THE APPLICATION OF THE HAMMETT EQUATION TO CYCLOPHOSPHAZENES

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THE APPLICATION OF THE HAMMETT EQUATION TO CYCLOPHOSPHAZENES

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The applicability of the extended Hammett equation to substituted cyclophosphazene pK_a values taken from the literature is demonstrated. Steric effects were shown to be absent or constant by correlation with the LDS form of the extended Hammett equation. The magnitude and composition of the electrical effects in the cyclotriphospha-triazenes is generally comparable to that observed for 2-substituted pyrimidines and 6-substituted-2,4-diamino-1,3,5-triazines, and differs significantly from that observed for 2- and 4-substituted pyridines. The data were also correlated with the Kabachnik equation. The results that were obtained with the extended Hammett equation were at least as good as those obtained with the Kabachnik equation.

Some time ago we investigated the application of the extended Hammett equation

$$Q_X = L\sigma_{IX} + D\sigma_{RX} + h \qquad (1)$$

to the effect of substituents at phosphorus on the reactivity of tetrahedral $P(V)$ compounds.[1] In the course of that work we briefly examined the correlation of pK_a's for $P_3N_3X_6$ and $P_4N_4X_8$ with Eq. 1. We now present a more detailed study of the correlation of pK_a's of several sets of substituted cyclo-phosphazenes. Our objective is to provide new insights into the application of correlation analysis to systems bearing a substituent bonded to phosphorus.

Shaw and coworkers[2] have proposed a set of sub-stituent constants α_X and γ_X which represent the effect of substituents in the α and γ positions of cyclotriposphatriazene, I, respectively.
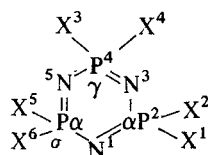
(I) X = any substituent unless otherwise noted

(II) $X^1 = X^2 = X^5 = X^6 = Me_2N$ or EtNH

(III) $X^1 = X^3 = X^4 = X^5 = Me_2N$ or EtNH

(IV) $X^1 = X^3 = X^5 = NMe_2$

In this work we examine the relationship between these constants and the substituent parameters σ_I and σ_R which are commonly used to represent the

localized (field and/or inductive) and delocalized (resonance) effects of substituents bonded to carbon. Our recent results[3] suggest that in the correlation of pK_a's for acids of the type $XPO(OH)_2$ and $X^1X^3PO(OH)$, a steric term is required. We have therefore made use of the localized, delocalized, and steric effects (LDS) equation,

$$Q_X = L\sigma_{IX} + D\sigma_{RX} + S\nu_X + h \qquad (2)$$

in which the parameter ν^4 is a measure of the steric effect of the X group. The α_X and γ_X values used in the correlations are reported in Table I. The σ_I constants required are from our collection[5] whenever possible. The σ_R values are calculated from the equation

$$\sigma_R = \sigma_p - \sigma_I \qquad (3)$$

using σ_p values taken from the compilation of McDaniel and Brown.[6] Values of σ_I and σ_R from other sources are given in Table III. The ν parameters required are taken from our previous work when available. Other values of ν have been estimated assuming additivity. Thus, the value of ν for the EtO group can be estimated as follows—the effect of the Et group is determined by the difference between ν_{CH_3} and ν_{CH_2Et}. This $\Delta\nu$ is then added to the value of ν for the OH group.

$$\nu_{CH_2Et} - \nu_{CH_3} = 0.68 - 0.52 = 0.14 \qquad (4)$$

$$\nu_{OEt} = \nu_{OH} + 0.14 = 0.32 + 0.14 = 0.46 \qquad (5)$$

These ν values, while only approximate, nevertheless, represent an improvement over our previous method

which assumed that the ν value was determined by the van der Waals radius of that atom of the substituent closest to the reaction site. Results of the best correlations are reported in Table II.

