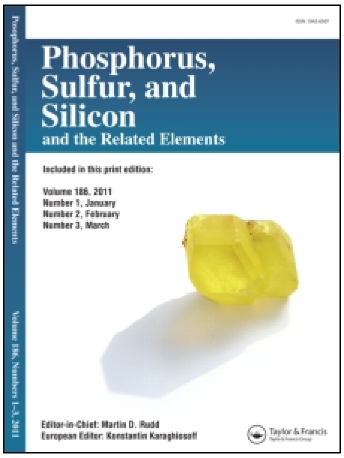

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SUBSTITUENT EFFECTS OF ORGANOPHOSPHORUS ESTERS IN STRUCTURE REACTIVITY STUDIES

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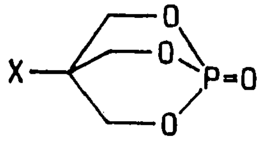
Abstract An empirical approach for the estimation of substituent polar and steric parameters of organophosphorus compounds was suggested by experimental measurements and theoretical calculations.

INTRODUCTION

In QSAR studies of organic compounds it is necessary to evaluate the contribution of polar(electronegativity, field, resonance, polarizability) and steric effects of the substituents directly bonded to the reaction centre. For the chemistry of carbon compounds, there are some sets of parameters including Hammett σ, Taft σ^{*}, Es and Charton's υ. In the field of organophosphorus chemistry, Kabachnik and his coworkers introduced a new scale (σ_{Φ}) for the polarity of substituents based on the pKa measurement of various kinds of phosphorus acids.[1,2] In recent years we extended this method for the evaluation of the substituent effects of long chain alkyl and alkoxyl groups.[3] We demonstrated that as an empirical parameter, σ^{Φ} is useful, at least in certain extent, in QSAR studies by correlation analyses including IR, NMR spectroscopic investigations,[3] alkaline hydrolysis[4] as well as metal extraction reactions[5,6] by organophosphorus esters. However, the σ^{Φ} parameters reflect not only polar but also other structural effects, since the contribution of the steric effect could not be excluded in such treatments. It is therefore very interesting to examine the substituent effect of organophosphorus compounds in more strict manner.

SUBSTITUENT POLAR EFFECT

The structural effect of 4-substituted-2,6,7-trioxa-1-phosphabicyclo-[2,2,2]octane-1-oxide (**1**), in which the influence of steric effect of substituent on position 4 can be eliminated, was evaluated on the basis of the difference of chemical shift in ^{31}P NMR between methanol and deuterated as represented by $\Delta\delta_{\text{acetone}}\,^{31}P$ NMR was investigated.



1

X = Et, Pr, i-Pr, s-Bu, s-Am, t-Bu, MeO, EtO, Cl, NO_2,
COOEt, COOH, CH_2OH, CMe_2OH, MeCH=CH, CH_2=CMe_2.

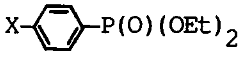
The $\Delta\delta\ ^{31}P$ obtained from Equation 1 may be considered as a quantitative measure of the proton affinity or the Lewis basity of phosphoryl oxygen of the compounds under investigation. It was observed that the $\Delta\delta\ ^{31}P$

$$\Delta\delta\ ^{31}P = \delta\ ^{31}P(MeOH) -- \delta\ ^{31}P[(CD_3)_2CO] \qquad (1)$$

values of alkyl substituted bicyclic phosphate are almost the same. therefore, the average $\Delta\delta\ ^{31}P$ value for alkyl groups is taken as reference, from which $\Delta\Delta\delta\ ^{31}P$ can be derived by subtracting $\Delta\delta\ ^{31}P$ of methyl group. Such parameter may be used as a measurement of polar effect of group studied relative to alkyl radical.

Since the correlation analyses involving $\Delta\delta\ ^{31}P$ and q_o obtained from MNDO calculation provide excellent results, it is reasonable to conclude that the $\Delta\delta\ ^{31}P$, as suggested in this paper, is a function of the charge density of phosphoryl oxygen. On the other hand, as shown by us, $\Delta\delta\ ^{31}P$ is correlated linearly with σ value of the substituents.

For investigating the substituent polar effect in conjugated phosphorus esters, a series of diethyl p-substituted phenylphosphonates(2)



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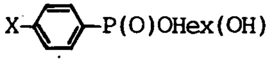


3

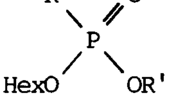
X = H, Me, Et, i-Pr, n-Bu, i-Bu, t-Bu, n-Oct, MeO,
Me_2N, Cl, COOEt.

and corresponding mono-hexyl esters (**3**) was synthesized and studied in the similar manner. Experimental data showed that the q_o calculated by MNDO method for various alkyl groups are almost the same. In the meantime, regression analyses of q_o with $\Delta\delta\ ^{31}P$ gave only poor cofficients. However, $\Delta\delta\ ^{31}P$ is linearily dependent on E_{HOMO}. For the acidic phosphorus esters (**3**), Both pKa and $\Delta\delta^{31}P$ are the function of σ constants of the nuclear substituents.

