

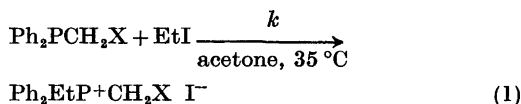
Substituent Effects on Phosphorus Nucleophilicity in Phosphinoacetic Acid Derivatives

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Tertiary phosphines, although generally powerful nucleophiles, vary considerably in reactivity depending on the substituents on phosphorus. Davies and Lewis¹ and later Henderson and Buckler² have measured relative nucleophilicities toward EtI of a series of phosphines and the rate constants have, with limited success, been correlated with Taft σ^* values² or Kabachnik σ^{Ph} values.³ The phosphines examined by Henderson and Buckler contained mostly unsubstituted radicals and, to our knowledge, no quantitative measurements of the influence of substituents in alkyl radicals on the nucleophilicity of phosphines have been published.

One of us has prepared some (cyanomethyl)phosphines, $\text{R}_n\text{P}(\text{CH}_2\text{CN})_{3-n}$, which show very low nucleophilic reactivities towards EtI.^{4,5} This property is conventionally thought to reflect the strong $-I$ effect of the cyano group. In order to obtain more insight in the factors which influence phosphorus nucleophilicity we have measured the nucleophilic reactivity of some diphenylphosphinoacetic acid derivatives towards EtI in acetone (eqn. 1).



$\text{X} = \text{COOH}, \text{COOEt}, \text{CONH}_2, \text{CONMe}_2, \text{CN}$

There is conflicting evidence in the literature concerning the reactivity of these phosphines towards alkyl halides. It is stated that $\text{Ph}_2\text{PCH}_2\text{COOH}$ does not react with MeI, whereas $\text{Ph}_2\text{PCH}_2\text{COOEt}$ does,⁶ and that $\text{Ph}_2\text{PCH}_2\text{CN}$ reacts with EtI.⁴ We have found that all of the above mentioned phosphines react with EtI in acetone, and have determined the rate constants at 35 °C (Table 1). The rate constants do not correlate too well with the $\sum\sigma^*$ values (best least squares fit, $r=0.93$, see Fig. 1), but the trend in nucleophilic reactivity, $\text{Ph}_2\text{PCH}_2\text{CONMe}_2 > \text{Ph}_2\text{PET} \sim \text{Ph}_2\text{PCH}_2\text{CONH}_2 > \text{Ph}_2\text{P} \sim \text{Ph}_2\text{PCH}_2\text{COOH} \sim \text{Ph}_2\text{PCH}_2\text{COOEt} > \text{Ph}_2\text{PCH}_2\text{CN}$, is reasonable if mainly inductive effects are operating. A correlation with Kabachnik's σ^{Ph} substituent coefficients, which contrary to the σ^* values are derived from reactions of phosphorus compounds is not possible because of lack of data for the substituents of interest here.

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Table 1. Rate constants for quaternization,^a Taft σ^* values of substituents, and phosphorus lone-pair ionisation potentials of diphenylphosphinoacetic acid and related phosphines.

| Compound | $k \times 10^5 / \text{l mol}^{-1} \text{s}^{-1}$ | $\sum\sigma^*{}^c$ | I.P. e |
|---|---|--------------------|----------------------|
| $\text{Ph}_2\text{PCH}_2\text{COOH}$ | 4.1 | 2.25 | 8.22 |
| $\text{Ph}_2\text{PCH}_2\text{COOEt}$ | 3.9 | 1.91 | 8.16 |
| $\text{Ph}_2\text{PCH}_2\text{CONH}_2$ | 10.7 | 1.61 ^d | 8.18 |
| $\text{Ph}_2\text{PCH}_2\text{CONMe}_2$ | 17.7 | | 8.05 |
| $\text{Ph}_2\text{PCH}_2\text{CN}$ | 0.40 | 2.91 | 8.44 |
| Ph_2PMe | | 1.20 | 8.05 |
| Ph_2PEt | 11.2 ^b | 1.10 | 7.98 |
| Ph_3P | 3.2 | 1.80 | 7.88 |
| | (3.8 ^b) | | (7.88 ^f) |

