

O-protonation and considerably favored over edge protonation. The various protonated species are in equilibrium with each other, and this intramolecular equilibrium is probably somewhat faster than the ring opening. Intermolecular equilibrium among the protonated species may well be faster still. The three postulated mechanisms are similar in transition state energies for oxaziridine itself, but N-alkylation can be expected to favor eq 1 (O-protonation followed by O-N bond cleavage) over the others. Since it is observed that substitution of an aryl group at the carbon changes the products from those expected for eq 1 to those which would be expected for eq 2 or 3 and since aryl substitution is predicted to favor eq 3 far more than it does eq 2, it seems probable that the observed products result from eq 3 rather than 2. The previously accepted mechanism involving O-protonation followed by C-O bond cleavage is less supported by the calculations than is the mechanism involving N-protonation followed by C-N bond cleavage.

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Supplementary Material Available: A complete listing of the optimized geometry parameters of species 1–21 (8 pages). Ordering information is given on any current masthead page.

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Steric Effects. 12. Substituents at Phosphorus

Marvin Charton* and Barbara I. Charton

Department of Chemistry, Pratt Institute, Brooklyn, New York 11205

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Ionization constants of four sets of alkyl-substituted phosphorus oxy acids, rate constants for hydrolysis of four sets of alkyl-substituted phosphorus oxy acid esters, rate constants for the reaction of 22 sets of XZ(PO)Cl with water, and rate constants for the reaction of a set of trialkylphosphines with ethyl iodide have been correlated with both the ν and the ν' steric parameters by means of the modified Taft equation. The pK_a s gave best results with the ν parameters, in accord with the tetrahedral geometry of the acids. The rate constants for the reaction of XZ(PO)Cl with water are best correlated by the ν' constants, the results in agreement with a transition state exhibiting trigonal-bipyramidal geometry with the nucleophile and leaving group at opposite positions. The success of the correlations with the ν or ν' steric parameters shows that significant steric effects occur in the acidity of phosphonic and phosphinic acids, the reaction of derivatives of these acids with nucleophiles, and the reaction of trialkylphosphines with ethyl iodide. Furthermore, steric parameters evaluated from reactions of carbon compounds may be successfully applied to the reactivity of compounds of phosphorus. The $\sigma\phi$ constants proposed by Kabachnik for use with substituents at phosphorus were correlated with $\sigma\phi_X = L\sigma_{IX} + D\sigma_{RX} + S\nu_X + c$ with excellent results. The steric term was significant at the 99.9% confidence level. The results show clearly that substituents exert the same types of electrical effects at phosphorus that they do when bonded to carbon. They also provide verification for the conclusion that ν values for alkoxy, alkylthio, and dialkylamino groups are on the same scale as the ν values for other substituents.

We have hitherto studied the steric effect of alkyl substituents attached to oxygen¹ and to nitrogen² in carbonyl compounds and alkyl groups attached to sulfur³ in a variety of compounds. In this work we turn our attention to steric effects of alkyl groups attached to phosphorus. We have examined the correlation with the modified Taft equation¹⁻³

$$Q_X = S\nu_X + h \quad (1)$$

with the pK_a s for four sets of alkyl-substituted phosphorus oxy acids; four sets of rate constants for the hydrolysis of esters of alkyl-substituted phosphorus oxy acids; 22 sets of rate constants for reactions of alkyl-substituted acyl chlorides of phosphorus oxy and thio acids with water; and one set of rate constants for the reaction of trialkyl phosphines with ethyl iodide. The data used in the correlations are reported in Table I. We have considered only steric effects on the reactions studied because the magnitude of the localized (field and/or inductive) electrical effect as measured by reliable σ_I values⁴ for nine alkyl groups (Me, Et, Pr, *i*-Pr, Bu, *i*-Bu, *s*-Bu, and *t*-Bu) is -0.01 ± 0.02 . The magnitude of the delocalized (resonance) electrical effect as determined by reliable σ_R

values⁴ for four alkyl groups is -0.16 ± 0.02 . These values lead to the inexorable conclusion that the electrical effects of alkyl groups are constant and independent of alkyl group structure. This view is supported by our previous work.^{5,6}