Our results revealed that both the inductive constants[7] or Hammett's parameters widely used in the chemistry of carbon compounds are applicable in correlation analysis of organophosphorus esters, or probably for organophosphorus compounds in general. Consequently, it seems unnecessary to define a new set substituent polar parameters in phosphorus chemistry.

SUBSTITUENT STERIC EFFECT

a significant difference of the substituent steric parameters of organophosphours esters from carbon compounds was evidenced by poor results in correlation analyses using Taft's Es or Charton's υ in the alkaline hydrolysis of alkylphosphonates resulted from the larger steric influences of the substituents for phosphonates than that for carboxylates. It may be rationalized by the fact that in the process of alkaline hydrolysis of a carboxylate involves the transformation from trigonal carbon to tetrahedral carbon while the hydrolysis of alkylphosphonate proceedes from tetrahedral to bipyramidal phosphorus atom. Therefore, since the structural change between ground state and transition state in the carboxylate hydrolysis is completely different from the phosphonate hydrolysis, the steric influence of substituent might be quite different too. On the other hand, to our surprise, the structural effect of R or RO group on $\delta\ ^{31}P$ or pKa of compounds **4**, in which the substituents are directly bonded to phosphorus, is not interpretative in term of Es or υ.



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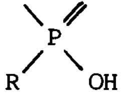


5

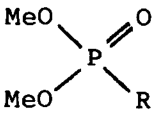
4 R' = H or Hex, R = Me, Pr, i-Pr, Bu, i-Bu, s-Bu, t-Bu,
Am, i-Am, Oct, i-Oct, s-Oct.

5 R = Oct, Me_3C, $EtCMe_2$, $HexCMe_2$

As an empirical substituent steric parameter, E_s^P was suggested for organophosphorus esters based on ^{31}P NMR and pKa investigation of **4** and **5**.

For the evaluation of the substituent steric effect on the hydrolytic process of alkylphosphonates, Molecular Mechanics Calculation (Allinger's 1977 force field, MM2, 1985 version) was applied. Our results indicate that the difference of energy between the tetracoordinated and pentacoordinated species represents a good measurement of the steric effect of substituents in phosphorus compounds[8].

In order to find the most stable conformation of dialkyl alkylphosphonates, the lower homologue, dimethyl methylphosphonate **6** was taken as a model compound, and the most stable conformation of alkylphosphonates with large alkyl group can thus be estimated by substitution of Me with alkyl group. The most stable conformation of **6** possesses two RO groups gauche to P=O (**6a**) and the most stable conformation of its pentacoordinated species **7** has two OH groups in axial position in the trigonal bipyramid (**7a**). From the steric energies of **6a** and **7a** the ΔE_R and $\Delta\Delta E_R$



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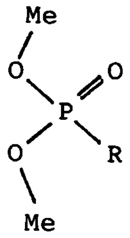
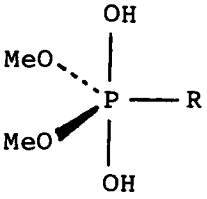


6a



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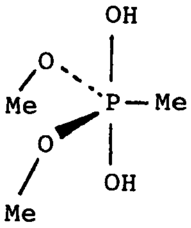

7a

of the reaction can be evaluated. As demonstrated by us $\Delta\Delta E_R$ works well as steric parameter, which is significantly better than Es, υ , and υ' scales, in the multiple regression analysis of organophosphorus compds.

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REFERENCES

1. M.I.Kabachnik Tetrahedron **9** 10 (1960)
2. T.A.Mastryukova and M.I.Kabachnik J. Org. Chem. **36** 1201 (1971)
3. C.Y.Yuan, S.S.Hu Acta Chimica Sinica **44** 590 (1986)
4. C.Y.Yuan, S.G.Yuan and S.S.Hu Acta Chimica Sinica **46** 159 (1988)
5. C.Y.Yuan and S.S.Yuan Scientia Sinica (B) **31** 137 (1988)
6. C.Y.Yuan, Q.R.Xu,S.G.Yuan, H.Y.Long, D.Z.Shen, Y.T.Jiang, H.Z.Feng, F.B.Wu and W.H.Chen Solv. Extr. and Ion Exch. **6** 393 (1988)
7. M.Charton J. Org. Chem. **29** 1222 (1964)
8. S.S.Li, X.G.Liao and C.Y.Yuan J. Phys. Org. Chem. **2** 146 (1989)