PHOSPHINIC ACIDS AND DERIVATIVES. 4. LINEAR FREE ENERGY
RELATIONSHIPS IN DISPLACEMENT AT PHOSPHINYL PHOSPHORUS[1]

Paul Haake, David R. McCoy,[2] William Okamura,[2] Sigma R. Alpha,[2]
Shi-Yin Wong,[2] Donald A. Tyssee,[2] Jean P. McNeal, and Robert D. Cook[3]

Department of Chemistry, University of California, Los Angeles, California, 90024,
and Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457

There has been considerable recent interest in the mechanism of displacement at phosphorus
in phosphinates,[4] in the nature of pi bonding to phosphorus,[5] and in linear free energy (LFE)
relationships in phosphorus compounds.[6] We have studied the hydrolysis of some aryl diaryl-
phosphinates. We report here some results particularly important to the above problems.

The rates of alkaline hydrolysis of three sets of compounds, 1, 2, and 3, have been
measured. Displacement at phosphorus[7] has been shown to be sensitive to the basicity of the
attacking nucleophile,[8] i.e., phosphorus acts as a hard acid.[9] Hydroxide, the nucleophile, is
a hard base.[9] Therefore, the rate of attack by hydroxide should be quite sensitive to electron
density at phosphorus. Some previous studies of LFE relationships in organophosphorus
compounds have depended on measurement of acidity of SH or OH groups bonded to phosphorus.[6b]
That is, the reaction (ionization) takes place one bond away from phosphorus. In alkaline
hydrolysis of a phosphinate, hydroxide attacks the phosphorus center directly,[7] so this experi-
mental technique should be a sensitive indication of the nature of electronic interactions of the
substituted aryl rings in 1, 2, and 3 with phosphorus.
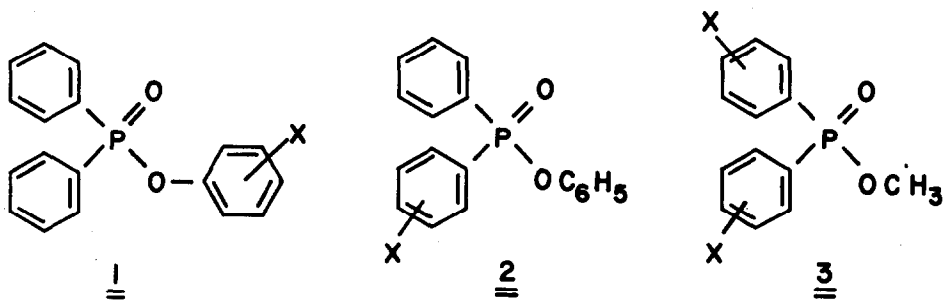
Second order rate constants (k) were evaluated for the alkaline hydrolysis of $\underline{1}$, $\underline{2}$, and $\underline{3}$ by titration, by pH-stat measurements, and in a few cases by conductivity. The compounds were prepared by straightforward methods[10] and confirmatory analyses and spectra were obtained.

The data for $\underline{1}$, (in 60% acetone-40% H_2O) are given in Fig. 1. The plot of log $k(\underline{1})$ against σ values[11] is a good straight line (ρ = 2.2). However, when the log $k(\underline{1})$ are plotted against pK's of phenols (in H_2O),[12] significant deviation is observed for the p-acetyl compound although the other five points define a good straight line with slope = 1.0. This point for the p-acetyl compound is particularly important, for it indicates that significant negative charge is probably not developed on the phenolic oxygen in the transition state, i.e., the structural change, ground state → transition state for $\underline{1}$, does not resemble the structural change, phenol → phenoxide for ArOH. The rather large slopes in Fig. 1 may be due to partial delocalization of the unshared pairs of electrons on the phenolic oxygen toward phosphorus. The substituted aryl rings in $\underline{1}$ would alter this delocalization toward phosphorus and therefore change the electron density at phosphorus significantly.

The log $k(\underline{2})$ (in 35% dioxane-65% H_2O) data correlate acceptably with σ values (ρ = 0.7) as shown in Fig. 2. An important observation is the fit of the p-methoxy compound with the rest of the data. This strongly indicates resonance type interaction since the inductive effect alone of the p-methoxy group would tend to accelerate the rate. The log $k(\underline{2})$ data do not correlate with σ_I. The known rates of alkaline hydrolysis of ethyl benzoates in 85% ethanol[11] also give an LFE correlation (Fig. 2) with the log $k(\underline{2})$ (slope = 0.6) and the p-CH_3O point again fits with the other data. Therefore, substituents effects appear to be similar for benzoates and arylphosphinates. The similarity of the two reactions related by this LFE plot and the relatively well understood interactions of substituted aryl rings with carbonyl groups makes this approach important in determining the nature of aryl-phosphinyl interactions.

The rates of alkaline hydrolysis of $\underline{3}$ (in 60% 1,2-dimethoxyethane-40% H_2O) were evaluated at a number of different temperatures and related to the rate of alkaline hydrolysis of methyl diphenylphosphinate ($\underline{3}$, X = H) at 75°. Fig. 3 shows correlations of log $k_{relative}$ ($\underline{3}$) with the same parameters used in Fig. 2. The straight lines and the correlation of the data for the p-$(CH_3)_2N$ compound with the rest of the data lead to the same conclusions as from the data for $\underline{2}$ - aryl-phosphinyl interactions are similar to aryl-carbonyl interactions, and there are, therefore, electronic effects of the resonance type in aryl-phosphinyl compounds.

