$$k_{\text{uni}} = \frac{Q_1{}^\dagger}{hQ_1Q_2}\exp(-E_0/RT)\Delta E^\dagger \sum_{i=1}^{i_{\max}} \frac{G(E^\dagger)\exp(-E^\dagger/RT)}{1 + \left(\frac{Q_1{}^\dagger}{Q_1}\right)k(E^*)/fk_s[\text{M}]} \tag{6}$$

and eq 8b should read

$$E^* = E_0 + E^\dagger \tag{8b}$$

The above corrections apply only to the equations stated in the paper. The correct equations were used in the actual calculations. (b) For additional discussion of the amine association reactions, see P. V. Neilson, M. T. Bowers, M. Chau, W. R. Davidson, and D. H. Aue, *J. Am. Chem. Soc.*, **100,** 3649 (1978). (c) W. N. Olmstead and J. I. Brauman, *ibid.*, **99,** 4219 (1977). (d) O. I. Asubiojo and J. I. Brauman, *ibid.*, in press.

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Mechanism of Base-Promoted Phosphonium Salt Hydrolyses. Kinetics and Multiple Substituent Effects for a Nucleophilic Attack at Phosphorus

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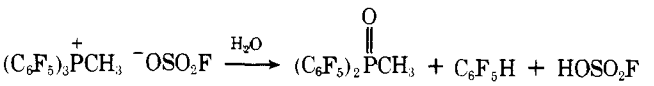
Abstract: Hammett analysis of substituent effects on the kinetics of the hydroxide-promoted conversion of phosphonium salts ($R_4P^+X^-$) into phosphine oxides (R_3PO) and hydrocarbons (RH) supports a mechanism with a transition state that varies along the path for each class of R groups studied. An intermediate hydroxyphosphorus adduct (R_4P-OH) that was originally proposed by Ingold is supported by kinetic and pH measurements. A kinetic analysis is offered to clarify previous mechanistic proposals. The hydrolytic lability of a new, reactive methyltris(perfluorophenyl)phosphonium salt is described.

Introduction

Reported herein are mechanistic interpretations of results from analysis of multiple substituent effects on the kinetics of hydrolysis of quaternary phosphonium salts in aqueous methanolic solutions. Studies concerning the effects of substituents on phosphorus ylides in Wittig reactions have led us to the observation that methyltris(pentafluorophenyl)phosphonium fluorosulfonate is hydrolytically extremely labile. Cleavage of this quaternary phosphonium salt to methylbis(pentafluorophenyl)phosphine oxide and pentafluorobenzene occurs at room temperature with the addition of just 1 equiv of water. In comparison, alkyltriphenylphosphonium salts are stable in aqueous solutions, as exemplified by benzyltriphenylphosphonium bromide, which may in fact be recrystallized from water.[2] The conditions normally required for the hydrolysis of these salts are added base and/or elevated temperatures.[3]



$$(C_6F_5)_3\overset{+}{P}CH_3\ {}^{-}OSO_2F \xrightarrow{H_2O} (C_6F_5)_2\overset{\overset{\displaystyle O}{\|}}{P}CH_3 + C_6F_5H + HOSO_2F$$

In 1929, Marvel and Ingold[2] separately published the first mechanistic suggestions for the formation of phosphine oxides and hydrocarbons from phosphorus ylides and water, or quaternary phosphonium salts and aqueous base, respectively. Ingold's detailed mechanism, in which initial hydroxide attack at the phosphorus was originally purported to be rate limiting (step 1), is given in Scheme I. Since this original mechanism was proposed, several other related mechanisms have been suggested and reviewed.[3-7] Results largely from the work of McEwen and VanderWerf,[6] Allen,[7] and Hoffmann[4a] have led to the current belief that the mechanism for alkaline hydrolysis

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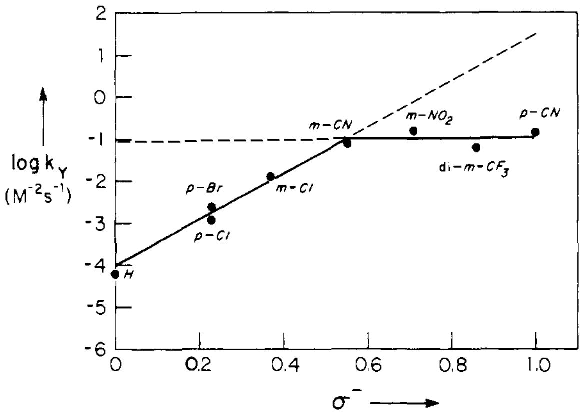


Figure 1. Graph of log k_Y vs. σ^- for Y substituents in the hydrolysis of Y-benzyltriphenylphosphonium bromides (X = H). The ρ values for the solid lines are +5.6 and +0.4.