The confidence level of the "t test" for the significance of S in Eq. 2 shows that S is not significant for both the α and the γ substituent constants. Using our previous criteria for the possible existence of steric effects,[6] we are forced to the conclusion that steric effects are either absent or constant in the protonation of cyclotriphosphatriazenes. In the absence of experimental values for the compounds in which X = H it is not possible to distinguish between no steric effect and a constant steric effect,[6] at least by any method now known to us. Correlation of pK_a's for the other cyclophosphazene sets studied (Table I) with the LDS equation showed that in all cases, S was not significant and therefore steric effects were absent or constant. Correlation of the data with the extended Hammett equation (Eq. 1) gave better results. The results are very much improved by the exclusion of the value for X = CF_3CH_2O from these sets, sets 1, 2. This is shown by the values of the confidence level of the F test and of $100R^2$. The latter quantity increases from 83.1 to 97.0 for the α and from 85.6 to 97.0 for the γ substituent constants.

The first ionization constants of cyclotriphosphatriazenes and cyclotetraphosphatetrazenes (sets 11, 12; Table I) were then correlated with Eq. (1) giving excellent results. Correlation of the second ionization constants of the cyclotetraphosphatetrazenes (set 13). Correlation with Eq. (1) gave results which were not significant.

The first ionization constants of the geminal $N_3P_3(NMe_2)_4X_2$ and $N_3(_3(NHEt)_4X_2$, sets 14 and 15, were also studied. In correlating these ionization constants we considered the possibility of annular tautomerism suggested by Shaw and his coworkers.[2] From our correlations with Eq. (1) of the pK_a's of $N_3P_3X_6$, the NMe_2 and EtNH groups behave as electron donors relative to the other substituents in sets 14 and 15. Thus, in II, the site of protonation ought to be the ring nitrogen atom with the highest electron density. This is N^1 which is flanked by NMe_2 groups attached to its two adjacent phosphorus atoms. When X is NMe_2 or NHEt, an appropriate statistical factor of 3 is required, as N^1, N^3, and N^5 are equivalent in that case. The results obtained for set 14 are fair while those for set 15 are not significant as determined by the confidence level of the F test. This poor correlation is undoubtedly due to the fact that each set contains only four points. To circumvent

TABLE I

Data used in the correlations

1. Values of $\alpha_\chi{}^a$
   NHMe, 5.8; NMe₂, 5.6; 4-MeC₆H₄, 4.5; Ph, 4.2; 4-ClC₆H₄, 3.7; EtS, 3.6; OMe, 3.6; PhS, 3.0; PhO, 3.1; OCH₂CF₃, 1.0

2. Values of $\gamma_\chi{}^a$
   NHMe, 3.1; NMe₂, 2.8; Ph, 2.3; 4-ClC₆H₄, 2.0; EtS, 1.8; MeO, 1.8; PhS, 1.5; PhO, 1.3; OCH₂CF₃, 0.3

11. pK_a, $N_3P_3X_6$ in $PhNO_2$ at 25°[a-f]
    EtO, 0.20; PhCH₂O, −2.10; EtS, −2.75; PhCH₂S, −4.15; PhS, −4.80; Et, 6.40; Ph, 1.50; Me₂N, 7.60; EtNH, 8.20; MeNH, 8.80; NEt₂, 8.50; 4-ClC₆H₄, −1.35; OMe, −1.9; OPh, −5.8; NHPh, 1.2; OBu, 0.1; OiPr, 1.4

12. pK_a, $N_4P_4X_8$ in $PhNO_2$ at 25°[b-e]
    EtO, 0.60; Et, 7.60; Ph, 2.20; Me₂N, 8.30; EtNH, 8.10; MeNH, 8.20; Et₂N, 8.30; PhCH₂O, −1.6; MeO, −1.0; PhO, −6.0; BuO, 0.7; iPrO, 2.1

13. pK_{a₂}, $N_4P_4X_8$ in $PhNO_2$ at 25°[b,c]
    NHMe, 3.4; NHEt, 3.8; NMe₂, 0.6; NEt₂, −0.9; Ph, −5.8; Et, 0.2

14. pK_a, gem $N_3P_3(NMe_2)_4X_2$ in $PhNO_2$ at 25°[g,h]
    EtS, 4.7; PhS, 4.0; Ph, 6.2; NMe₂, 7.1[i]

15. pK_a, gem $N_3P_3(NHEt)_4X_2$ in $PhNO_2$ at 25°[d,g,h]
    Ph, 7.4; NHEt, 7.70;[i] OCH₂CF₃, 3.7; Cl, 3.2