^a With EtI in acetone, 35 °C. ^b Ref. 2. ^c $\sigma^* = 0.60$ for Ph, 0.00 for Me, -0.10 for Et, 1.05 for CH_2COOH , 0.71 for CH_2COOEt ,⁹ and 1.71 for CH_2CN .¹⁰ ^d $\sigma^* = 0.41$ for CH_2CONH_2 , calculated from the σ^* given^c and $\text{p}K_{\text{A}}$ -values for $\text{CH}_2(\text{COOH})_2$, $\text{EtOCOCH}_2\text{COOH}$, $\text{H}_2\text{NCOCH}_2\text{COOH}$, and NCCH_2COOH (2.78, 3.35, 3.64 and 2.47, resp.).¹¹ ^e Vertical ionisation potentials, eV. ^f Ref. 12.

Phosphorus lone-pair ionisation potentials (IP) have been suggested⁷ as an alternative measure of the relative nucleophilicity of phosphines. We have measured the vertical IP's of the diphenylphosphinoacetic acid derivatives and of three related phosphines by He(I) photoelectron spectroscopy (Table 1) and correlated the rate constants for quaternization with these IP values (Fig. 2). The best least squares fit ($r=0.91$) excepting triphenyl phosphine which

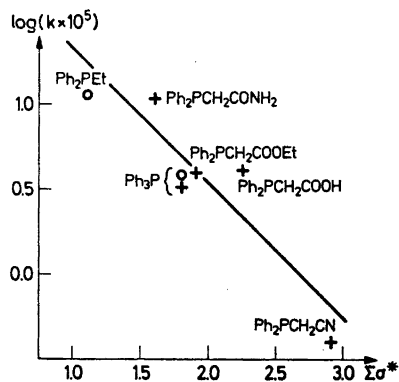


Fig. 1. Plot of rate constant versus Taft σ^* values for the reaction $\text{R}_3\text{P} + \text{EtI} \rightarrow \text{R}_3\text{EtP} + \text{I}^-$, solvent acetone, 35 °C. + = This study, O = Henderson and Buckler.²

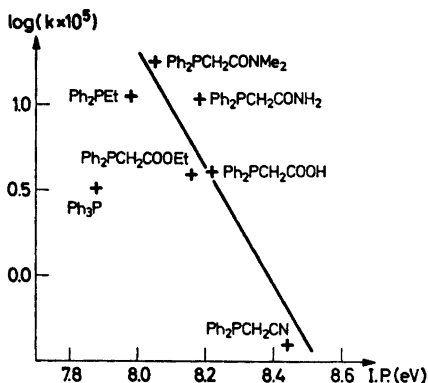


Fig. 2. Plot of rate constant versus lone-pair ionisation potential for the reaction $R_3P + EtI \rightarrow R_3EtP^+ + I^-$, solvent acetone, 35 °C.

does not belong to the series Ph_2PCH_2X is shown in the figure.

While it is obvious that the deviations from linearity do exceed the experimental error it is also evident that IP's as a measure of nucleophilic reactivities of phosphines are not less reliable than the σ^* values. On the other hand a perfect linear correlation between IP's and free energies of activation can hardly be expected. IP's according to Koopmans theorem represent one-electron orbital energies. The latter quantities are related to activation energies through the general perturbation equation for reactions between soft acids and bases.⁸ Even accepting the validity of both relations for the present case the correlation implies two rather crude approximations. IP's are recorded in the gas phase and may change to a varying degree on transfer of the compounds to acetone solution as a result of conformational changes and/or solvation effects. The perturbation treatment neglects the entropy contribution to the free energy of activation and is thus valid only to the extent that this contribution remains constant through the series compared.

In conclusion, we have shown that rate of quaternization does depend on the measured quantity, lone-pair ionisation potential, for the phosphines studied. However, the rather weak correlation indicates that additional factors influence the reaction rates and further data are needed in order to separate these. The present study further shows that a cyanomethyl group is the most potent of the radicals studied with respect to decreasing the nucleophilic reactivity of a tertiary phosphine, and that it exerts its effect largely by increasing the lone-pair ionisation potential of phosphorus.