There are two different sets of ν parameters for alkyl groups available: the ν values derived from rate constants for esterification of carboxylic acids^{7,8} and the ν' values derived from the reaction of alkyl carbonyl bromides with bromide ion.⁹ These constants differ in their sensitivity to branching in the alkyl group.¹⁰ The ν parameters reflect steric effects in a tetrahedral species while the ν' parameters represent steric effects in the S_N2 transition state which may be considered as a trigonal bipyramid. We have examined the correlation of all the data with both types of steric parameter and some results of the correlations for those sets with five or more points. [For complete statistics for all the sets studied, see the paragraph at the end of this paper about the supplementary material.] Sets designated A were correlated with ν and sets designated B were correlated with ν' values. We found it necessary to estimate a value of ν' for the *s*-Bu group for use with several of the sets studied. To accomplish this, we have assumed addi-

Table I. Data Used in the Correlations

1,2. pK_{a1} , pK_{a2} of $XPO(OH)_2$ in H_2O at $25^\circ C^a$ Me, 2.38, 7.74; Et, 2.43, 8.05; Pr, 2.49, 8.18; <i>i</i> -Pr, 2.66, 8.44; Bu, 2.59, 8.19; <i>s</i> -Bu, 2.74, 8.48; <i>i</i> -Bu, 2.70, 8.43; <i>t</i> -Bu, 2.79, 8.88; <i>t</i> -BuCH ₂ , 2.84, 8.65	Me, 82.1; Et, 30.07; Pr, 25.58; <i>i</i> -Bu, 17.4
3. pK_a , $X(PO)H(OH)$ in H_2O at $25^\circ C^a$ Me, 3.08; Et, 3.29; Pr, 3.46; <i>i</i> -Pr, 3.56; Bu, 3.41; <i>t</i> -Bu, 4.24	19. 10^3k_r , $X(EtO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $10^\circ C^g$ Me, 137.3; Et, 52.50; Pr, 42.08; <i>i</i> -Pr, 1.77
4. pK_a , $X_2PO(OH)$ in 75% EtOH-H ₂ O ^b Me, 4.72; Bu, 5.24; <i>i</i> -Bu, 5.60; <i>s</i> -Bu, 5.75; <i>t</i> -Bu, 6.26	20. 10^3k_r , $X(EtO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $20^\circ C^g$ Me, 235.0; Et, 76.5; Pr, 68.33; <i>i</i> -Pr, 3.15; <i>i</i> -Bu, 39.2
5. k_{rel} , $XPO(O-i-Pr)_2 + OH^-$ in H_2O^c Me, 1; Et, 0.16; Pr, 0.062; Bu, 0.039; <i>t</i> -Bu, 0.002	21. 10^3k_r , $X(EtO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $30^\circ C^g$ Me, 337.8; Et, 114.9; Pr, 101; <i>i</i> -Pr, 6.05; <i>i</i> -Bu, 62.3
6. k_{rel} , $XPO(O-i-Pr)_2 + H_3O^+$ in H_2O^c Me, 1.0; Et, 0.5; Pr, 0.5; Bu, 0.33; <i>t</i> -Bu, 0.33	22. 10^3k_r , $X(ClCH_2CH_2O)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $0^\circ C^g$ Me, 187.2; Et, 68.3; <i>i</i> -Pr, 2.58; <i>s</i> -Bu, 2.47
7. 10^3k_r , $X_2PO(OMe)$ in 60% dimethoxyethane-H ₂ O at $75^\circ C^d$ Me, 500; Et, 10.9; Bu, 3.08; <i>i</i> -Pr, 0.3	23. 10^3k_r , $X(ClCH_2CH_2O)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $10^\circ C^g$ Me, 331; Et, 104.0; <i>i</i> -Pr, 4.24; <i>s</i> -Bu, 4.31
8. 10^2k_r , $XMe(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $0^\circ C^e$ Et, 5560; Pr, 3093; <i>i</i> -Pr, 83.7; Bu, 2968; <i>i</i> -Bu, 1360	24. 10^3k_r , $X(ClCH_2CH_2O)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $20^\circ C^g$ Et, 169.7; <i>i</i> -Pr, 7.03; <i>s</i> -Bu, 7.07
9. 10^2k_r , $XEt(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $0^\circ C^e$ Me, 5560; Et, 551; Pr, 445	25. 10^3k_r , $X(ClCH_2CH_2O)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $30^\circ C^g$ Et, 233.0; <i>i</i> -Pr, 11.67; <i>s</i> -Bu, 11.03
10. 10^2k_r , $XPr(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $0^\circ C^e$ Me, 3093; Et, 445; Pr, 371	26. 10^3k_r , $X(i-PrO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $0^\circ C^g$ Me, 41.5; Et, 16.76; Pr, 14.65
11. 10^2k_r , $X(PO)Cl_2 + H_2O$ in 95% v/v MeAc-H ₂ O at $0^\circ C^e$ Me, 3847; Et, 793; Pr, 671; <i>i</i> -Pr, 30.4; <i>s</i> -Bu, 28.1	27. 10^3k_r , $X(i-PrO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $10^\circ C^g$ Me, 74.7; Et, 26.15; Pr, 23.63
12. 10^3k_r , $X(EtS)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $0^\circ C^f$ Me, 202; Et, 74.2; <i>i</i> -Pr, 2.84; <i>s</i> -Bu, 2.51	28. 10^3k_r , $X(i-PrO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $20^\circ C^g$ Me, 120.1; Et, 42.58; Pr, 41.55
13. 10^3k_r , $X(ClCH_2CH_2S)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $0^\circ C^f$ Me, 814; Et, 258; <i>i</i> -Pr, 8.47; <i>s</i> -Bu, 6.48	29. 10^3k_r , $X(i-PrO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $30^\circ C^g$ Me, 196.0; Et, 67.5; Pr, 56.52; <i>i</i> -Pr, 3.81
14. 10^3k_r , $X(MeO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $0^\circ C^g$ Me, 135.6; Et, 60.6; Pr, 51.47; <i>i</i> -Pr, 2.48; Bu, 36.1	30. 10^3k_r , $X_3P + EtI$ in MeAc at $34.97^\circ C^h$ Me, 2.24; Et, 1.54; Pr, 1.36; Bu, 1.62; <i>i</i> -Bu, 0.138; BuCH ₂ , 1.58
15. 10^3k_r , $X(MeO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $10^\circ C^g$ Me, 200.6; Et, 82.3; Pr, 82.15; <i>i</i> -Pr, 4.19; Bu, 58.1	31. 10^4k_r , $X(PO)(OEt)(OC_6H_4NO_2^{4-}) + OH^-$ in H_2O (pH 8.3) at $37.5^\circ C^i$ Me, 24.2; Et, 5.06; Pr, 4.17; Bu, 4.23; BuCH ₂ , 3.62; BuCH ₂ CH ₂ , 3.56; <i>i</i> -Pr, 1.07; <i>i</i> -Bu, 2.34; <i>i</i> -PrCH ₂ CH ₂ , 2.45; <i>i</i> -Pr(CH ₂) ₃ , 3.62; <i>t</i> -Bu, 0.032; ^j <i>t</i> -Bu(CH ₂) ₃ , 3.41; ^k <i>c</i> C ₆ H ₁₁ , 0.307
16. 10^3k_r , $X(MeO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $20^\circ C^g$ Me, 319.6; Et, 134.5; Pr, 134.2; <i>i</i> -Pr, 6.55; Bu, 99.0	
17. 10^3k_r , $X(MeO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $30^\circ C^g$ Me, 469.5; Et, 193.5; Pr, 185.3; <i>i</i> -Pr, 9.69; Bu, 147.6	
18. 10^3k_r , $X(EtO)(PO)Cl + H_2O$ in 95% v/v MeAc-H ₂ O at $0^\circ C^g$	

