

THE DISPERSION OF SUBSTITUENT EFFECTS IN ORGANOPHOSPHORUS COMPOUNDS

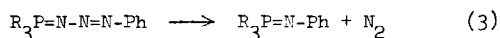
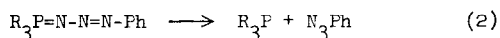
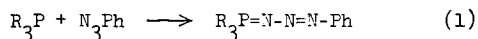
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Linear free energy relationships sometimes disperse into separate lines characteristic of different classes of substituent. Although ad hoc explanations of this phenomenon are readily devised in terms of the general theory of free energy relationships (1), the dispersion effects are still not predictable. Since the effects are not predictable, usable experimental results are almost always the by-product of other lines of research and are, therefore, not only quite scarce, but sometimes not recognized as pertinent. In this paper, we report one example from our own laboratory and several from the literature, all involving organophosphorus compounds.

The first example is from the Staudinger reaction of a wide variety of trivalent organophosphorus compounds with phenyl azide in benzene (2,3). The mechanism for triarylphosphines (3), and very probably for the other trivalent phosphorus compounds, is given by equations 1-3.



Although the rates in some cases deviate considerably from second order, the apparent second order rate constant is adequate for our present purpose since we are concerned only with very large effects. When the intermediate complex is sufficiently unstable for the steady state approximation to apply, the apparent second order rate constant is given by equation (4) and

$$k_{2nd\ order} = \frac{k_1 k_2}{k_2 + k_3} \quad (4)$$

is concentration independent. For several of the triarylphosphine reactions with various azides,

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it has been possible to evaluate the individual rate constants  $k_1$ ,  $k_2$  and  $k_3$  separately (3). The largest phosphine substituent effects are on  $k_1$  with  $\rho$  equal to -1.07. The contribution of the small substituent effect on the other rate constants to  $k_{2nd}$  will be still further reduced by partial cancellation (see equation 4), so that large substituent effects on  $k_{2nd}$  are probably due mostly to large substituent effects on  $k_1$ .<sup>†</sup>

Our approximate overall second order rate constants (2,3) are listed in Table I. Reactivities and substituent effects for all compounds in Table I can be compared by applying the Taft polar  $\sigma^*$  constant for  $RCH_2$  to the phosphines  $R_1R_2R_3P$ .<sup>††</sup> Previously untabulated  $\sigma^*$  values were calculated from ionization constants of the acid  $RCH_2COOH$ .<sup>†††</sup> The logarithms of the rates in Table I are plotted vs. polar substituent constants in Figure 1. The separate correlations for various classes of phosphines obtained using Hammett  $\sigma$  values are summarized in Table II.

Instead of defining a single line, the points in Figure 1 lie on two parallel straight lines, and possibly on a third one. The line furthest to the right with a slope of -2.41 and intercept on the log k axis of +1.540 (correlation coefficient 0.997) is for phosphites, phosphonites, and phosphinites, compounds with one or more phosphorus-oxygen bonds. Points for triarylphosphines, diarylphosphinous chlorides, and arylphosphinous dichlorides fall on the middle line with slope -2.43 and intercept +0.128 (correlation coefficient 0.997). These compounds have at least one aryl group attached to phosphorus but contain no phosphorus-oxygen bonds. The two straight lines are parallel within 99.7% confidence limit. The 1.41 log unit separation corresponds to a difference in free energy of activation of 1.93 kilocalories per mole. Points for the two trialkylphosphines lie to the left of these two lines, possibly on a

<sup>†</sup> We hope that it will prove to be feasible to obtain  $k_1$  values for trivalent phosphorus compounds other than triarylphosphines, but this has not yet been attempted.

<sup>††</sup> This corresponds to choosing  $PH_3$  as a reference compound. Because of experimental difficulties with the reactions used for defining  $\sigma^*$  constants, values for substituents such as chloro and methoxy are unavailable. Using  $\sigma^*_{RCH_2}$  constants avoids these difficulties and at the same time gives polar substituent constants free from resonance and other  $\alpha$ -effects.