Experimental. He(I) photoelectron spectra were obtained on a Perkin-Elmer PS 18 spectrometer. Calibrations were performed by measuring the 2P_{3/2} peaks of Ar and Xe present

along with the samples. The phosphines are serious contaminants in the analyzer and therefore the calibration peaks were recorded immediately before and after the phosphine first I.P. in order to minimize spectrum drift. The I.P.'s were reproducible within ± 0.03 eV. NMR spectra were run on a Bruker HX-90 E spectrometer. The δ values are given as positive for lowfield shifts and refer to internal TMS for δ_H and external 85% H_3PO_4 for δ_P . The kinetic measurements were performed as described earlier⁴ using the conductivity method of Henderson and Buckler.² The solvent was acetone (Merck, "zur Analyse") and dissolved oxygen was removed by boiling and cooling under nitrogen giving a conductivity of 0.1–0.2 μS . The solvent was not dried because the earlier described method⁴ and other attempts (Al_2O_3 , neutral, molecular sieves) caused substantial condensation to diacetone alcohol. Liquid phosphines were handled under nitrogen, and small amounts of hydroquinone were added to all solutions of phosphines in order to minimize oxidation. Solutions of phosphines were checked (¹H NMR) after the kinetic measurements and contained only a few percent phosphine oxides for the most oxidizable phosphines. Ph_3P (Fluka) was purified by recrystallization from EtOH, m.p. 79.5–80.5 °C. The following compounds were prepared according to literature methods: Ph_2PMe ;¹³ Ph_2PCH_2COOH ;⁹ m.p. 123.5–124.5 °C (MeOH-H₂O), lit.⁶ 120–121 °C. NMR [(CD₃)₂CO]: δ_P –18.4; δ_H 3.17 (CH_2 , ² J_{PH} 0.3 Hz); Ph_2PCH_2COOEt ;⁶ b.p. 135–137 °C/0.15 mmHg, lit.⁶ 183–185 °C/5 mmHg. NMR (CDCl₃): δ_P –16.8; δ_H 3.11 (P-CH₃, ² J_{PH} 0.5 Hz); $Ph_2PCH_2CONH_2$;¹⁴ m.p. 182.5–184 °C (CH_3CN), lit.¹³ 173–174 °C. NMR [(CD₃)₂SO]: δ_P –17.5; δ_H 3.06 (CH_2 , ² J_{PH} 1.1 Hz); Ph_2PCH_2CN ;⁴ $Ph_3P^+ I^-$;² $Ph_2EtP^+CH_2CN I^-$;⁴ Ph_2PEt was prepared in the same way as Ph_2PMe (60 %).

N,N-Dimethyl diphenylphosphinoacetamide was prepared in the same way as Ph_2PMe .¹³ Ph_3P (13.1 g, 0.05 mol) was added to a stirred solution of Na (2.3 g, 0.10 mol) in liq. NH₃ (100 ml) at –78 °C. After 15 min NH₄Cl (2.7 g, 0.05 mol) was added and then ClCH₂CONMe₂ (6.1 g, 0.05 mol). The reaction mixture was left overnight for NH₃ to evaporate and then treated with H₂O (50 ml) and CH₂Cl₂ (100 ml). The CH₂Cl₂ solution was dried (CaCl₂) and evaporated to give crude $Ph_2PCH_2CONMe_2$ (13 g). Recrystallization from dry ether gave the pure compound, m.p. 99.5–100.5 °C (8.9 g, 65 %). Anal. C₁₆H₁₈NOP: C, H, N. NMR (CDCl₃): δ_P –19.0; δ_H 3.16 (CH_2 , ² J_{PH} 0.5 Hz); δ_H 2.90, 2.96 (CH_3). The compound is stable towards air in the solid state.