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tivity of the effects of branching. Five different estimates were made in the following manner:

- $v'_{Pr} - v'_{Et} = \beta_{CH_2} = 0.04$
 $v'_{i-Pr} + \beta_{CH_2} = v'_{s-Bu} = 0.62 + 0.04 = 0.66$
- $v'_{i-Pr} - v'_{Et} = \alpha_{CH_2} = 0.62 - 0.38 = 0.24$
 $v'_{Pr} + \alpha_{CH_2} = v'_{s-Bu} = 0.42 + 0.24 = 0.66$
- $v'_{i-Bu} - v'_{Et} = 0.55 - 0.38 = 0.17 = 2\beta_{CH_2}$, $\beta_{CH_2} = 0.09$
 $v'_{i-Pr} + \beta_{CH_2} = v'_{s-Bu} = 0.62 + 0.09 = 0.71$
- $v'_{t-Bu} - v'_{Et} = 2\alpha_{CH_2} = 1.23 - 0.62 = 0.61$, $\alpha_{CH_2} = 0.31$
 $v'_{Pr} + \alpha_{CH_2} = v'_{s-Bu} = 0.42 + 0.31 = 0.73$
- $v'_{Et} - v'_{Me} = \alpha_{CH_2} = 0.03$, $v'_{Pr} - v'_{Me} = \alpha_{CH_2CH_2} = 0.07$
 $v'_{Me} + \alpha_{CH_2} + \alpha_{CH_2CH_2} = v'_{s-Bu} = 0.45$