Table I. Summary of Kinetic Data

X substituent	$3\sigma^{a,b}$	log k_X (Y = *p*-nitro)^{c,d}	log k_X (Y = *m*-nitro)^{e,f}
p-methoxy	−0.81	−2.85	
p-*tert*-butyl	−0.60	−1.99	
p-methyl	−0.51	−2.37	
m-methyl	−0.21	−1.51	−1.98
H	0.00	−1.21	−0.80
p-fluoro	0.18	−0.15	
m-methoxy	0.36	−0.66	−0.25
p-chloro	0.69	0.58	1.61
m-chloro	1.11	1.26	3.14
p-trifluoromethyl	1.62	2.53	4.99

[a] Sum of Hammett σ values for X substituents. [b] Reference 11. [c] ρ = 2.2. [d] k_X is an overall second-order rate constant, first order in hydroxide. [e] ρ = 3.8. [f] k_X is an overall third-order rate constant, second order in hydroxide.

of phosphonium salts consists of those steps shown in Scheme I with rate-limiting carbanion expulsion (step 3). However, the aggregate collection of data presently available in the literature is not consistent with just this single mechanism having only one rate-limiting step, in that either second- or third-order kinetics may be observed for phosphonium salts with similar structures. Our results now demonstrate that the rate-determining step is variable and the *overall* transition state may more resemble the intermediates shown in steps 2 or 3 of Scheme I, depending upon the ability of the leaving group to stabilize an incipient negative charge on carbon and the ability of the remaining groups to stabilize an octet-expanded phosphorus.

Scheme I

$$R_4P^+ + {}^-OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_4P{-}OH \qquad (1)$$

$$R_4P{-}OH + {}^-OH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_4P{-}O^- + H_2O \qquad (2)$$

$$R_4P{-}O^- \xrightarrow{k_3} R_3P{=}O + R^- \qquad (3)$$

$$R^- + H_2O \overset{\text{fast}}{\rightleftharpoons} RH + {}^-OH \qquad (4)$$

Results

Solutions of meta- and para-substituted benzyltriphenylphosphonium bromides in basic 50% (v/v) aqueous methanol produced X-substituted triphenylphosphine oxides and Y-substituted toluenes at room temperature, as shown. The pH of each solution was adjusted by adding potassium hydroxide to a KH_2PO_4 buffer. The pH was measured with a conventional glass electrode calibrated with aqueous solutions. Relative pH values should be reliable, although highly accurate absolute values would be unknown.[8]

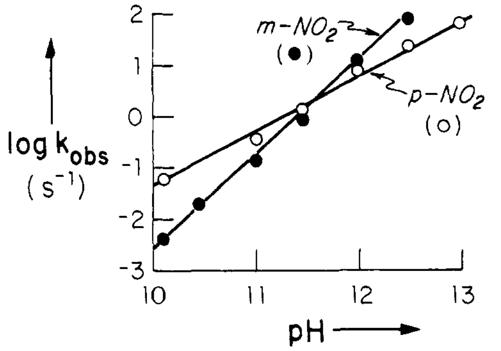
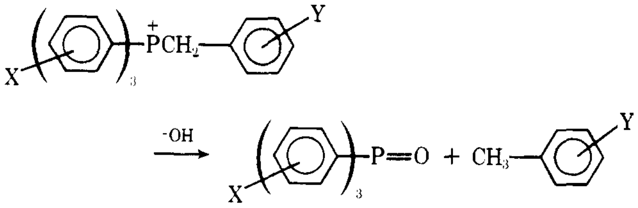


Figure 2. Graph of log k_{obsd} vs. pH for *m*- (●) and *p*- (○) nitrobenzyltris(*p*-trifluoromethylphenyl)phosphonium bromide hydrolyses.



Hydrolysis rates were measured for a series of compounds with fixed X and variable Y substituents. With the exception of the compounds in which Y was *p*-nitro, all reactions were second order in hydroxide, first order in substrate, and third order overall. A Hammett analysis in which σ^- for substituents on the benzyl group (Y) are graphed against log k_Y, where k_Y is the third-order rate constant, rendered the nonlinear correlation shown in Figure 1. For weakly electron-withdrawing substituents, ρ has the value of +5.6, whereas for more strongly electron-withdrawing substituents ρ is more than an order of magnitude smaller, +0.4. No significant buffer catalysis or ionic strength effects were observed up to 0.1 M in electrolyte concentration.

