

Linear free energy relationship and deuterium kinetic isotope effect observed on phospho and thiophosphoryl transfer reactions in some organophosphorous compounds

B J Lumbiny¹, Z Hui², M A Islam¹, M A Quader³ and M Rahman¹

¹ Department of Chemistry, University of Rajshahi, Rajshahi 6205, Bangladesh

² Department of Chemistry, Inha University, Incheon 402-751, South Korea

³ Department of Chemistry, University of Dhaka, Dhaka 1000, Bangladesh

E-mail: blksjahan@yahoo.com

Abstract. Tetracoordinated organophosphorous compounds were synthesized, characterized and nucleophilic substitution reaction were investigated by varying substituents around phosphorous centre or in nucleophile considering its utility in biological and environmental system. The reactivity is expressed in terms of second-order rate constant, k_2 and measured conductometrically. Linear Free Energy Relationship (LFER) tools mainly Hammett (ρ), Brönsted (β) LFER coefficients and deuterium kinetic isotope effects (KIEs) being determined for the pyridinolysis of 4 - chlorophenyl 4 - methoxy phenyl chlorophosphate, **1** in acetonitrile at 5.0 °C. The experimental data's were compared with those of structurally similar organophosphorous compounds reported earlier in quest for the mechanistic information. Nice linear correlation being found for Hammett ($\log k_2$ vs σ_x), having negative value of the $\rho_x = -5.85$ and Brönsted ($\log k_2$ vs $pK_{a(x)}$) plots having large positive value for $\beta_x = 1.18$ for **1** can be interpreted as S_N2 process with greater extent of bond formation in transition state (TS) of **1**. The observed k_H/k_D values of **1** is 1.00 ± 0.05 and *net* KIE, 1.32 suggests the primary KIE and indicates frontside nucleophilic attack through the partial deprotonation of pyridine occurs by the hydrogen bonding in the rate-determining step.

1. Introduction

Tetracoordinated organophosphorous species play a key role in a wide range of organic and biological processes [1a]. Phosphate is a strong tribasic acid and is ionized at neutral pH in aqueous environments. So it has quite natural availability as biomolecules like phospholipids and very significantly form the monomeric unit of DNA/ RNA by linking up to ribose and heterocyclic nitrogenous base (*e.g.* adenosine, figure.1). Phosphate can link up to two groups as ester in nucleic acid and still remain ionized as shown in figure. 1. Phosphate esters and anhydrides, *e.g.* ATP, are thermodynamically unstable and kinetically stable, which is a hallmark of life [1b]. So Phosphoryl transfer reactions play a fundamental role in a wide range of biological processes including basic metabolism, energy transduction, gene expression, and cell signalling [1]. Besides Certain organophosphorous compounds are widely used as pesticides, neurotoxin, and other biologically active substances. So new findings on organophosphorous compounds have been withdrawn much attention to the synthetic chemist as well as in drug designing.

Tetracoordinated organophosphorous compounds were synthesized, characterized and nucleophilic substitution reactions were investigated by varying substituents around phosphorous

¹ B J Lumbiny, Department of Chemistry, University of Rajshahi, Rajshahi 6205, Bangladesh.

² M A Islam, Department of Chemistry, University of Rajshahi, Rajshahi 6205, Bangladesh.



centre or in nucleophile. All of the classically used tools of physical organic chemistry mainly linear free energy relationship (LFER) and heavy atom (deuterium) kinetic isotope effect (KIEs) have been used in this study to interpret the (thio)phosphoryl group transfer reaction. LFER and KIEs methods are both powerful tools for the diagnosis of organic reaction mechanism, and relatively few reactions have been studied combining both methodologies.