An average value of 0.64 is obtained from the five approximations. We have used the value of 0.66 obtained with approximations 1 and 2 as a reasonable estimate of v'_{s-Bu} .

Five of the sets studied have tetrahedral (sets 1-4) or close to tetrahedral (set 30) geometry throughout the course of the reaction being studied. For sets 1-4, best results were obtained on correlation with the ν values. This is in agreement with the

fact that ν is defined from a reaction involving a tetrahedral intermediate. Excellent correlations were obtained for all four sets (sets 1A-4A). It must be noted that the $X_2PO(OH)$ acids of set 4 are disubstituted, thus the equation

$$Q_{X^1X^2} = S\Sigma\nu + h \quad (2)$$

would presumably be required, where

$$\Sigma\nu = \nu_{X^1} + \nu_{X^2} \quad (3)$$

As in this set $X^1 = X^2$,

$$\Sigma\nu = 2\nu_{X^1} \quad (4)$$

and

$$Q_{X^1X^2} = S\nu_X + H \quad (5)$$

$$= S'\nu_X + h \quad (6)$$

Thus, the correlations were carried out with eq 6. Set 30 gave somewhat better results with ν' than with ν , although the two correlations were significant at the same confidence level. We are unable to account for this at the present time. Inspection

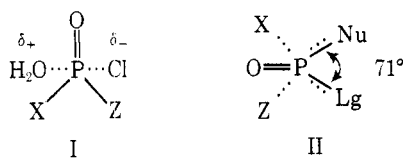
Table II. Results of Correlations with Equation 1

Set	S	h^A	100r ²	S	h^B	100r ^{2a}	n ^b
1	0.521	2.17	89.5	0.413	2.36	61.9	9/8
2	1.04	7.44	82.3	1.06	7.69	79.7	9/8
3	1.50	2.39	98.0	1.13	2.86	93.3	6
4	1.98	3.75	97.2	1.49	4.56	81.7	5
5	-3.18	1.12	87.6	-2.30	0.0659	76.7	5
6	-0.432	0.0047	40.6	-0.283	-0.154	28.9	5
8	-1.80	4.47	15.2	-6.53	6.27	85.4	5
11	-4.13	5.37	75.5	-6.45	5.58	95.8	5
14	-5.74	5.19	72.3	-6.20	4.23	98.6	5
15	-5.41	5.17	69.2	-5.94	4.31	97.8	5
16	-5.42	4.38	68.2	-6.01	4.55	98.0	5
17	-5.41	5.54	68.9	-5.97	4.69	98.2	5
20	-1.87	2.94	24.2	-5.48	4.18	83.4	5
21	-1.74	3.05	24.4	-5.09	4.19	83.2	5
30	-2.60	1.81	88.4	-6.17	2.62	92.5	6
31	-3.29	2.80	79.7	-2.84	1.93	94.3	12/7

^a Percent of data accounted for by the correlation equation. ^b Number of points in A/B set. When only one number is given, it applies to both A and B sets.

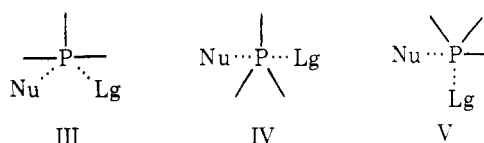
of the S values obtained for sets 1–4 and comparison with the ν values of the constant substituents attached to the phosphorus atom suggests that the magnitude of S is more dependent on the electrical effect of the constant substituent than upon its steric effect.