If Y were *m*-nitro and X were varied (data in Table I), a good linear free energy correlation (r = 0.99) is obtained from graphs of log k_X vs. 3σ for the X substituents. Similarly, σ correlates well (r = 0.99) with log k_X for the hydrolysis of derivatives in which Y is *p*-nitro and X is variable (data in Table I). In the case where Y is *m*-nitro, k_X is a third-order rate constant as before (second order in hydroxide and first order in substrate). However, if Y is *p*-nitro, then overall second-order kinetics are observed (first order in both hydroxide and substrate). Of the derivatives studied, the *p*-nitrobenzylphosphonium salts all uniquely exhibited second-order kinetics in this alkaline cleavage reaction.

From these Hammett plots using 3σ for the abscissa, the ρ values, which were determined from several sets of experiments in which X was variable, while Y remained constant for a series of several Y substituents, clustered into two groups. Reactions that are second order in hydroxide (Y is weakly or moderately electron withdrawing, *m*-NO_2, *m*-CN, *p*-CN) all have ρ values of 3.7 ± 0.1; if Y is the strongly electron-withdrawing *p*-nitro group, derivatives which exhibit first-order kinetics with respect to hydroxide, then ρ has a smaller value of 2.2 ± 0.1.

Results from stopped-flow kinetics experiments in which the hydrolysis rates of both *p*- and *m*-nitrobenzyltris(*p*-trifluoromethylphenyl)phosphonium bromides (X = *m*- or *p*-NO_2; Y = *p*-CF_3) are compared as a function of pH over the range

10–13 revealed no apparent deviations from the respective first- and second-order kinetics with respect to hydroxide. As shown in Figure 2, the slopes of log k_{obsd} vs. pH are 1.1 ± 0.1 (r = 0.998) and 1.8 ± 0.2 (r = 0.999), respectively. At pHs below 11.6 the observed pseudo-first-order rate constant, k_{obsd}, is greater for the p-nitro derivative than for the m-nitro derivative. Above pH 11.6 hydrolysis of the m-nitro substrate is faster.

The mixing of neutral methanolic solutions of the p-nitrobenzylphosphonium salt with solutions of buffer in this pH range produces a transient red solution (λ_{max} 535 nm), characteristic of ylide formation. The rates of ylide depletion and product formation at a given pH are the same within experimental error. In preparative-scale reactions, stable ylides precipitated from the mixture of base and p-nitrobenzylphosphonium salts in this pH range.[3,9] No color is visible for the m-nitro analogue.

Experiments to identify and characterize a neutral pentacoordinate phosphorus intermediate of the general structure R_4POH (a pseudobase adduct of the quaternary phosphonium salt) have been carried out. Under no circumstances was a stable compound isolated.[10] However, titration of 0.01 M p-methoxybenzyltris(p-trifluoromethylphenyl)phosphonium bromide in aqueous methanol with potassium hydroxide gave an inflection at pH 11.0 ± 0.5, suggesting a pK_a at that value. The uncertainty in the pK for pseudobase formation (no visible color correlatable with ylide formation could be observed) is a consequence of pH drift due to hydroxide consumption from hydrolysis.

Discussion

The nonlinear Hammett relation[11] shown in Figure 1 may be dissected into two linear portions. For weak electron-withdrawing Y groups the ρ value for the slope (+5.6) is in agreement with that for the hydrolysis of substituted benzylphenylphosphonium salts in 25% aqueous 2-propanol (+4.6)[4a] and in 50% aqueous 1,2-dimethoxyethane (+3.6),[6a] and, as well, with those for other known base-promoted reactions (ρ values of +4 to +5) in which benzylic carbanions in hydroxylic solvents are proposed as intermediates.[12-14] Thus, the transition state for these phosphonium salt hydrolysis reactions likely occurs in step 3 of the mechanism outlined in Scheme I, where a carbanion is generated. Consistent with this postulate is the fact that second-order kinetics, with respect to hydroxide, are observed for these reactions. Two equivalents of hydroxide is consumed in the prior equilibrium steps, 1 and 2. Based on pK_a estimates for weakly stabilized benzylic carbanions (between 35 and 45 in Me_2SO)[12] and the strength of carbon–phosphorus bonds, the Y-substituted toluene anions should be relatively poor leaving groups. Thus, it is not unexpected that the step in which they are formed is rate limiting. Concomitant with carbanion formation and cleavage of the phosphorus–carbon bond is the development of a new stable phosphorus–oxygen bond in the product phosphine oxide. Thus, the spontaneity associated with the formation of the phosphorus–oxygen double bond provides the driving force for carbanion expulsion.