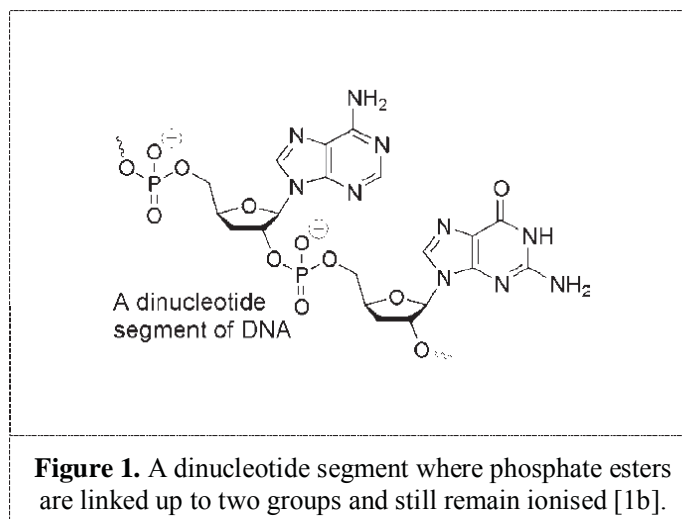
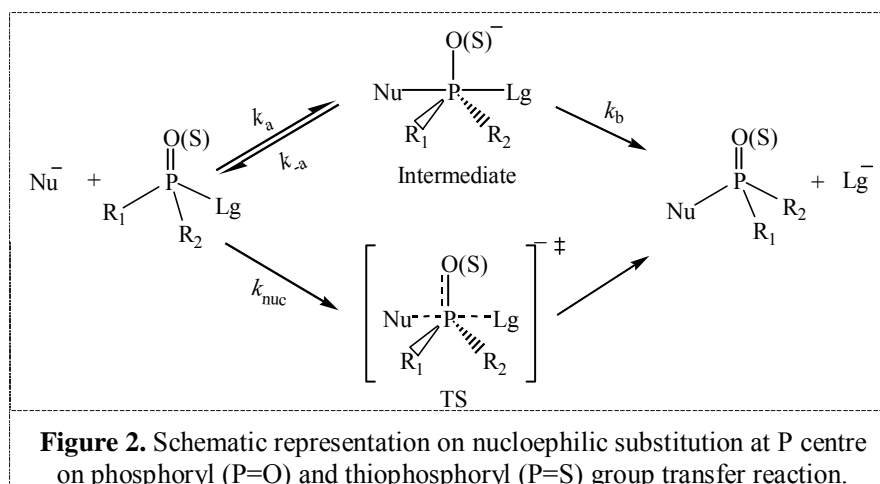


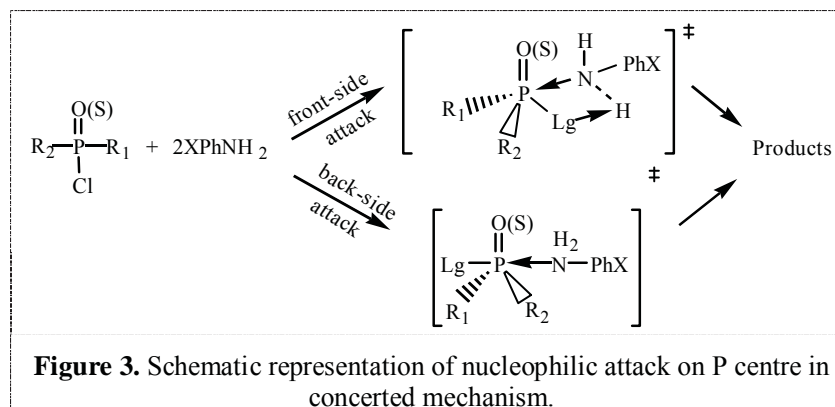
Figure 1. A dinucleotide segment where phosphate esters are linked up to two groups and still remain ionised [1b].