16. pK_a, gem $N_3P_3(NR^1R^2)_4X_2$ in $PhNO_2$ at 25° (combination of sets 14 and 15)

17. pK_a, $N_3P_3(NMe_2)_4X_2$ non-gem, in $PhNO_2$ at 25°[f,g]
    PhS, 2.8; PhO, 3.3; EtS, 3.8; Me₂N, 7.41;[j] Cl, −1.4

18. pK_a, $N_3P_3(NHEt)_4X_2$ non-gem in $PhNO_2$ at 25°[d,g]
    Cl, 1.4; CF₃CH₂O, 2.7; EtNH, 8.0[j]

19. pK_a, non-gem, $N_2P_3(NR^1R^2)_4X_2$ in $PhNO_2$ at 25°. (combination of sets 17 and 18)

20. pK_a, non-gem, $N_3P_3(NMe_2)_3X_3$ in $PhNO_2$ at 25°[f-h]
    OPh, 1.05; Me, 7.3; NMe₂, 7.6; Ph, 4.1; Cl, −5.5

[a] Ref. 2.

[b] D. Feakins, W. A. Last and R. A. Shaw, *Chem. Ind. (London)* 510 (1962).

[c] D. Feakins, W. A. Last, N. Neemuchwala and R. A. Shaw, *Chem. Ind. (London)*, 164 (1963).

[d] D. Feakins, W. A. Last and R. A. Shaw, *J. Chem. Soc.*, 444 (1964).

[e] D. Feakins, W. A. Last, N. Neemuchwala and R. A. Shaw, *J. Chem. Soc.*, 2804 (1965).

[f] D. Feakins, W. A. Last, S. N. Nabi and R. A. Shaw, *J. Chem. Soc.* A, 1831 (1966).

[g] D. Feakins, W. A. Last, S. N. Nabi, R. A. Shaw and P. Watson, *J. Chem. Soc.* A, 196 (1969).

[h] D. Feakins, R. A. Shaw, P. Watson and S. N. Nabi, *J. Chem. Soc.*, A, 2468 (1969).

[i] Includes statistical factor 3.

[j] Includes statistical factor 3/2.

this problem, the data from the two sets were combined into a single set (set 16). The justification for this is that the electrical effects of the dimethylamino and the ethylamino groups are about the same ($\sigma_I = 0.10, 0.10$; $\sigma_R = -0.93, -0.94$) respectively. Steric effects were shown, above, to be absent in the

ionization of $N_3P_3X_6$. Results of the correlations with Eq. (1) are very much improved, the confidence level obtained for the F test of the combined sets (set 16) is 99.5%. The results are somewhat improved by the exclusion of the pK_a for X = Ph, R^1 = Et, R^2 = H, as is shown by the values of $100R^2$, 92.6 and 96.8, respectively.

Considering the first ionization constants of the non-geminal $N_3P_3(NMe_2)_4X_2$ which have structure III (set 17), the possibility of annular tautomerism again occurs. Arguing as before, that the ring nitrogen atoms with the highest electron density are those flanked by the greatest number of R^1R^2—N groups, we conclude that protonation will occur preferentially at N^3 and N^5. Correlation with Eq. (1) gave a poor but significant result. Again, the problem seems to be the small number of points in the set. To overcome this difficulty we have once more resorted to the combination of pK_a's for III, R^1 = R^2 = Me (set 17) with those for III, R^1 = Et, R^2 = H (set 18).

Correlation of the combination set (set 19) with Eq. (1) gave excellent results as is shown by the confidence level of the F test. Exclusion of the value for X = Cl, R^1 = R^2 = Me very much improved the results as is shown by the values of $100R^2$ of 91.8 and 98.9, respectively.

Finally, we have examined the first ionization constants of non-geminal $N_{3(3}X_3(NMe_2)_3$ (set 10), IV. In these compounds, the three ring nitrogen atoms are completely equivalent. Correlation with Eq. (1) was fair. Once again, the results would undoubtedly have been improved had more points been available.

