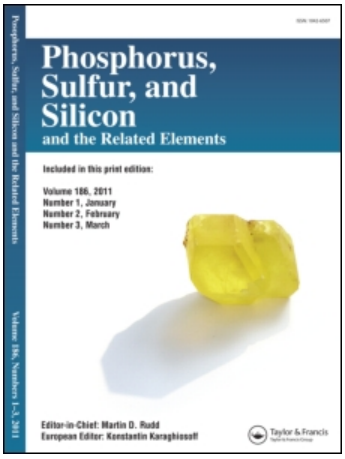

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Computational and Theoretical Chemistry in Structure-Reactivity Studies of Organophosphorus Compounds

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Computational multivariation analysis, molecular orbital calculation as well as molecular mechanics study were used for the qualitative and quantitative evaluation of the relationship between chemical structure and reactivity of organophosphorus compounds.

Keywords: computational chemistry; molecular orbital calculation; molecular mechanics; organophosphorus compounds

INTRODUCTION

Organophosphorus compounds comprise an important group of organic moleculeswith remarkable biological and technological significances. Structure-reactivity studies which usually provide an empirical or theoretical basis for the design of new compounds, attract great interest of chemists. As one of important fields of application of phosphorus compounds, extractive separation of metals may be regarded as a multi-componental coordination process between heterogenous phases. The limitation of SRS based on univariation analysis is understandable. Early in the eightieth a computational multivariation analysis, pattern recognition processing was introduced by us for the evaluation of contribution of chemical structure to extraction behaviour of uranium by phosphorus-based ligand.[1] Later on new approaches consisting cluster and factor analyses were reported for SRS of acidic phosphorus esters in rare earth separation[2]. HMO and MNDO are helpful for such investigation.[3] Some foundamental aspects in phosphorus chemistry including ^{31}P NMR chemical shifts, rate of hydrolysis as well as asymmetric addition of phosphorus esters were examined by molecular mechanics calculation.

RESULTS AND DISCUSSIONS

MNDO and MM2(85) methods were used to study the conformation and structure reactivity relationship of neutral and acidic phosphorus esters. The calculation results indicate that for the most stable conformation, the

charge density of phosphoryl oxygen(q_o) is determined not only by the electronegativity of the substituents, but also by the conformation of the alkoxy group on phosphorus atom. Meanwhile, the conformation of the alkoxy group provides, as a rule, more important influence on q_o. However, the energy of the highest occupied molecule orbital (E_{HOMO}) is basically dependent on the electronegativity of the substituent, while the donating ability or the withdrawing property of the neutral phosphorus compounds is mainly governed by E_{HOMO} but not the q_o.

For quantitative structure-activity relationship study (QSAR), as the result of our systematic investigation[4-6] an equation for regression analysis was introduced by us.

$$\log K_{ex} = \rho\Sigma\sigma + \delta\ \Sigma Es + P \qquad (1)$$

Where σ is the polar parameter, as shown by us[7], the polar substituen effect in organophosphorus compounds parallels that of carbon compounds Es is the steric parameter that is related to the configuration of the complex formed during extraction process. A new set of such paramters is listed in Table 1. P is the partition constant of the ligand.

TABLE 1

Substituent Steric Parameters

Group	$E_s^P(R)$	$E_s^P(RO)$	$E_{s,ex}(R)$	$E_{s,ex}(RO)$	ν	E_s
Me	0.50	0.38	-0.037	0.0	0.52	-1.24
Et	0.75	0.62	0.0	0.003	0.56	-1.31
n-Pr	0.85	0.72	0.007	0.003	0.68	-1.60
i-Pr	1.12	0.98	0.216	0.021	0.76	-1.71
n-Bu	0.91	0.77	0.010	0.003	0.68	--
i-Bu	1.05	0.91	0.053	0.015	0.98	--
s-Bu	1.17	1.02	0.246	0.102	1.02	-2.37
t-Bu	1.36	1.21	0.545	--	1.24	-2.78
n-Am	0.91	0.77	0.010	0.010	0.68	--
i-Am	0.92	0.78	--	--	0.68	--
cyc-Hex	1.07	0.93	0.218	--	6.87	-1.01
n-Oct	0.90	0.76	0.011	0.012	0.68	--
i-Oct	1.10	0.96	0.058	0.023	1.01	--
s-Oct	1.25	1.05	0.277	0.169	1.05	--

Abbreviation i-Oct and s-Oct denotes $BuCHEtCH_2$- and HeptCHMe- respectively.