LFER is an empirical observation which can be derived when the shapes of the potential energy surfaces (PES) of a reaction are not substantially altered by varying the substituents [2]. LFER have been very useful in delineating the degree of nucleophilic participation and the extent of leaving group bond fission in the transition states (TS) of the reaction. The measurement of the KIEs has been found widespread use in mechanistic study of various reactions as KIEs are one of the few experimental probes for the TS of the rate limiting step of a reaction [3]. KIEs of atoms at different positions within a molecule can provide details of the TS structures. It is also very insightful and convenient tool for studies of reaction mechanisms. A library of new organophosphorus compounds being synthesized and series of kinetics and mechanism of nucleophilic substitution reactions on phosphoryl group (P=O) and thiophosphoryl group (P=S) have been reported for long from the research group acknowledged [4-13]. The above studies are relied on physical organic chemistry methods; Hammett and Brönsted LFER, cross interaction constants (CICs), heavy atom kinetic isotope effects (KIE) which have provided unambiguous evidence for the interpretation of the mechanistic pathway.

It has been reported that nucleophilic substitution at a phosphoryl (P=O) or thiophosphoryl (P=S) centre generally proceeds either through stepwise mechanism with a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate (upper route in figure 2) or an S_N2 mechanism with TBP-5C TS (lower route in figure 2), where the attacking and leaving groups occupy apical positions, *i.e.*, backside nucleophilic attack toward the leaving group [4-14].



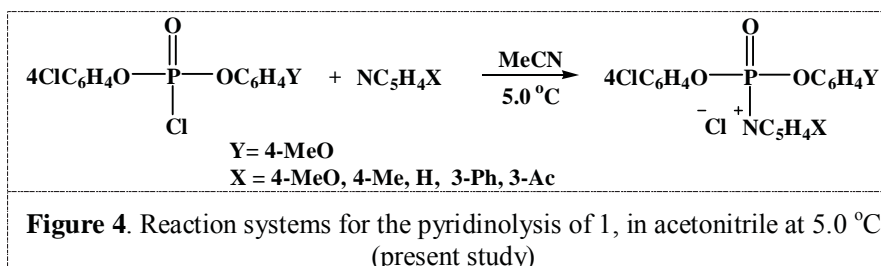
Our very recent studies show that in case of concerted mechanism the nucleophile can approach towards reaction centre in two different ways. Front and back-side nucleophilic attack on the substrates is proposed mainly based on the deuterium kinetic isotope effects. A hydrogen-bonded, four-center type transition state is suggested for a frontside attack while the TBP-5C TS is suggested for a back-side attack as shown in figure 3 [5, 7, 12].



The nucleophile attacks the backside toward the leaving group in most phosphoryl transfers, *i.e.*, the attacking and the leaving groups occupy apical positions [ap(Nu)-ap(Lg)] causing inversion of configuration. However, when the nucleophile attacks frontside toward the leaving group, *i.e.*, when the nucleophile and the leaving groups occupy apical and equatorial positions [ap(Nu)-eq(Lg)], or equatorial and apical positions [eq(Nu)-ap(Lg)], respectively, the configuration is retained [5, 12]. When backside and frontside nucleophilic attacks occur simultaneously, the relative importance of each reaction pathway leads to products with inversion or retention of the configuration, depending on the nucleophile, the leaving group, and the reaction conditions [5, 12]

This is also very strongly claimed from previous studies as the substituents around the P centre varies in leaving or nonleaving group, or substituents around nucleophilic centre, the reactivity, selectivity, stereochemistry and finally mechanistic pathway for S_N reaction varies a lot. Continuing our studies on phosphoryl transfer reactions the tetracoordinated organophosphorus compound 4-chlorophenyl 4-methoxy phenyl chlorophosphate [4-ClPhOP(=O)(4-MeOPhO)Cl], **1**, being

synthesized, characterised by spectrometric methods and element analysis and aminolyses reaction with substituted pyridines have been carried out at 5.0 °C in acetonitrile (figure 4). Recently the pyridinolysis of some organophosphorous compounds, structurally similar of those of 1, 4-chlorophenyl 4-methyl phenyl chlorophosphate [4-ClPhOP(=O)(4-MePhO)Cl], 2, 4-chlorophenyl phenyl chlorophosphate [4-ClPhOP(=O)(OPh)Cl], 3, in acetonitrile at 5.0 °C, and *O*-aryl phenyl phosphonochloridothioates [PhP(=S)(OPh-Y)Cl], 4, in acetonitrile at 35.0 °C were observed. The substituents around phosphorus centre (Y in 4) or in nucleophile (X with 2, 3, 4) being varied and compared with those of 1. The reported mechanism according to LFER is S_N2 without any change in mechanism for the system 2, 3 and 4 [4, 6, 13]. Comparing the reactivities, the linear free energy selectivity parameters and deuterium KIEs with the above comparable systems this study could be a further evidence to clarify aminolyses mechanism and stereochemistry to propose plausible TS structure.



