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# Nucleophilic Substitution at Thiophosphoryl Center (P=S)

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**Abstract** Two main types of displacement processes are well known at neutralthiophosphoryl group transfer reactions: concerted involving displacementat phosphorus through a single pentacoordinate transition state (TS) and stepwise mechanism involving a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate. In some cases mechanistic change from concerted to stepwise or *vice versa* has been reported. This paper includes a review on mechanism of nucleophilic substitution at phosphorus center with P=S substrates. For example the reactions of aryl phenyl chlorothiophospahtes with anilines were reported as concerted whereas the reactions between thiophosphinyl and thiophosphonyl chlorides and $R_2NH$ proceed through stepwise mechanism forming thiophosphene intermediates. In case of reactions of *O*-aryl methylphosphono chloridothioates with anilines the mechanism reported as change from concerted to stepwise. These conclusions were done based on Hammett and Brönsted constants, Cross-interaction Constants and Kinetic Isotope Effects. The papers reported from 1994-2014 were reviewed in this article.

**Keywords** Thiophosphoryl transfer reaction, Aminolysis, Pyridinolysis, Concerted, Stepwise

## 1. Introduction

Organothiophosphorous compounds are useful in agricultural, pharmaceuticals and Textile chemicals [1a, b]. Organothiophosphorous compounds are used as pesticides in crop production in agriculture. These substances are also used as flame retardant agent in Textiles. Considering its wide uses in different sectors the displacement reactions at P=S center has become significant in the field of reaction mechanism. The chemistry of organothiophosphate compounds is very important because of greater interest. A significant number of works have been reported on thiophosphoryl (P=S) transfer reactions. Because predicting the effects of replacing the oxygen atom in the phosphoryl group (P=O) with sulfur is necessary. Two main types of displacement processes are well known at neutralthiophosphoryl group transfer reactions: concerted involving displacementat the phosphorus through a single pentacoordinate transitionstate (TS) and stepwise mechanism involving a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate (Scheme 1). In some cases mechanistic change from concerted to stepwise or *vice versa* has been reported. This paper includes a review on mechanism of nucleophilic substitution at phosphorus center with P=S substrates. Most recent and updated papers have been reviewed in this article to get a clear idea of researchers in this field.

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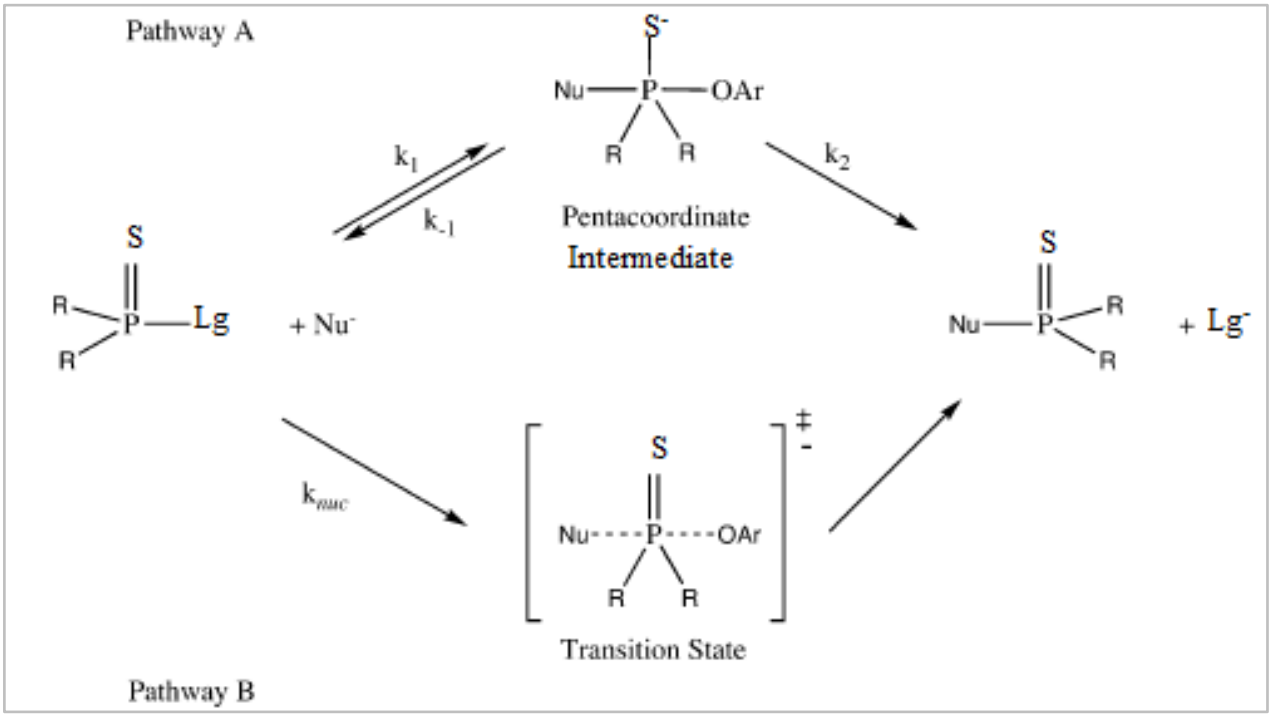
## 2. Results and Discussion