Based on eq. 1 and Table 1 we can calculated the Kex value and corresponding separation factor. Our theoretical prediction is well supported by experimental data. Among phosphorus acids and esters studied, the unique performance of Cyanex 272 in Co/Ni separation and in rare earths extraction was demonstrated and discussed.

^{31}P NMR spectroscopy plays an important role in structure elucidation of phosphorus compounds. As in ^{13}C NMR studies, Quin[8] figured out the substituent parameters (β- and γ-)as empirical rules to rationalize the substituent effect on ^{31}P NMR chemical shifts. However why did the substituent β-effect produced large deshielding (downfield) effect on ^{31}P NMR chemicalshifts, while the substituent γ-effect produced smaller shielding (upfield) effect? Gorenstein's stereoelectronic effect was only illustrated for some of alkyl phosphates.[9] Our MM studies on ^{31}P NMR chemical shifts reveal that such effect for organophosphorus compounds including alkyl-phosphines, -phosphine oxides, -phosphinates, -phosphonates and phosphates are mainly governed by the local van der Waals(VDW) steric energy of phosphorus nucleus of compounds studied. Our results [10,11] showed that all of the β-substituent to phosphorus nucleus largely increase the local VDW steric energy of phosphorus nucleus ($E_{VDW,P}$) i.e. increase the VDW repulsion interaction, to produce large downfield effect and all of the γ-substituent decrease the $E_{VDW,P}$, i.e. increase VDW attraction interaction, to yied upfield effect, which is smaller than that of β-substituent effect in their quantity. A linear relationship between the $E_{VDW,P}$ and ^{31}P NMR chemical shifts (δ_P) of various types of organophosphorus compounds was established.

$$\delta_P = b_k + C_{k.VDW}E_{VDW,P} \qquad (2)$$

Our findings are not only important for understanding the nature of substient effect on ^{31}P NMR, but can be used successfully for structure analysis of phosphorus-based diasterisomers.[12]

It was found that there is a significant difference in hydrolytic behaviour between phosphorus esters and carboxylic esters. The commonly used structural parameters including Es, υ, υ and σ* provide not very good results in regression analyses though υ' was suggested by Charton for phosphorus compounds.[13] By using the difference between the most stable conformation of the substrate and the transition state, we have

$$\log k = \delta\Delta E + \rho\sigma^* + C \qquad (3)$$

The regression results showed that Eq. 3 gives better correlation factor (γ) than that with υ' and σ* for phosphinates, phosphonates and phosphoryl chlorides. The ΔΔE can also be used to account the ring size effect on the hydrolytic reaction of cyclic phosphonic ester.[14]

The asymmetric induced addition of dialkylphosphite to aldimine fromed by condensation of chiral 1-methylbenzylamine with aldehyde was studied by MM calculation. It is the unique way for understanding the reaction mechanism and the factors that influence the de value. According to the transition state of the reaction, the attack direction of the phosphorus atom determines the absolute configuration of the product. When the P-atom attackes the C=N carbon from the top of the plane will produce R configuration of the product, while the bottom attack will yield S configuration. The ratio (ρ) of R to S can be estimated by Boltzman distribution(4). The de values are easily obtained from Equation 5.

$$\rho = (\Sigma e^{-E_r/RT})/(\Sigma e^{-E_s/RT}) \quad (4) \qquad de = (R-S)/(R+S)X100\% \quad (5)$$

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