2. Experimental

2.1. Materials

GR grade starting materials (4-Chlorophenyl dichlorophosphate, 4-methoxy phenol, triethylamine) substituted pyridines, deuterated pyridine ($\text{C}_5\text{D}_5\text{N}$; 99 atom% D), CDCl_3 (99.8 atom % D, 0.03% v/v TMS), from Aldrich, USA, were purchased and used. HPLC grade acetonitrile (less than 0.005% H_2O content) were used to prepare nucleophile solution to study.

2.2. Synthesis and characterization [4 -13]

Equimolar proportion of the starting materials were taken with methylene chloride and stirred in ice bath for 2 hrs. The compound 1 is obtained from the reaction mixture by column chromatography and characterized in the following way.

4-Chlorophenyl 4-methoxyphenyl chlorophosphate: Yellowish liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 9.2$ Hz, 2H), 7.26-7.19 (m, 4H), 6.90 (d, $J = 9.2$ Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.81, 148.26, 143.21, 131.97, 130.10, 121.84, 121.32, 114.97, 55.65 (OCH_3); ^{31}P NMR (162 MHz, CDCl_3) δ 0.66 (s, 1P); IR (neat, cm^{-1}) 3003 (C-H, aromatic), 2951 ($-\text{CH}_3$ Asym), 2844 ($-\text{CH}_3$ Sym), 1388 (P=O), 1239, 1160, (C-O-Ar) 1066, 990, 843 (P-O-Ar str); m/z, 332 (M^+); Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{O}_4\text{PCl}_2$: C, 46.87; H, 3.33; Found: C, 46.92; H, 3.58.

2.3. Kinetics [4-13]:

Reactions were carried out under pseudo first-order conditions at 5.0 °C in which amine concentrations were at least 20 times greater than the substrate concentration. Thus the pseudo first- order rate (k_{obsd}) was obtained experimentally by using Guggenheim equation [equation (1)] by nonlinear curve fitting method in ORIGIN program.

$$\lambda_t = \lambda_\infty - (\lambda_\infty - \lambda_0)e^{(-k_{\text{obsd}}t)} \quad (1)$$

[where, λ_0 = initial conductivity, λ_t = conductivity at any time, λ_∞ = conductivity at infinity]

This will ultimately produce second-order rate constant (k_2) from the slope of the plots (see table 1) of k_{obsd} vs [Nu], in equation (2) which gave very good linearity in all cases (regression > 0.997) reproducible to within $\pm 3\%$.

$$k_{\text{obsd}} = k_0 + k_2 [\text{Nu}] \quad (2)$$

Similarly deuterated pyridine were treated to obtain k_2 , values for deuterium effect. In this study k_{H} is expressed as average of second order rate constants with pyridine and k_{D} indicates average of second order rate constant with deuterated pyridine. If $k_{\text{H}} \neq k_{\text{D}}$ a kinetic isotope effect (KIE) exists, expressed as the ratio, $k_{\text{H}}/k_{\text{D}}$ [3]. Standard error being measured by the following equation (3)

$$\text{Standard error} \{= 1/k_{\text{D}}[(\Delta k_{\text{H}})^2 + (k_{\text{H}}/k_{\text{D}})^2 \times (\Delta k_{\text{D}})^2]^{1/2}\} \quad (3)$$

Another significant measure is net KIE which is determined by the relation below

$$(k_{\text{H}}/k_{\text{D}})_{\text{net}} = (k_{\text{H}}/k_{\text{D}})_{\text{obsd}}/(k_{\text{H}}/k_{\text{D}})_{\text{expd}} \quad (4a)$$

$$\log(k_{\text{D}}/k_{\text{H}})_{\text{expd}} = \beta_{\text{X}} \times \Delta \text{p}K_{\text{a}} \quad (4b)$$

Perrin and his coworkers reported that the basicities of β -deuterated analogs of benzylamine, *N*, *N*-dimethylaniline and methylamine increase roughly 0.02 $\text{p}K_{\text{a}}$ units per deuterium and these effects are additive [15, 16]. For five deuterium atoms in *d*-5 pyridine this gives an expected $\Delta \text{p}K_{\text{a}}$ of approximately +0.1 unit.