<sup>†††</sup> New  $\sigma^*_{RCH_2}$  values are for R = p-chlorophenyl (+0.281), m-tolyl (+0.195), p-tolyl (+0.166), p-methoxyphenyl (+0.137), p-dimethylaminophenyl (-0.026), p-chlorophenoxy (+0.886), m-tolyloxy (+0.832), p-tolyloxy (+0.824), p-methoxyphenoxy (+0.801), n-butyl (-0.141), n-octyl (-0.185).

Table I

Rate Constants: Trivalent organophosphorus compounds plus phenyl azide in benzene at 25°

Compound Number	Compound, R <sub>3</sub> P	$k_{2nd}^{-1} \text{ sec}^{-1}$ a	$\Sigma\sigma^b$	$\Sigma\sigma^*_{RCH_2}$ c
1	tris( <u>p</u> -chlorophenyl)phosphine	0.0115 ± 0.0008	0.681	0.843
2	<u>p</u> -chlorophenyldiphenylphosphine	0.0237 ± 0.0001	0.227	0.711
3	triphenylphosphine	0.0343 ± 0.0010	0.000	0.645
4	<u>m</u> -toloydiphenylphosphine	0.0367 ± 0.0007	-0.069	0.625
5	<u>p</u> -toloydiphenylphosphine	0.0499 ± 0.0002	-0.170	0.596
6	tri- <u>m</u> -tolylphosphine	0.0387 ± 0.0029	-0.207	0.585
7	<u>p</u> -methoxyphenyldiphenylphosphine	0.0687 ± 0.0054	-0.268	0.567
8	tri- <u>p</u> -tolylphosphine	0.0856 ± 0.0036	-0.510	0.498
9	tris( <u>p</u> -methoxyphenyl)phosphine	0.128 ± 0.038	-0.804	0.411
10	<u>p</u> -dimethylaminophenyldiphenylphosphine	0.144 ± 0.014	-0.830	0.404
11	tri- <u>p</u> -chlorophenyl phosphite	1.42 ± 0.00 x 10 <sup>-5</sup>	0.681	2.658
12	triphenyl phosphite	2.29 ± 0.17 x 10 <sup>-5</sup>	0.000	2.550
13	tri- <u>m</u> -tolyl phosphite	3.25 ± 0.29 x 10 <sup>-5</sup>	-0.207	2.496
14	tri- <u>p</u> -tolyl phosphite	3.69 ± 0.41 x 10 <sup>-5</sup>	-0.510	2.472
15	tri- <u>p</u> -methoxyphenyl phosphite	5.37 ± 0.26 x 10 <sup>-5</sup>	-0.804	2.403
16	dimethyl <u>p</u> -chlorophenylphosponite	0.0247 ± 0.0002	0.227	1.321
17	dimethyl phenylphosponite	0.0378 ± 0.0056	0.000	1.255
18	dimethyl <u>p</u> -methoxyphenylphosponite	0.0648 ± 0.0021	-0.268	1.177
19	phenylphosponous dichloride	3.12 ± 0.05 x 10 <sup>-6</sup>	0.000	2.315
20	<u>p</u> -methoxyphenylphosponous dichloride	3.77 ± 0.03 x 10 <sup>-6</sup>	0.268	2.237
21	trimethyl phosphite	0.00344 ± 0.00010	-----	1.560
22	diphenyl phenylphosponite	0.00129 ± 0.00004	-----	1.915
23	phenyl diphenylphosphinite	0.0210 ± 0.0017	-----	1.380
24	diphenylphosphinous chloride	5.97 ± 1.00 x 10 <sup>-4</sup>	-----	1.480
25	tri- <u>n</u> -butylphosphine	0.227 ± 0.022	-----	-0.423
26	tri- <u>n</u> -octylphosphine	0.165 ± 0.070	-----	-0.555

<sup>a</sup>The limits are either two standard deviations for values based on four or more runs, or the total observed range. It should be noted that these limits, in some cases, include real effects due to the deviation from strictly second order kinetics, as well as experimental error. <sup>b</sup>Hammett constants for substituents in aryl rings. <sup>c</sup>Taft  $\sigma^*$  constants for substituents RCH<sub>2</sub>.