Sets 8–29 involve the reaction of water with compounds of the type $XZ(PO)Cl$ where Z is a constant substituent. Of the 22 sets studied, seven gave significant correlation with the ν parameters and 15 did not. Furthermore, five of the seven significant correlations were poor. By contrast, 16 of the sets gave significant correlation (five excellent, three very good, four good, two fair, and two poor) with the ν' constants whereas six sets did not give significant correlation (of which three sets had only three points). Clearly then, much better results are obtained with ν' than with ν . These results are in agreement with a transition state such as I for the reaction of $XZ(PO)Cl$ with water.

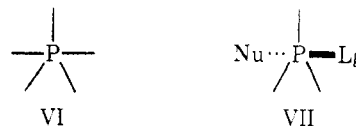


Transition state I has trigonal-bipyramidal geometry. The argument upon which this statement is based is that the steric effect of an unsymmetrical substituent, a category into which most alkyl groups fall, upon a rate constant is dependent upon the geometry of the transition state for reaction which is occurring. When transition states have similar geometry (that is, are of the same geometric type, although bond lengths may differ) the rate constants for the corresponding reactions should be correlated by the same type of substituent constant. Differences in bond lengths would then be reflected in differences in the coefficient, S .

There does not seem to be a consensus in the literature as to the mechanism of nucleophilic attack on $XZ(PO)Lg$ where X and Z are substituents and Lg is a leaving group. Kirby and Warren¹¹ state that three structures have been suggested for the transition state in nucleophilic attack on tetrahedral pentacoordinate phosphorus: (1) a square pyramide with $d_{x^2-y^2}$, p_x , p_y , and p_z hybrid bonds; (2) the structure II with three sp^3 bonds and two long ($1/4sp^3-d_{xy}$) bonds to the entering and leaving groups, Nu and Lg ; and (3) trigonal bipyramids in which the entering and leaving groups may occupy either opposite or adjacent positions. Three such transition states can be written, III, IV, and V. I is of course equivalent to IV.



Osterheld¹² is of the opinion that the most probably bimolecular mechanism for this type of reaction involves a pentacoordinate *intermediate* of the trigonal bipyramid type, VI. The



location of the groups in VI is not shown since by appropriate pseudorotation any two groups may occupy either opposite or adjacent positions. Emsley and Hall¹³ feel that the bimolecular mechanism is probably of the S_N2 type. The mechanism of these reactions has also been discussed by Benkovic¹⁴.

Although a better correlation with ν' is suggestive of a rate-determining step involving either I or the transition state VII which leads to the intermediate VI, it cannot be regarded as conclusive at the present. Steric effects can however distinguish between associative mechanisms such as the $S_N2(P)$ and dissociative mechanisms such as the $S_N1(P)$. The former will have more repulsions between the substituent and the rest of the molecule in the transition state than are present in the substrate. The result is steric hindrance, which is indicated by a negative value for S . In the latter type of mechanism there are more repulsions in the substrate than the transition state, and therefore the result is steric acceleration, indicated by a positive value of S .

The last group of sets studied represents the reaction of esters of alkyl-substituted phosphorus oxy acids with hydronium ion, water, or hydroxide ion (sets 5–7, 31). The reaction of the diisopropyl phosphonates with hydronium ion (set 6) did not give a significant correlation with either the ν or the ν' constants and their reaction with hydroxide ion (set 5) was best correlated by the ν constants giving good results. The reaction of the ethyl *p*-nitrophenyl phosphonates with hydroxide ion (set 31) was best correlated by the ν' constants, however. Although correlations with both ν and ν' were significant at the 99.9% confidence level, CL, the former accounted for 79.6% of the data while the latter accounted for 94.4% of the data. The difference in behavior between the two

types of ester may possibly be due to the differences in leaving group character between the *p*-nitrophenoxy group and the isopropoxy group, the former being a much better leaving group. Further work is required before we can make use of the steric effect of alkyl groups to indicate the geometry of the transition state in the reaction of esters of phosphorus oxy acids with nucleophiles. The dialkyl methyl phosphinates (set 7) give somewhat better correlation with ν (poor results) than with ν' (results not significant).