2.4. Tools to interpret mechanism (theory)

In the early part of twentieth century the quantitative study of LFER was introduced by the Danish scientist Johannes Nicolaus Brönsted (1923) and Swedish scientist Louis Plack Hammett (1937).

2.4.1. Hammett Equation [2, 17, 18]

It treats the electronic effect of substituents on the rate or equilibria of organic reactions, can be expressed as follows equation 5(a) and 5(b)

$$\log(k_{\text{X}}/k_{\text{H}}) = \sigma \rho \quad (5a)$$

$$\log(K_{\text{X}}/K_{\text{H}}) = \sigma \rho \quad (5b)$$

k_{X} or K_{X} is the rate or equilibrium constant, respectively, for the given reaction of *m*- or *p*- $\text{XC}_6\text{H}_4\text{COOH}$, k_{H} or K_{H} refers to the reaction of $\text{C}_6\text{H}_5\text{COOH}$, i.e., $\text{X} = \text{H}$, σ is the substituent constant, ρ is the reaction constant or Hammett coefficients and obtained by plotting $\log k_2$ vs. σ_{X} .

2.4.1.1 Significance of Sign and Magnitude of ρ

The susceptibility of the reaction to substituents, (+ve) sign; a reaction favored by EWS and $\rho < 1$ indicates negative charge is built, (–ve) sign and $\rho > 1$ suggest reverse situation.

2.4.2. The Brönsted equation [19, 20]

The Gibbs free energy for proton dissociation is proportional to the activation energy (equation 6a, 6b) for the catalytic step. When the relationship is not linear, the chosen group of catalysts do not operate through the same reaction mechanism.

$$k_{\text{b}} = G_{\text{b}}K_{\text{b}}^{\beta} = G_{\text{b}}(K_{\text{W}}/K_{\text{a}})^{\beta} = G_{\text{b}}K_{\text{a}}^{-\beta} \quad (6a)$$

$$\text{or} \quad \log k_{\text{b}} = \beta \text{p}K_{\text{a}} + \text{Constant} \quad (6b)$$

The Brönsted correlations of rate constants with nucleophile $\text{p}K_{\text{a}}$ (β_{X}) is one measure of the degree of nucleophile bond formation in the rate determining TS. Reactions that have low values for proportionality constants (β_{X}) are considered to have a transition state closely resembling the reactant with little proton transfer, with a high value, resembles product.

2.4.3. Kinetic isotope Effects (KIEs)

Kinetic isotope Effects (KIEs) is a kinetic method that can in principal tells about bonding changes in the rate limiting step of a reaction as the rate of reaction varies when an atom is replaced by a different (usually heavier atom) [3b]. Isotopic substitution does not affect the PES of the molecule nor does it

perturb the electronic energy levels. It is only those properties that are dependent upon atomic masses which are affected; for chemical purposes, the perturbation can be considered to be limited to vibrational frequencies [3c]. Vibrational energy will usually change during the course of a reaction or between reagent and transition state since some bonds are in the course of reaction being broken or made and their associated frequencies will be affected. Isotopic substitution should therefore affect reaction rates. The extent to which this occurs depends greatly upon the relative masses of the isotopes, and the mass of D doubles to that of H (greatest) so hydrogen isotope effects are the most thoroughly examined, the following discussion will refer to this case, rate constants being denoted, k_H , k_D , but the same principles apply to any pair of isotopes.

