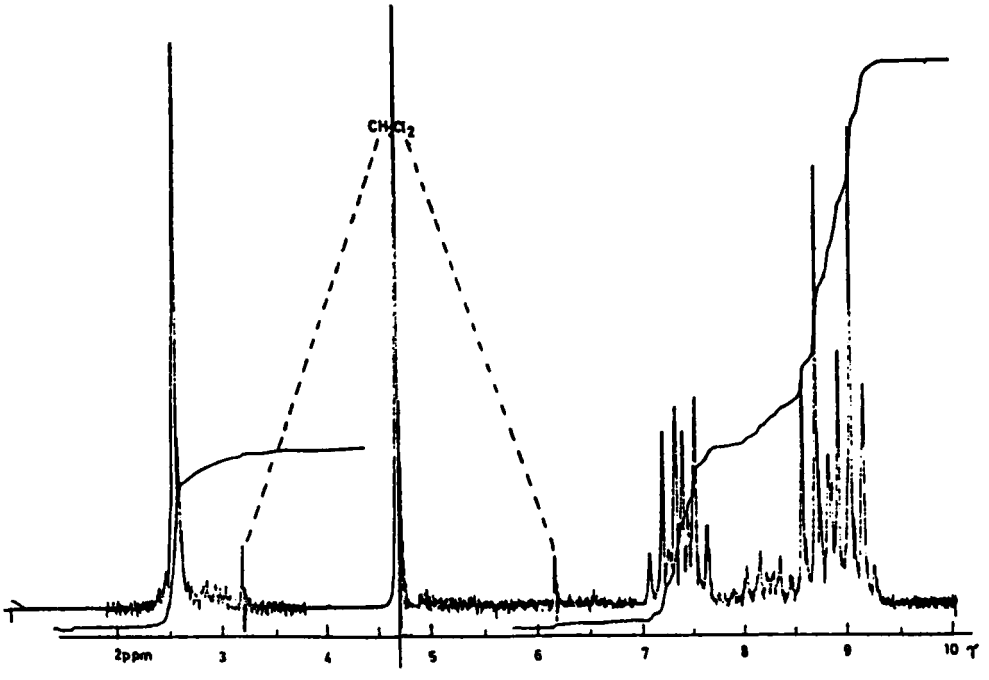
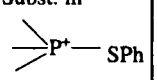
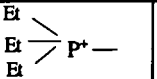
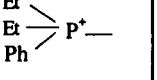
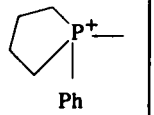
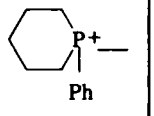
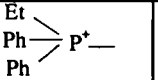
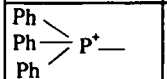


FIGURE 2 NMR-spectrum (60 MHz) of $Et_3P^+SPhCl^-$ in chloromethane (CH_2Cl_2).

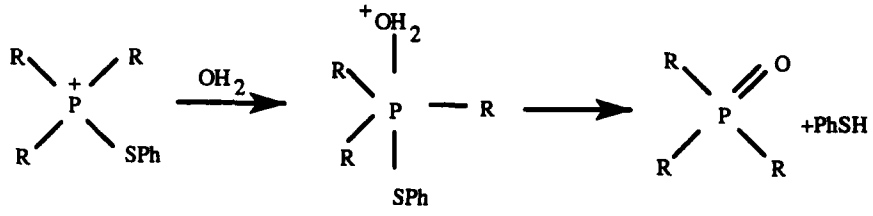
TABLE I

Solvolysis of various alkylphenyl thiophenoxyphosphonium chlorides in 50 volume % water/methanol

Subst. in 	UV max. nm react.	React. conc. M/l	Rate constant, k x 10^3 s^{-1} 7,5°C	15°C	20°C	25°C	35°C	Activation parameters E_a cal/M	ΔS^* e.u.
	238	$8x10^{-4}$	-	5,90	-	16,0	42,6	17.5	-10.1
	265 271.5	$2.5x10^{-3}$	6.27	12.5	20.5	34.0	-	16.0	-13.6
	266 271,5	$1.8x10^{-3}$	11.7	24.2	38.8	-	-	15.6	-13.8
	265 272.5	$2.0x10^{-3}$	-	1.15	-	2.85	-	15.5	-15.7
	265 272	$1.7x10^{-3}$	10.2	19.2	25.5	35.9	-	11.7	-27.8
	267.5 274	$1.4x10^{-3}$	-	11.2	13.1	15.4	20.5	5.7	-49.6