Our successful correlation of the pK_a s of phosphonic and phosphinic acids with steric parameters suggested to us that it might be useful to reexamine the $\sigma\phi$ constants of Kabachnik.¹⁵ These constants were defined from the pK_a s of phosphorus oxy acids and are intended to represent the effect of substituents at a phosphorus atom. It had previously been shown by one of us that¹⁶ $\sigma\phi$ is a function of σ_I and σ_R ; thus for 20 substituents,

$$\sigma\phi = L\sigma_I + D\sigma_R + c \quad (7)$$

Mastryukova and Kabachnik¹⁷ reinvestigated the correlation of values with eq 1 and reported a value of r of 0.931. Thus the correlation accounted for only 86.7% of the data although it was significant at the 99.9% CL. They ascribed this failure to account for more of the data to a difference in resonance effects between a substituent bonded to phosphorus and a substituent bonded to carbon. We have examined the correlation of $\sigma\phi$ values with the equation

$$\sigma\phi_X = L\sigma_{IX} + D\sigma_{RX} + S\nu_X + c \quad (8)$$

The σ_I and σ_R values were taken from our compilation;⁴ the ν_X values were from our previous work¹⁰ whenever possible. The σ_I value for *i*-PrCH₂CH₂ was assumed equal to the average value of -0.01 found for nine alkyl groups (only reliable values were considered). The σ_R values for *i*-Bu, *s*-Bu, *c*-C₆H₁₁, *i*-PrCH₂CH₂, and *t*-BuCH₂ were assumed equal to the average value of -0.16 found for nine alkyl groups. Again, only reliable values were considered. The σ_I values for CHCl₂ and CHPh₂ were calculated from the equation

$$\sigma_{I,CHX^1X^2} = 0.318\Sigma\sigma_{IX} + 0.005 \quad (9)$$

The σ_{R,CH_2Cl_2} value was estimated graphically from a plot of σ_R vs. the number of chlorine atoms for CCl_{*n*}H_{3-*n*} groups. The σ_R value for *i*-PrO, BuO, *i*-PrCH₂CH₂O, and *c*-C₆H₁₁O was assumed equal to the average σ_R value of -0.57 for OR groups. The σ_I values for BuCH₂O, *i*-PrCH₂CH₂O, and *c*-C₆H₁₁O were assumed equal to the average σ_I value of 0.28 for OR groups. The σ_I value of *i*-PrS and the σ_R value of PrS were assumed to be equal to the average values for SR groups of 0.26 and -0.27 , respectively. The σ_R value for the Ph₂CH group was obtained from the equation

$$\sigma_R = \sigma_P - \sigma_I \quad (10)$$

using a σ_P value reported by Little et al.¹⁸ The ν value for the PhO group was estimated from the equation

$$\nu_{OX} = 0.959\nu_{CH_2X} - 0.100 \quad (11)$$

to be 0.57. The $\sigma\phi$ values are taken from Mastryukova and Kabachnik. Of the 41 values of $\sigma\phi$ reported by these workers, we have used 38, excluding the values for the phenyl, vinyl, and Me₃SiCH₂ groups. These groups were not included in the correlation due to either uncertainty in or lack of the appropriate ν parameters. The results of the correlation with eq 8 are L , 4.09; D , 1.34; S , -0.551 , c , -0.428 ; correlation coefficient, 0.959; F , test for significance of regression; 131.5 (99.9% CL); partial correlation coefficients of σ_I on σ_R , σ_I on ν , σ_R on ν , 0.381 (95.0% CL), 0.167 (<90.0% CL), 0.405 (98.0% CL); standard errors of the estimate, L , D , S , and c , 0.191, 0.213 (99.9% CL), 0.155 (99.9% CL), 0.113 (99.9% CL), 0.112 (99.9% CL), 38 points. The correlation obtained is excellent and accounts for 92.1% of the data. This represents a significant improvement over the results of Mastryukova and Kabachnik and indicates that *most* of the effect of a substituent attached to phosphorus can be accounted for in terms of the *same electrical effects and steric effects which the substituent exerts when attached to carbon*. The 7.9% of the data which remains unaccounted for may be due in part at least to errors in determining $\sigma\phi$ constants for strong acceptor groups such as F, Cl, DFa, and CCl₃. We find it particularly significant and rewarding that values for such a wide range of substituent effects give a correlation with significant at the 99.9% confidence level as this substantiates the argument that ν values for alkoxy, alkylthio, and dialkylamino groups are indeed on the same scale as the other ν values.

Supplementary Material Available: Complete statistics for all of the sets studied (2 pages). Ordering information is given on any current masthead.

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