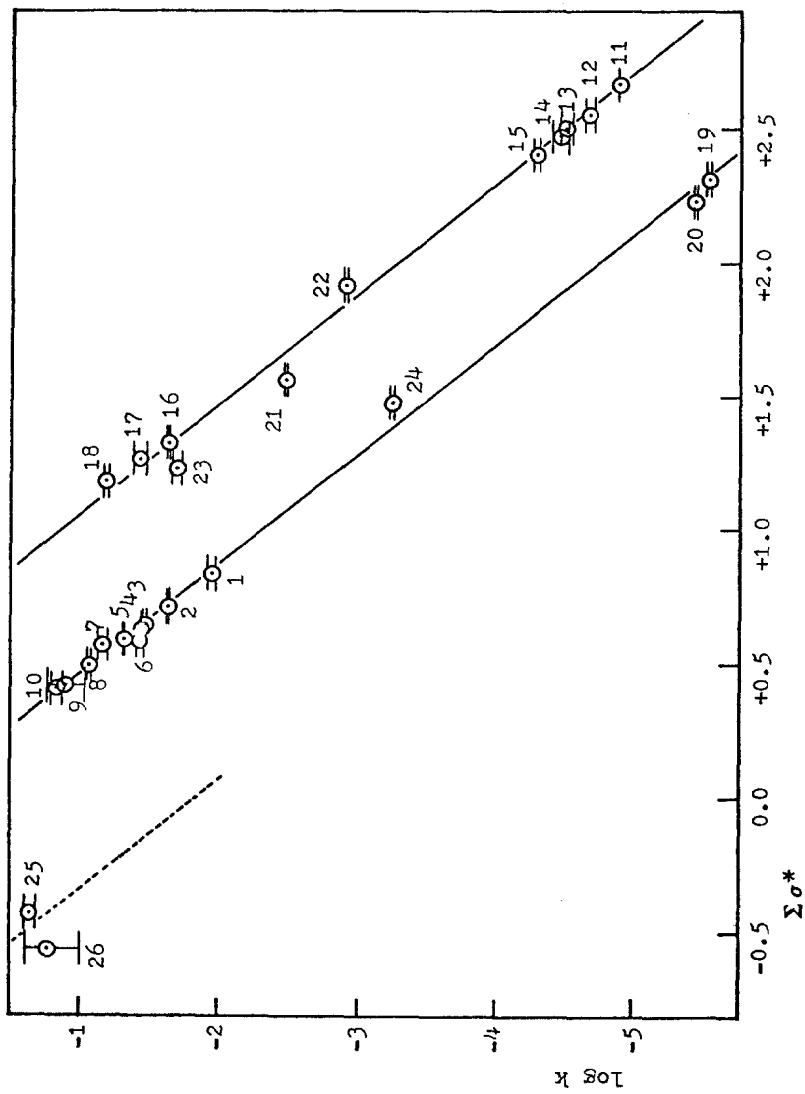


FIG. 1

Reaction rates of trivalent phosphorus compounds with phenyl azide in benzene at 25° versus Taft sigma-star constants. Numbers refer to compounds in Table I.

Table II

Hammett Equation Correlations

Series	No. of Compounds in Series	Correlation Coefficient, r	Reaction Constant, $\rho$	$\log k_0$
$\text{Ar}_3\text{P}$	10	0.988	-0.73	-1.46
$\text{ArPh}_2\text{P}$	6	0.987	-0.76	-1.45
$\text{P}(\text{OAr})_3$	5	0.989	-0.38	-4.60
$\text{ArP}(\text{OCH}_3)_2$	3	(1.000)	-0.85	-1.42
$\text{ArPCL}_2$	2	-----	-0.31	-5.51

third parallel line with an intercept of about -1.8.