An increase in the electron-withdrawing ability of the Y substituents decreases the pK_a of the toluene products.[12] These more stable carbanions are certainly better leaving groups. Thus, the observed decrease in ρ (from 5.5 to 0.4) would reflect the increased relative ease for departure of the toluene anions.[11] The overall transition state, then, has shifted to a structure that more resembles the conjugate base (R_4PO^-) of the proposed pentacoordinate hydroxyphosphorus intermediates than a benzylic carbanion and a phosphine oxide. The insensitivity (ρ = 0.4) of the hydrolysis rates on those Y substituents whose σ^- values are above 0.5 is consistent with such a transition state inasmuch as the inductive effects of the Y groups on oxy-anion stability should be greatly reduced by the insulating methylene group. A transition state structure similar to R_4PO^- is also consistent with the second-order dependence on hydroxide observed for these compounds. Although individually step 1 is likely to be slower than step 2 for the mechanism shown in Scheme I, the highest energy point on the reaction coordinate can occur in step 2. The observed rate constant then reflects an unfavorable equilibrium process (step 1) preceding a proton transfer (step 2).[15] Two hydroxides are required to reach the overall transition state.

The fact that the p-nitrobenzyl derivatives exhibit first-order kinetics with respect to hydroxide initially suggested that the p-nitro substituent caused the overall transition state to shift once again, this time such that step 1 in Scheme I (which would require only one hydroxide) is rate limiting.[5] However, the following argument stands as support of the hypothesis that pseudobase formation, k_1 (step 1), *in the mechanism shown* is not rate limiting for the p-nitro derivatives. In experiments that required stopped-flow kinetic determinations, the rates for hydrolysis of both m- and p-nitrobenzyltris(p-trifluoromethylphenyl)phosphonium bromides were compared over the pH range 10–13. The comparison between m- and p-nitrobenzyl groups was utilized, because both substituents have similar σ values, 0.71 and 0.78, respectively. Thus, relative to the X substituents on the three phenyl groups attached to the central phosphorus, which should have a large effect on k_1, these two similar substituents on the benzyl group may reasonably be assumed[11] to exert a negligible (or at most small) differential influence on the value of k_1 in Scheme I.

As illustrated in Figure 2, graphs of log k_{obsd} vs. pH for the two hydrolysis reactions show no significant deviation from first- and second-order kinetics with respect to hydroxide ion over the pH range investigated.[8] Below pH 11.6, the p-nitro derivative is hydrolyzed more rapidly than the m-nitro species; however, above that pH the inverse applies. If pseudobase formation, as shown in the mechanism in Scheme I, were rate limiting for the p-nitro compound, then the structurally analogous m-nitro phosphonium salt should not hydrolyze faster, as that process (step 1) common to both derivatives would be the upper limit for the overall observed rate constant. Clearly this is not the case. Indeed, if pseudobase formation were rate limiting, then at the pH where the observed pseudo-first-order rate constants intersect (pH 11.6) the m-nitro isomer should have exhibited an inflection point and followed kinetics, first order in hydroxide, at higher pHs. The fact that a crossover occurs with no apparent deviation from the specific kinetic order with respect to hydroxide provides evidence that the p-nitro derivatives undergo alkaline cleavage through a different mechanism subject to a separate kinetic scheme. The present evidence is insufficient to unambiguously identify the new mechanism.[17]

A feature of the phosphonium salt (R_4P^+) hydrolysis reaction, well established in many laboratories,[2-7,18] is that the group most able to accommodate a negative charge subsequent to carbon–phosphorus bond cleavage is the product hydrocarbon (RH) source. Thus, the hydrolytic lability of methyltris(pentafluorophenyl)phosphonium fluorosulfonate is now clear. Relative to p-CF_3 on a phenyl group, which has a σ^+ value of 0.61, the perfluorination of the phenyl group ($C_6F_5^-$) produces a considerably more electron-withdrawing functionality with a estimated σ^+ value of 0.90.[19] Moreover, pentafluorobenzene is comparable in acidity[20] to p-nitrotoluene, which has a pK_a of 20.5 in Me_2SO.[12] The resultant combination of these features may reasonably be expected to produce a reactive salt that would eject a perfluorophenyl anion in preference to a methyl anion. The reactivity of this salt would need be only slightly greater than that of p-nitrobenzyltris(p-trifluoromethylphenyl)phosphonium bromide, which required stopped-flow kinetics to measure reaction rates at the usual pHs, and which exhibited measurable rates (half-lives on the order of minutes) at pHs below 8, to account for its lability.