The following types of isotope effect are distinguished [3]

- (a) primary kinetic isotope effect (PKIE): in which the bond to the isotopic atom is broken in the rate determining step, $k_H/k_D \gg 1$;
- (b) secondary kinetic isotope effect (SKIE), in which the bond to the isotopic atom (s) remains intact throughout the reaction, $k_H/k_D < 1$ or k_H/k_D , around, 1;
- (c) solvent isotopic effects, which result from isotopic differences in the medium, e.g., if the solvent is changed from H_2O to D_2O , then $k_{(H_2O)} / k_{(D_2O)}$ is obtained as solvent isotope effect.

More precisely The net KIE of less than unity, $(k_H/k_D)_{net} < 1$, implies the secondary inverse KIE while the net KIE of greater than unity, $(k_H/k_D)_{net} > 1$, implies a primary KIE [21]. The primary KIE suggests that partial deprotonation of nucleophile occurs by hydrogen bonding in the rate-determining step retaining the configuration whereas The secondary inverse KIE is ascribed to the increment of out-of-plane bending vibrational frequencies of C–H(D) bonds in the TS because of steric congestion of the hydrogen (deuterium) atom in the C–H(D) moiety in the bond-making step and inversion of configuration is found.

4. Results and Discussion

The second-order rate constants ($k_2 \times 10^3/M^{-1}s^{-1}$) of the pyridinolysis [4-ClPhOP(=O)(4-MeOPhO)Cl], 1, [4-ClPhOP(=O)(4-MePhO)Cl], 2, [4-ClPhO)PhOP(=O)Cl], 3, with $Y = H$: (PhO)PhP(=S)Cl, 4, obey the following order of reactivity respectively (see table 1, k_2 is given upto three significant figures)

$$3 (31.6, P=O) > 2(26.2, P=O) > 1(24.0, P=O) > 4 (11.2, P=S)$$

At a glance, the reaction rates seem to be proportional to the positive charge on reaction center P. However, it is well known that P=O substrates are more reactive than P=S because of electronegativity difference between O and S, favoring O over S. Also the presence of electron donating substituent, 4-MeO in 1 retards the rate of reaction most than that of 2 and 3 follow the expected trend of nucleophilic substitution reaction.

The Hammett plots for substituent (X) variations in the nucleophile ($\log k_2$ vs. σ_X , figure 5) and Bronsted plots ($\log k_2$ vs. $pK_a(X)$, figure 6) show linearity for 1, 2, 3, same as 4 suggesting no change in mechanism.

The reactivity selectivity parameters for 1, 2, 3, 4 are compiled in table 1 and compared. The obtained $\rho_X = -5.78$, and $\beta_X = 1.17$ for 2, $\rho_X = -5.66$, and $\beta_X = 1.14$ for 3, $\rho_X = -4.35$ to -4.75 , and $\beta_X = 0.87$ to 0.95 , of 4 are somewhat smaller than those in the present work, $\rho_X = -5.85$, and $\beta_X = 1.18$ in 1. The reaction mechanism for the pyridinolysis of 2, 3, and 4 follow S_N2 mechanism as reported earlier. The comparable ρ_X and β_X of 1 with those of 2, 3, 4 indicates concerted S_N2 mechanism for system 1, with a similar but later transition state structure (TS) i.e., a greater extent of bond-formation in (Figure 7).

Table 1. Second-Order Rate Constants, k_2 ($\times 10^2$ /M⁻¹ s⁻¹) and Selectivity Parameters for the Pyridinolysis of [4-ClPhOP(=O)(4-MeOPhO)Cl], **1**, [4-ClPhOP(=O)(4-MePhO)Cl], **2**, (4-ClPhO)PhOP(=O)Cl, **3**, (YPhO)PhP(=S)Cl, **4**.