The remarkable thing about Figure 1 is not just the dispersion, but the fact that the introduction of a single oxygen atom (changing from  $\text{Ar}_3\text{P}$  to  $\text{Ar}_2\text{POR}$ ) causes a sharp discontinuity, while the second and third oxygens (changing to  $\text{ArP}(\text{OR})_2$  and  $\text{P}(\text{OR})_3$ ) do not. It would be of great interest to identify the interaction mechanisms responsible for this effect.

Basolo and co-workers have recently reported rates of displacement of carbon monoxide from  $\pi$ -cyclopentadienyldicarbonylrhodium (4) and nitrosyltricarbonylcobalt (5) by trivalent phosphorus nucleophiles. Although interpretation of these rate data is complicated by the sensitivity of the reactions to steric effect, plots of  $\log k$  vs. polar substituent constants clearly exhibit dispersion into two approximately parallel lines. Phosphites lie on one line and phosphines (with alkyl, aryl and chloro substituents) lie on another, displaced to slower rates by about 1.4 log units (1.9 kilocalories per mole) for the rhodium compound and 1.7 log units (2.4 kilocalories per mole) for the cobalt complex.

When the  $1200\text{-}1300\text{ cm}^{-1}$  phosphoryl stretching band in the infrared spectra of  $\text{R}_3\text{P}=\text{O}$  compounds (6) is plotted against  $\Sigma\sigma^*_{\text{RCH}_2}$ , a figure consisting of two straight lines is obtained. The lower-frequency line correlates data for compounds with aryl-phosphorus and chlorine-phosphorus bonds, but no oxygen-phosphorus bonds; the other line contains points for compounds with one, two and three oxygen-phosphorus bonds. The lines are not quite parallel, the separation being about  $45\text{ cm}^{-1}$  at  $\Sigma\sigma^* = 0.7$  and about  $20\text{ cm}^{-1}$  at  $\Sigma\sigma^* = 2.5$ .

Ramirez and co-workers (7) recently noted that oxidation of alkyl- and arylphosphines causes the  $^{31}\text{P}$  magnetic resonance to occur at lower field strength, while oxidation of phosphite and phosphonite esters causes shifts to higher fields. This difference between the two classes of compounds (with and without oxygen substituents) was attributed to differences in  $p_{\pi}-d_{\pi}$

bonding in the oxidized derivatives. However, a plot of  $^{31}\text{P}$  chemical shifts vs. polar substituent constants suggests that the explanation lies in the phosphines rather than in the oxides. Points for the oxides fall close to a straight line, indicating that for these compounds  $\delta^{31}\text{P}$  is a well-behaved quantity determined mainly by a single polar effect. Points for the trivalent compounds fall in two separate groups (on parallel lines?) containing, respectively, compounds with and without oxygen-phosphorus bonds. Additional  $^{31}\text{P}$  nmr data taken from the literature (8) substantiate these relationships. Recent theoretical interpretations of  $^{31}\text{P}$  chemical shifts have attributed deviations from additivity to a combination of  $\pi$  interactions between substituents and the phosphorus atom (9) and bond angle (hybridization) changes (9,10).

There are other reactivity studies in the literature in which the structural variation in the phosphorus compounds is too limited to reveal dispersion into parallel lines. Inspection of such reports in the light of the present findings, however, shows that the special effect of oxygen-phosphorus bonds can be detected in every pertinent case examined. For example, Ramirez and co-workers noted that diphenyl phenylphosphonite reacts with  $\alpha$ -dicarbonyl compounds more rapidly than either triphenylphosphite or triphenylphosphine (11), whereas in the absence of a dispersion effect, it would have been expected to react at an intermediate rate. We suspect that a further investigation of this reaction would show dispersion into two lines, one for triarylphosphines and a separate one for the phosphites and phosphonites.

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