A problem of interest to us is that of the magnitude of L and D for substituents at the 2 and 4 positions. We can obtain the values of L_4 and D_4 for the geminal $N_3P_3(NR^1R^2)_4X_2$, II, very easily as the effect of the substituents on the reacting ring nitrogen is given by

$$pK_a\ X = 2L_4\sigma_{IX} + 2D_4\sigma_{RX} + h \qquad (6)$$

$$= L_g\sigma_{IX} + D_g\sigma_{RX} + h \qquad (7)$$

From the values of L_g and D_g in Table II (Set 16),

$$L_4 = -4.68, \qquad D_4 = -0.805$$

Values of L_2 and D_2 for the non-geminal $N_3P_3(NR^1R^2)_4X_2$ may be calculated as follows: the effect of the substituents on the ring nitrogen undergoing protonation is given by

$$pK_a = L_a\sigma_{IX} + L_4\sigma_{IX} + D_2\sigma_{RX} + D_4\sigma_{RX} + h \qquad (8)$$

$$= L_{ng}\sigma_{IX} + D_{ng}\sigma_{RX} + h \qquad (9)$$

Assuming that $L^4{}_{gem} = L^4{}_{non\text{-}gem}$, $D^4{}_{gem} = D^4{}_{nobgem}$ and substituting into the equations

$$L_{ng} = L_2 + L_4; \qquad D_{ng} = D_2 + D_4 \qquad (10)$$

using the values of L_{ng} and D_{ng} given in Table II (Set 19), gives

$$L_2 = -6.12; \qquad D_2 = -2.71$$

In each of the above sets there are constant NR^1R^2 groups. Constant substituents are known to have an effect upon the values of L and D. Thus, the values of L and D for the $N_3P_3X_6$ and the non-geminal $N_3P_3(NMe_2)_3X_3$ differ from those above. The ratios L_2/L_4 and D_2/D_4 should remain approximately constant, however. These ratios are

$$L_2/L_4 = 1.31; \qquad D_2/D_4 = 3.36$$

The substituent effects in the $N_3P_3X_6$ are given by

$$pK_a = 4L_2\sigma_{IX} + 2L_4\sigma_{IX} + 4D_2\sigma_{RX} + 2D_4\sigma_{RX} + h \qquad (11)$$

$$= L'\sigma_{IX} + D'\sigma_{RX} + h \qquad (12)$$

Since

$$L' = 4L_2 + 2L_4; \qquad D' = 4D_2 + 2D_4 \qquad (13)$$

and L and D are known, set 11, We have $L_2 = -5.96$; $L_4 = -4.56$; $D_2 = -1.96$; $D_4 = -0.582$. For the non-geminal $N_3P_3(NMe_2)_3X_3$ for which the substituent effect may be written

$$pK_a = 2L_2\sigma_{IX} + L_4\sigma_{IX} + 2D_2\sigma_{RX} + D_4\sigma_{RX} + h \quad (14)$$

$$= L''\sigma_{IX} + D''\sigma_{RX} + h^{\cdot\cdot} \qquad (15)$$

Making use of the relationships

$$L'' = 2L_2 + L_4; \qquad D'' = 2D_2 + D_4 \qquad (16)$$

and the values of L'' and D'' in Table II (Set 20) $L_2 = -8.43$, $L_4 = -6.44$; $D_2 = -2.39$, $D_4 = -0.710$.

Finally, we can estimate L_4 in $N_4P_4X_6$ by making the assumption that L_2 for this system is equal to L_2 for $N_3P_3X_6$. The effect of the substituents in $N_4P_4X_8$ is given by

$$pK_a = 4L_2\sigma_{IX} + 4L_4\sigma_{IX} + 4D_2\sigma_{RX} + 4D_4\sigma_{RX} + h \qquad (17)$$

$$= L'''\sigma_{IX} + D'''\sigma_{RX} + h \qquad (18)$$

and

$$L''' = 4L_2 + 4L_4 \qquad (19)$$

TABLE II

Results of correlations with Eq. (1) and Eq. (2)