Y/X	4-MeO	4-Me	H	3-Ph	3-Ac	$-\rho_X$	β_X
σ	-0.27	-0.17	0.00	0.06	0.38	<i>Hammett</i>	<i>Bronsted</i>
p <i>K_a</i> (py)	6.47	6.00	5.17	4.87	3.26	<i>coefficient</i>	<i>coefficient</i>
4-MeO, 1	101	20.7	2.40	0.656	0.016	5.85	1.18
4-Me, 2	111	23.5	2.62	0.709	0.020	5.78	1.17
H, 3	121	27.8	3.16	0.918	0.026	5.66	1.14
H, 4			1.12			4.35-4.75	0.87-0.95

The observed k_H/k_D values of **1** (1.00) is unity (see table 2) so there is a chance to be secondary kinetic isotope effect (SKIE). The *net* KIE of **1**, **2**, **3**, **4**, $[(k_H/k_D)_{\text{net}} = (k_H/k_D)_{\text{obsd}}/(k_H/k_D)_{\text{expd}}]$ are 1.32, 1.31, 1.30, 1.35 respectively suggesting primary kinetic isotope effect (PKIE).

Table 2. Deuterium kinetic isotope effects (k_H/k_D) and *net* KIE for the Pyridinolysis of [4-ClPhOP(=O)(4-MeOPhO)Cl], **1**, [4-ClPhOP(=O)(4-MePhO)Cl], **2**, (4-ClPhO)PhOP(=O)Cl, **3**, (YPhO)PhP(=S)Cl, **4**.

Y	k_H ($\times 10^2$ / M ⁻¹ s ⁻¹)	k_D ($\times 10^2$ / M ⁻¹ s ⁻¹)	$(k_H/k_D)_{\text{obsd}}$	$(k_H/k_D)_{\text{expd}}$	<i>net</i> KIE $(k_H/k_D)_{\text{obsd}}/$ $(k_H/k_D)_{\text{expd}}$
4-MeO, 1	2.40 ± 0.07	2.40 ± 0.07	1.00 ± 0.05	0.762	1.32
4-Me, 2	2.62 ± 0.06	2.62 ± 0.06	1.04 ± 0.04	0.764	1.31
H, 3	3.16 ± 0.20	3.04 ± 0.14	1.04 ± 0.08	0.769	1.30
H, 4	1.12 ± 0.2	1.01 ± 0.1	1.11 ± 0.02	0.820	1.35

The primary KIE and indicates frontside nucleophilic attack through the partial deprotonation of pyridine occurs by hydrogen bonding in the rate-determining step. Taking into account the larger magnitude of *net* PKIE the extent of hydrogen bond formation in TS would be greater for **4** than for **1**, **2** and **3**.