(Carboxymethyl)diphenylethylphosphonium iodide. Ph_2PCH_2COOH (2 mmol) and EtI (6 mmol) were refluxed in acetone (3 ml) for 24 h. The solution was evaporated to dryness and the residue recrystallized from H₂O. After drying at 80 °C/0.1 mmHg for 2 h the m.p. was

152.5–153.5 °C (dec.). Anal. $C_{18}H_{18}IO_2P$: C, H, I. NMR $[(CD_3)_2SO]$: δ_P 25.6; δ_H 4.72 (CH_2COOH , $^2J_{PH}$ 13.7 Hz).

(Ethoxycarbonylmethyl)diphenylethylphosphonium iodide. The compound was prepared as above and had m.p. 129.5–130 °C (from 2-PrOH). Anal. $C_{18}H_{22}IO_2P$: C, H, I. NMR $[(CD_3)_2SO]$: δ_P 26.0; δ_H 4.88 (CH_2COOEt , $^2J_{PH}$ 14.2 Hz).

(Carbamidomethyl)diphenylethylphosphonium iodide. The compound was prepared as above, m.p. 165–167 °C (from H_2O). Anal. $C_{16}H_{19}INOP$: C, H, N, I. NMR $[(CD_3)_2SO]$: δ_P 26.4; δ_H 4.57 (CH_2CONH_2 , $^2J_{PH}$ 14.2 Hz).

(N,N-Dimethylcarbamidomethyl)diphenylethylphosphonium iodide. The compound was prepared as above, m.p. 235–237 °C (dec.; from EtOH). Anal. $C_{18}H_{23}INOP$: C, H, N, I. NMR $[(CD_3)_2SO]$: δ_P 26.3; δ_H 4.97 (CH_2CONMe_2 , $^2J_{PH}$ 13.3 Hz).

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Tropylium Ions. Part VIII.¹ General Base Catalysis in the Reaction of Phenyltropylium Ions with Water

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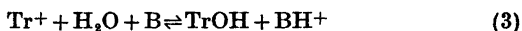
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There are divided opinions about the occurrence²⁻⁴ and importance⁵ of general base catalysis in the reaction of carbonium ions with water and consequently also of general acid catalysis in the reverse dissociation reaction. Direct observations have earlier been reported for reactions of triarylmethyl cations²⁻⁵ and for the hydration of *N*-substituted iminolactones.⁶⁻⁷ In this paper we wish to report our observations about general base catalysis in the reaction of a representative of another cation system, phenyltropylium cations.

When dissolved in aqueous B–BH⁺ buffer solution, phenyltropylium cations undergo the reactions



and if general base catalysis by B contributes, the one-step reaction



The observed pseudo first-order rate constant can be written as

$$k_{obs} = k_{H_2O} + k_{OH^-}[OH^-] + k_B[B] \quad (4)$$

where k_B is the second-order rate constant for catalysis by the base B. At constant buffer ratio (more exactly, at constant pH) the slope of the plot of k_{obs} vs. [B] gives k_B , and the intercept $k^{B=0}$ is $k_{H_2O} + k_{OH^-}[OH^-]$. If the intercepts $k^{B=0}$ measured at different buffer ratios are plotted as a function of $[OH^-]$, the values of k_{H_2O} and k_{OH^-} at zero concentration of buffer are obtained.

Data for the reaction of *p*-dimethylamino-phenyltropylium cation with water in Dabco (1,4-diazabicyclo[2.2.2]octane)–DabcoH⁺ and Et₃N–Et₃NH⁺ buffers are collected in Table 1. The rates were measured by stopped-flow technique at 25 °C and at constant ionic strength, regulated with potassium perchlorate.⁸ Examination of the data gives the values of 1.4 dm³ mol⁻¹ s⁻¹ and 2.3 dm³ mol⁻¹ s⁻¹ for catalysis by Dabco and Et₃N, respectively, a value 0.8×10^{-2} s⁻¹ for k_{H_2O} and a value 1.5×10^3 dm³ mol⁻¹ s⁻¹ for k_{OH^-} at ionic strength 0.02 mol dm⁻³, and a value 1.1×10^{-2} s⁻¹ for k_{H_2O} and a value 1.3×10^3 dm³ mol⁻¹ s⁻¹ for k_{OH^-} at ionic strength 0.1 mol dm⁻³. Slightly