<div align="center">REFERENCES</div>

1. Supported in part by grants from the National Science Foundation and by an Alfred P. Sloan Research Fellowship, 1964-67, to P.H. Inquiries should be addressed to P.H. at Wesleyan University.
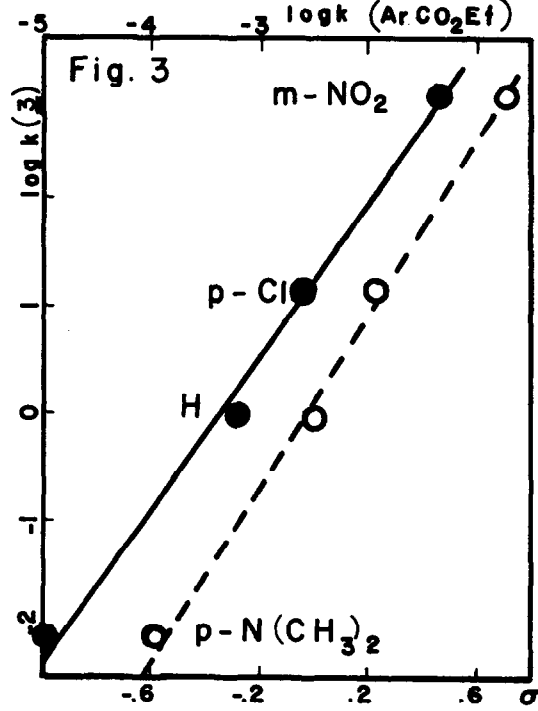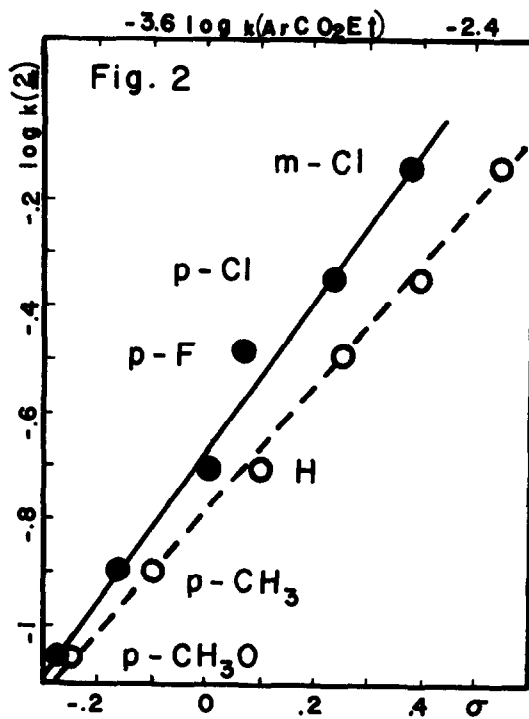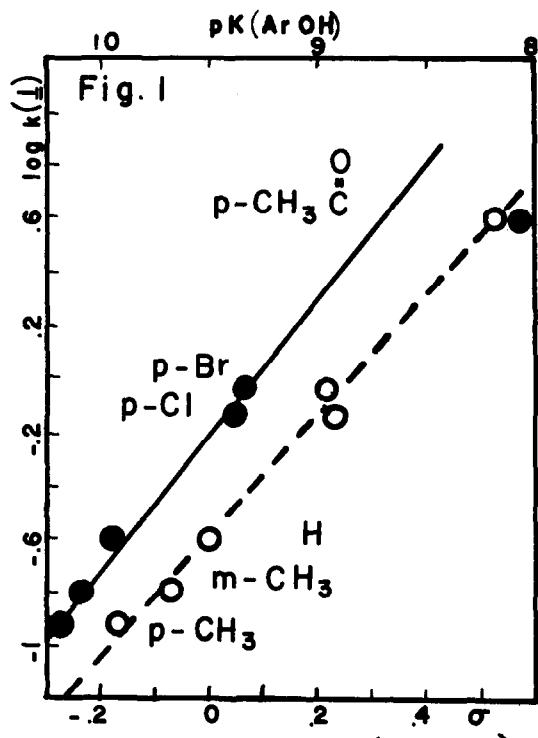
2. NSF undergraduate research participants.

Fig. 1

Fig. 2

Fig. 3

Fig. 1 Log k($\underline{1}$) plotted against
σ (– ◯– ◯–) and against pK (ArOH)
(●——●).

Fig. 2 Log k($\underline{2}$) plotted against
σ (●——●) and against log k for
alkaline hydrolysis of $ArCO_2C_2H_5$
(◯– ◯).

Fig. 3 Log k$_{relative}$($\underline{3}$) plotted against
σ (– ◯– ◯–) and against log k for
alkaline hydrolysis of $ArCO_2C_2H_5$
(●——●).

3.   Present address: Department of Chemistry, American University, Beirut, Lebanon.

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