Set	L	D	h	R^a	F^b	$r_{12}{}^c$	Set	$100R^{2r}$	$s_{est}{}^d$	$s_L{}^d$	$s_D{}^d$	$s_h{}^d$	n^e
1	−6.76	−1.78	4.7	0.985	95.58[k]	0.068	1	97.0	0.204	0.655[k]	0.210[k]	0.170[k]	9
2	−4.47	−0.802	2.6	0.985	79.92[k]	0.186	2	97.0	0.128	0.446[k]	0.141[f]	0.127[k]	8
11	−33.0	−8.99	3.2	0.980	171.8[k]	0.065	11	96.1	1.04	2.30[k]	0.836[k]	0.679[k]	17
12	−33.8	−7.07	5.1	0.981	116.1[k]	0.025	12	96.3	1.04	2.44[k]	1.06[k]	0.832[k]	12
13	−40.9	−9.1	−2.8	0.871	4.727[p]	0.638	13	75.9	2.21	20.9[m]	2.99[o]	1.79[h]	6
14	−11.4	−1.08	7.2	0.9992	332.7[g]	0.450	14	99.8	0.0994	0.595[g]	0.162[o]	0.155[i]	4
15	−12.3	−0.215	8.6	0.991	26.06[p]	0.340	15	98.1	0.565	1.83[o]	0.952[q]	0.780[o]	4
16	−9.36	−1.61	6.8	0.984	60.06[j]	0.497	16	96.8	0.389	1.23[f]	0.523[g]	0.481[k]	7
17	−16.8	−2.72	7.1	0.952	9.603[o]	0.645	17	70.6	1.36	6.32[m]	2.88[h]	2.93[m]	5
19	−10.8	−3.51	5.5	0.995	189.6[k]	0.756	19	98.9	0.318	1.39[f]	0.622[f]	0.671[f]	7
20	−23.3	−5.48	5.5	0.977	20.58[g]	0.091	20	95.4	1.65	3.78[g]	2.37[m]	1.35[o]	5

[a] Multiple correlation coefficient.

[b] F test for significance of regression. Superscript indicates confidence level (CL).

[c] Partial correlation coefficient of σ_I on σ_R.

Confidence levels less than 90.0% unless otherwise indicated by superscripts.

[d] Standard errors of the estimate, L, D, and h. Superscripts indicate the confidence level of the "Student t" test for significance of L, D, and h.

[e] Number of points in set.

[f] 99.0% CL.

[g] 95.0% CL.

[h] 50.0% CL.

[i] 98.0% CL.

[j] 99.5% CL.

[k] 99.9% CL.

[l] 97.5% CL.

[m] 80.0% CL.

[n] 20.0% CL.

[o] 90.0% CL.

[p] <90.0% CL.

[q] <20.0% CL.

[r] Percent of data accounted for by the correlation.

Substituting in 19, the value of L''' obtained from Table II (Set 12) and the value of L_2 obtained for $N_3P_3X_6$, we find

$$L_4 = -2.49$$

The assumption that $L_{2,N_3P_3X_6} = L_{2,N_4P_4X_8}$ is justified on the basis of the similarity in geometry between substituents in positions 2 and 6 of $N_3P_3X_6$ and positions 2 and 8 of $N_4P_4X_8$. This dependence on the similarity in structure will be true whether the electrical effect is largely inductive or largely field in nature. Unfortunately, D_2 and D_4 cannot be estimated for $N_4P_4X_8$ and D_2 in this system is not necessarily equal to D_2 for $N_3P_3X_6$.

We felt it would be interesting to compare the values of L and D obtained for the cyclophosphazenes with those obtained for appropriate aza-arenes. Such comparisons are made in Table IV. The aza-arenes chosen were 2-substituted pyrimidines, V, which provide a model of L_2 and D_2 and, 2-substituted

-4,6-diamino-1,3,5-triazines, VI. The X groups that are electron acceptors by the localized effect should cause protonation at N_5 and therefore provide an estimate of L_4 and D_4.
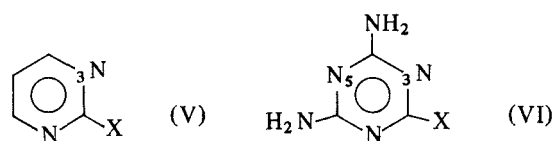
The magnitudes of L and D obtained for the aza-arenes are comparable to those obtained for the cyclophosphazenes. This is not conclusive in itself, however, as the cyclophosphazene data were determined in $PHNO_2$ while the aza-arene results were in water. It is also instructive to compare the results with those obtained for pyridine in water. Values of L and D for 2- and 4-substituted pyridines are also set forth in Table IV. Those values do not agree