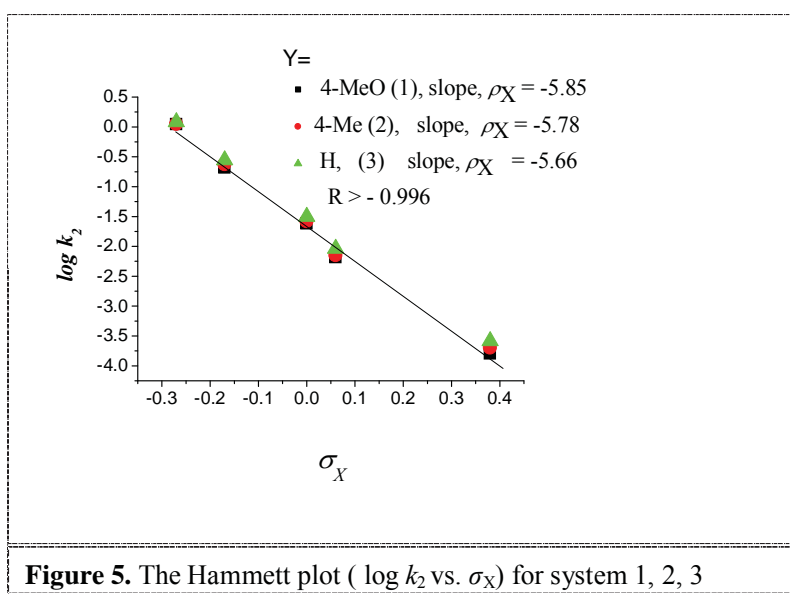


Figure 5. The Hammett plot ($\log k_2$ vs. σ_X) for system **1**, **2**, **3**

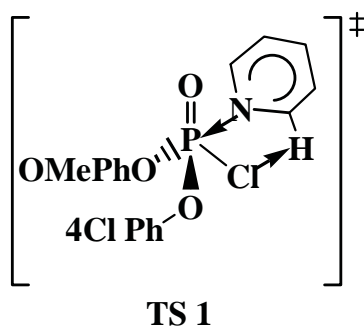
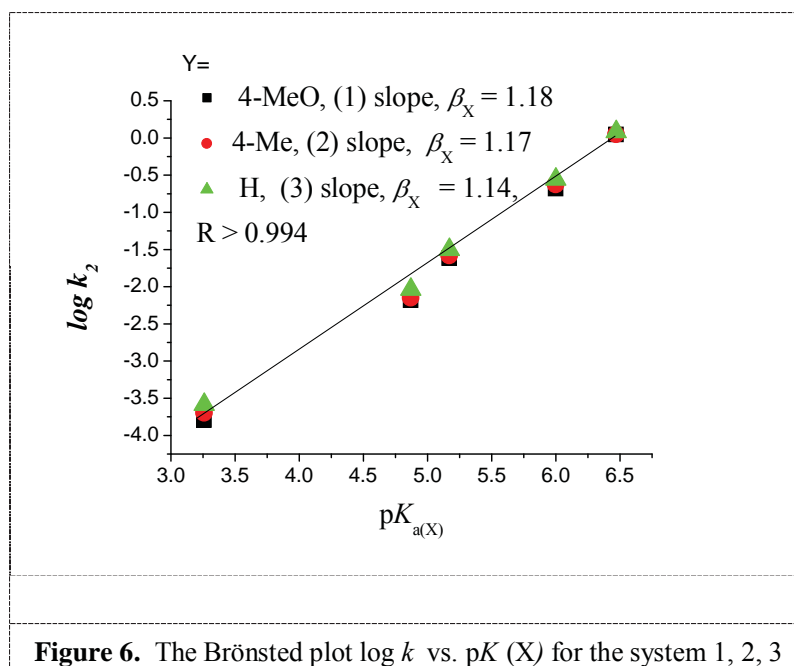


Figure 7. Plausible TS structure for 1

4. Conclusion

Physical organic chemistry methods; linear free energy relationship (LFER) and most recently developed technique heavy atom kinetic isotope effects (KIEs) have been used in quest for the mechanistic information of the pyridinolysis of 4-chlorophenyl 4-methoxy phenyl chlorophosphate [4-ClPhOP(=O)(4-MeOPhO)Cl], 1, at 5.0 °C in acetonitrile (figure 4). The experimental data being compared with those of some structurally similar organophosphorus compounds, 4-chlorophenyl 4-methyl phenyl chlorophosphate [4-ClPhOP(=O)(4-MePhO)Cl], 2, 4-chlorophenyl phenyl chlorophosphate [4-ClPhOP(=O)(OPh)Cl], 3, at 5.0 °C, and *O*-aryl phenylphosphonochloridethioates [PhP(=S)(OPh-Y)Cl], 4, at 35.0 °C in acetonitrile. Reaction kinetics of these nucleophilic substitution reactions were measured conductometric method and reactivity was obtained as second order rate

constant k_2 . These k_2 values being used up to study LFER and KIEs and to interpret the mechanistic pathway.

Nice linear correlation being found for Hammett plot ($\log k_2$ vs σ_x , figure 5), having negative value of the $\rho_x = -5.85$ and Brönsted ($\log k_2$ vs $pK_{a(x)}$, figure 6) plots having large positive value for $\beta_x = 1.18$ for 1 can be interpreted as S_N2 process with greater extent of bond formation in transition state (TS) of 1 (figure 7). The observed k_H/k_D values of 1 is 1.00 ± 0.05 and *net* KIE, 1.32 suggests the primary KIE and indicates frontside nucleophilic attack through the partial deprotonation of pyridine occurs by the hydrogen bonding in the rate-determining step.

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