ization of the salt is expected. This is also supported by the absence of the common ion effect. Thus, when the 0.1 M sodium acetate buffer normally used, was diluted to 0.05 M, and 0.05 M NaCl is added, in order to keep the ionic strength constant, the 0.05 M common ions (Cl^-) resulted in only 3% decrease in the rate of solvolysis of triethyl thiophenoxy phosphonium chloride. The effect of pH was also relatively small, as shown by the following rate data (in s^{-1}): Et_3P^+SPh: 0.018, 0.016, and 0.01, at pH 4.14, 4.70, and 10.2, respectively; and for Ph_3P^+SPh: 0.022, 0.016, and 0.008, at the same pH. The rate decrease with increasing pH rules out any participation of hydroxyl ions in the solvolysis. Since different buffers are used to obtain the pH-values, somewhat different effects on the rate of solvolysis are understandable.

The observed kinetics are in accord with rate Scheme 4. The rate determining step is assumed to be the formation of an unstable, trigonal bipyramidal intermediate, or an $S_N2(P)$ transition state, where the two most electronegative groups, the thiophenoxy group and water, occupy the axial positions. The intermediate is believed to decompose before pseudo-rotation can take place. This means that an intermediate, where the five-membered phospholane ring occupies axial and equatorial positions, must have the leaving thiophenoxy group in the equatorial position, and the displacement of the leaving group cannot benefit by apical attack of the water opposite



Scheme 4

the leaving group. Thus, the situation will be similar to the hydrolysis of phosphinate esters (Scheme 3).

The rate data in Table I might at first glance give the impression that the solvolysis of alkyl phenyl thiophenoxyphosponium compounds is little influenced by the P-substituents. However, rate measurements at different temperatures reveal that the activation parameters are very different. Thus, from the triethyl to the triphenyl substituted compounds the decrease of activation energy is 12 kcal/M, but the low activation energy is almost balanced by a 40 e.u. more negative activation entropy. The activation entropy is little influenced by the different substituents as long as only one phenyl group is linked to phosphorus. Introducing of two phenyl groups results in a strong negative drop of entropy, and even more for three phenyl groups. Models show that more than one P-phenyl group gives rise to steric hindrance and reduced accessibility of water during the solvolysis, thus reducing the probability of reaction.

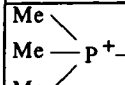
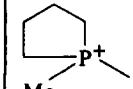
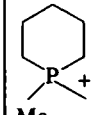
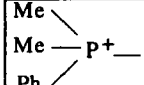
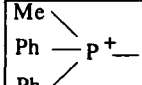
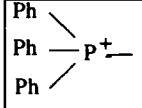
For comparison, the rates and activation parameters of the alkaline decomposition of alkyl phenyl phosphonium compounds are recorded in Table II. Whereas the rates differ only around 20 times in the solvolysis of different alkylphenyl thiophenoxyphosphonium compounds, the alkaline decomposition of the corresponding phosphonium compounds, where phenyl is the leaving group, exhibit 10^4 times rate differences. The entropy of activation in the solvolysis of the thiophenoxy group is negative for all substituents, a phenomenon which is typical for bimolecular reactions (Scheme 4). The displacement of phenyl in the alkaline decomposition of phosphonium salts (Scheme 1) is preceded by several equilibrium steps before the rate determining step, each of which contributes to the activation energy and entropy of the overall reaction. Thus, the first step, the reaction between opposite charged ions, as well as the rate determining monomolecular decomposition step of the phosphorane anion, contribute both to a positive overall entropy of 30–40 e.u. which is necessary to overcome the 30–40 kcal/M overall activation energy.

The "phospholane effect," the 10^3 times higher rate of alkaline decomposition of the cyclic phospholanium compound, is characterized by having 15 e.u. more positive entropy, compared with the corresponding six-membered ring derivative (Table II). In the solvolysis of the corresponding thiophenoxy substituted phosphonium compounds, which show little rate increase, the activation entropy is of comparable magnitude.

The present study shows that displacement reactions in phosphonium compounds are sensitive to P-substituents, in spite of the fact that substituent effects do not always give rise to strong rate differences. Therefore, discussion of substituent effects

TABLE II

Alkaline decomposition of alkyl phenylphosphonium bromide

Substituents in $\gtrless P^+ - Ph$	Rate constant, 80° C. k, $l^{-2}M^{-2}s^{-1}x10^{-2}$	Activation parameters $E_a$kcal/M	ΔS*e.u.
	3.95	35	+32
	8750	38	+55
	4.42	32	+40
	333	32	+37
	4330	31	+34
	36700	29	+33

on the basis of rate data obtained at one temperature only, might be deceitful, and can, as the rate data of the thiophenoxy substituted phosphonium compounds show, give an incorrect view of underlying reaction forces.

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