TABLE III

Values of σ_I and σ_R

X	σ_I	Ref.	σ_R	Ref.
NHMe	0.10	a		
NMe₂	0.10	c		
NHEt	0.10	d	−0.94	d
NEt₂	0.10	d	−0.93	d
4-MeC₆H₄	0.09	f	−0.14	g
4-ClC₆H₄	0.13	f	−0.05	g
PhS			−0.22	a
PhO			−0.53	e
OCH₂CF₃	0.37	h	−0.43	i
PhCH₂O	0.34	e	−0.57	e
PhCH₂S			−0.16	b
NHPh	0.15	a	−0.55	a
OiPr	0.26	a	−0.57	e

ᵃ Footnote 9.

ᵇ M. Charton, *J. Org. Chem.*, **36**, 882 (1971).

ᶜ M. Charton, *J. Org. Chem.*, **36**, 266 (1971).

ᵈ Assumed equal to the value for the corresponding N methyl group.

ᵉ M. Charton, *J. Org. Chem.*, **34**, 1877 (1969).

ᶠ Calculated from the pK_a of the appropriate acetic acid.

ᵍ From σ_p values given by E. Berliner and L. H. Liu, *J. Amer. Chem. Soc.*, **75**, 2417 (1953).

ʰ Calculated from the equation σ_{I,OCH_2CF_3} = 0.539 σ_{I,CH_2CF_3} + 0.29.

ⁱ From σ_{p,OCH_2CF_3} calculated by the method of Charton, *J. Org. Chem.*, **28**, 3121 (1963).

nearly as well with the cyclophosphazene values as those of V and VI.

Another property of interest is the composition

of the electrical effect for which we have proposed the quantity P_R as a measure.[8]

$$P_R = \frac{D \cdot 100}{L + D} \qquad (20)$$

Values of $P_{R^{,2}}$ and $P_{R^{,4}}$ are presented in Table IV. These values express the composition of the electrical effect of a substituent at positions 2 and 4, respectively, of the cyclotriphosphatriazene ring. The values of $P_{R^{,2}}$ are in good agreement with those for 2-substituted pyrimidines and pyridines. The value of $P_{R^{,4}}$ is about half that for the 1,3,5-triazine system and about one fourth that of the 4-substituted pyridines. Thus, the composition of the electrical effect at the 2 position of cyclotriphosphatriazenes is comparable to that in aza-arenes while this is not the case for the composition of the electrical effect in the 4 position.

Finally, we may consider the use of the Kabachnik[9] modification of the Hammett equation to correlate the data studied here. In this relationship, Eq. (21), special substituent constants are defined for substituents attached to tetrahedral phosphorus. The $\sigma_{\phi X}$ constants were defined from the pK_a values

$$pK_a = \rho_\phi \sigma_{\phi X} + h \qquad (21)$$

of disubstituted phosphinic acids in water at 25°. Kabachnik[10] has claimed that this equation is superior to Eq. (1) in correlating sets involving substitution at phosphorus. We have therefore correlated sets 11, 12, 16, 19 and 20 with Eq. (21). In all but set 20, it was necessary to exclude some points as

TABLE IV

Values of L, D, and P_R

System	$-L_2$	$-D_2$	$-L_4$	$-D_4$	P_{R_2}	P_{R_4}
P₃N₃X₆	5.96	1.96	4.56	0.582	24.7	11.3
P₃N₃(NR¹R²)₄X₂	6.12	2.71	4.68	0.805	30.7	14.7
P₃N₃(NMe₂)₃X₃	8.43	2.39	6.44	0.710	22.1	9.93
P₄N₄X₈	5.96		2.49			
2-substituted pyrimidines	6.30ᵃ	3.29ᵃ			34.3	
2-X-4,6-(NH₂)₂-1,3,5-C₃N₃ᵉ			4.29ᵃ	1.30ᵃ		23.3
2-subst.-pyridines	11.3ᵇ,ᶜ	2.31ᵇ,ᶜ			17.0ᶜ	
2-subst.-pyridines	9.18ᵇ,ᵈ	2.64ᵇ,ᵈ			22.3ᵈ	
4-subst.-pyridines			5.38ᵃ	5.11ᵃ		48.7

Cyclophosphazene data in PhNO₂ at 25°, aza-arene data in H₂O at 20–25°.