Further experiments are in progress to measure the enthalpies of reaction for conversion of substituted phosphines into the corresponding phosphine oxides, data which may offer insight into the extent that phosphine oxide bond formation may be coupled to, and provide the driving force for, carbon-phosphorus bond cleavage.

Experimental Section

General. Melting points are uncorrected as determined with a calibrated Thomas-Hoover Unimelt apparatus. UV data were collected from a Coleman/Perkin-Elmer 124 spectrophotometer, thermostated at 25.0 °C. NMR and pH measurements were taken from a Varian HFT-80 spectrometer using Me_4Si as an internal standard, and a London/Radiometer type 26 pH meter equipped with a type GK2320C combination electrode, standardized with calibrated pH 7, 10, and 14 aqueous buffers. Stopped-flow kinetics were carried out on a Durrum-D110 apparatus thermostated at 25.0 °C.

Materials. All compounds, except as noted below, were commercially available or prepared and purified in standard manner following literature procedures.[21] Physical and spectral properties of reaction products agreed with those for known materials. Solvents and salts used for kinetic studies were of high analytical grade and commercially available.

Kinetic Analyses. All measurements were performed in 50% (v/v) aqueous methanol solution buffered with 0.10 M potassium phosphate salts. An aliquot (5 μL) of substrate, dissolved in pure methanol (0.02 M), was added to 1.0 mL of buffer (equilibrated at 25.0 °C) in a semimicro quartz cell to give an initial substrate concentration of 10^{-4} M. Absorbance changes for conversion of phosphonium salts into phosphine oxide and hydrocarbon products were recorded on a strip chart for 5-10 half-lives at an optimal fixed wavelength between 245 and 265 nm. Linear least-squares regression analysis of ln $[(A_\infty - A_t)/(A_\infty - A_0)]$ vs. time (seconds) rendered slopes, equated to the pseudo-first-order rate constants, with correlation coefficients of 0.999 or greater. Error limits of reproducibility for k_{obsd} values were within 5%.

Stopped-flow experiments were carried out by mixing equal volumes of 2×10^{-4} M substrate dissolved in unbuffered 50% aqueous methanol with 0.1 M buffered 50% aqueous methanol. Controls established that substrates were stable in unbuffered solutions. The pH values recorded were those of effluent product solutions. Error limits averaged ±12%.

Methyltris(pentafluorophenyl)phosphonium Salt Hydrolyses. Solutions of the title compound were prepared by heating sealed NMR tubes containing 1 equiv each of tris(pentafluorophenyl)phosphine[21c] and methyl fluorosulfonate in $CDCl_3$ at 100 °C. NMR spectra were recorded over a 16-h period until complete conversion of methyl fluorosulfonate (singlet, δ 4.1) and phosphine (no ^1H NMR signals) into the title compound (doublet × septet, δ 3.7, $J_{HP} = 15$, $J_{HF} = 1.5$ Hz) had been achieved. Addition of 1 equiv of water at room temperature produced, on mixing, an NMR spectrum characteristic of methylbis(pentafluorophenyl)phosphine oxide[22] (doublet × quintet, δ 2.45, $J_{HP} = 15$, $J_{HF} = 2.0$ Hz). Preparative-scale reactions were carried out in an analogous manner, as follows. A solution of tris(pentafluorophenyl)phosphine (2.0 g, 3.8 mmol) and methyl fluorosulfonate (0.25 g, 2.2 mmol) in 30 mL of dry ethylene dichloride was heated in an argon atmosphere at reflux (~120 °C) for 16 h. The reaction mixture was cooled and addition of water, at 0 °C, caused 1.4 g (94%) of a light tan precipitate to form. Recrystallization from aqueous acetic acid produced 1.3 g (87%) of a white solid, methylbis(pentafluorophenyl)phosphine oxide, mp 134-135 °C (lit.[22] 131-133 °C), NMR as previously listed. Distillation of the ethylene dichloride reaction solvent at atmospheric pressure produced 0.5 g (79%) of a clear liquid, pentafluorobenzene, bp 85-88 °C (lit.[23] 86 °C), NMR ($CDCl_3$) δ 7.35 (multiplet).[24]

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