ᵃ M. Charton, unpublished results.

ᵇ M. Charton, *J. Org. Chem.*, **36**, 882 (1971).

ᶜ 25°.

ᵈ 20°.

ᵉ X may be any substituent.

TABLE V

Results of Correlations with the Kabachnik Equation

Set	ρ_ϕ	h	r[a]	F[b]	s_{est}[c]	s[c]	s_h[c]	$100R^2$	n[e]
11	7.78	−2.48	0.979	207.4[f]	0.972	0.540[f]	0.392[f]	95.8	11
12	7.83	−1.90	0.966	96.44[f]	1.34	0.797[f]	0.634[h]	93.2	9
16	1.87	4.09	0.991	110.7[g]	0.280	0.178[g]	0.143[f]	98.2	4
19	2.78	4.03	0.9999	7223.0[f]	0.0511	0.0327[f]	0.0255[f]	100.0	4
20	5.96	1.18	0.980	74.09[i]	1.23	0.692[g]	0.586[j]	96.1	5

[a] Correlation coefficient.
[b] F test for significance of regression. Superscript indicates confidence level.
[c] Standard error of the estimate, ρ_ϕ, and h. Superscripts indicate confidence level of the "Student t" test.
[d] Percent of data accounted for by correlation.
[e] Number of points in the set.
[f] 99.9% CL.
[g] 99.0% CL.
[h] 95.0% CL.
[i] 97.5% CL.
[j] 80.0% CL.

σ_ϕ values were unknown for the substituents. Groups excluded were:

11. $PhCH_2O$, $PhCH_2S$, PhS, $EtNH$, $NHMe$, $PhNH$
12. $EtNH$, $MeNH$, $PhCH_2O$
16. PhS, $NHEt$, OCH_2CF_3
19. PhS, OCH_2CF_3, $EtNH$

The results of correlations are set forth in Table V. Due to the difference in numbers of points in the majority of the sets the most useful statistic for comparison of correlations between Eq. (1) and Eq. (21) is $100R^2$. Comparing these values, we observe that Eq. (1) is superior in set 12, equivalent in sets 11 and 20 and somewhat inferior in sets 16 and 19. As sets 11 and 12 contain the greatest number of points and therefore provide the most rigorous test, we believe that the results show that for cyclophosphazenes at least, Eq. (1) is certainly as effective as Eq. (21). It is worth noting that these results were obtained with a special value of $\sigma_{\phi,OPh}$

for use in non-aqueous solvents, whereas the σ_I and σ_R constants used are for protonic solvents. Thus, this may be taken as support for our conclusion that Eq. (1) is as useful as the Kabachnik equation.

REFERENCES

1. M. Charton, *J. Org. Chem.* 34, 1877 (1969).
2. D. Feakins, W. A. Last, S. N. Nabi, R. A. Shaw and P. Watson, *J. Chem. Soc., A*, 196 (1969).
3. M. Charton and B. I. Charton, unpublished results.
4. M. Charton, *J. Am. Chem. Soc.* 97, 1552 (1975).
5. M. Charton, *J. Org. Chem.* 29, 1222 (1964).
6. M. Charton, *J. Org. Chem.* 40, 407 (1975).
7. M. Charton, *Chem. Tech.* 502 (1974).
8. M. Charton, *Prog. Phys. Org. Chem.* 10, 81 (1973).
9. T. A. Mastryukova and M. I. Kabachnik, *Russian Chem. Rev.* 38, 795 (1969).
10. T. A. Mastryukova and M. I. Kabachnik, *J. Org. Chem.* 36, 1201 (1971).
11. $\sigma_{\phi,OPh}$ = 0.28 in nonaqueous media. M. I. Kabachnik, private communication.