### 2.1. Concerted Mechanism

Dey et al. [1c] reported the mechanism of thiophosphoryl transfer, as well as to compare the reactivity when the oxygen atom in the phosphoryl group is replaced with sulfur, in the aminolyses of aryl phenyl chlorothiophosphates and 4-chlorophenyl aryl chlorothiophosphates with anilines in acetonitrile at 55.0°C. The aminolyses of aryl phenyl chlorothiophosphates and aryl 4-chlorophenyl chlorothiophosphates with X-anilines in acetonitrile at 55.0°C are studied. The cross-interaction constants, $\rho_{XY}$, are negative for both substrates. The obtained kinetic isotope effects ($k_H/k_D$) involving deuterated aniline ($XC_6H_4ND_2$) nucleophiles are greater than unity, $k_H/k_D > 1$, suggesting that the rate-determining step involves partial deprotonation of the aniline by hydrogen bonding. This is in line with a front-side attack concerted mechanism through a hydrogen-bonded four-center-type transition state. On the basis of the cross-interaction constant and primary kinetic isotope effects, authors proposed a concerted $S_N2$ mechanism with front- and back-side nucleophilic attack on substrate. A hydrogen-bonded, four-center TS is suggested for a front-side attack, while the TBP-5C TS is suggested for a back-side attack. The MO theoretical calculations of the model reactions of substrates with ammonia nucleophile are carried out. The charge densities calculated by the NPA18 are more negative and more positive for the leaving group (Cl) and the nucleophile, respectively, in the front-side attack TS than in the back-side attack TS, indicating that the degree of stabilization by specific solvation effects could be larger

in the front-side attack TS. This is supported by the results of NBO analysis at the B3LYP/ 6-311+G(d,p) level and the calculated activation energy barriersat the CPCM-MP2/6-31+G(d) level of theory.

Buncel et al. [2a] reported the nucleophilic displacement at the phosphorus center of [*O,O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothiate, by oxygen nucleophiles in aqueous solution at 25.0°C. In this paper authors concluded that the reactions between the substrate and oxygen nucleophioles proceed through concerted mechanism for nucleophilic attack at the phosphorus center. This conclusion was made based on the Brönstedplots, log$k_{Nu}$*vs.* p*K*a of nucleophilies shows a linear plot for the series of structurally related phenoxides in the p$K_a$ ranges 5.4-10.0, but curve obtained in the highly basic region corresponding to $CF_3CH_2O^-$ and $HO^-$ as nuleophiles. The $\beta_{Nu}$ value was 0.49 ± 0.01 ($R^2$ = 0.998). The linearity of the plot indicates a concerted mechanism for nucleophilic attack at the phosphorus center of the substrate. The log$k_{lg}$*vs.* p$K_a$ gave $\beta_{lg}$ = -0.39 ± 0.04 ($R^2$ = 0.973). The combined values of $\beta_{Nu}$ and $\beta_{lg}$ gave $\beta_{eq}$= 0.88 ($\beta_{Nu}$– $\beta_{lg}$) indicates that the TS for the symmetrical reaction has no significant phosphorylium ion character.




**Scheme 1.** Alternative Mechanisms, an Addition-Elimination ($A_N$ + $D_N$) Pathway with the Formation of a Pentacoordinate (Phosphorane) Intermediate (Pathway A) and a Concerted ($A_ND_N$) Reaction (Pathway B)

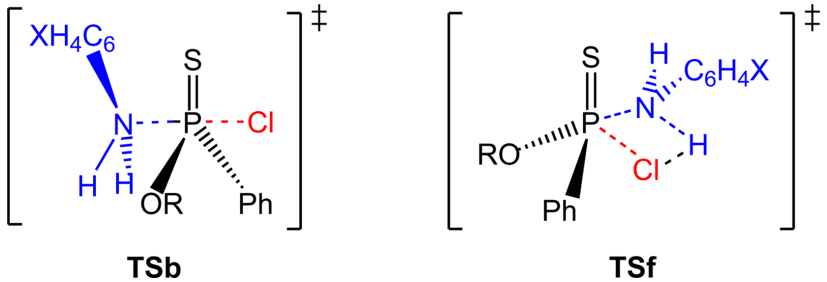
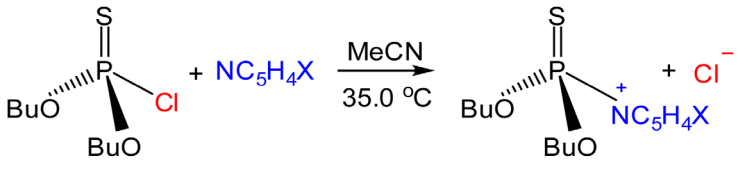



**Figure 1.** Backside Attack In-Line-Type TSb and Front-Side Attack Hydrogen Bonded, Four-Center-Type TSf




X = 4-MeO, 4-Me, 3-Me, H, 3-Ph, 3-MeO, 3-Cl, 3-Ac, 4-Ac, 3-CN, 4-CN

**Figure 2.** The Reactions of Dibutylchlorothiophosphate with X-pyridines in MeCN at 35.0°C

Hengge et al. [2b] reported a concerted mechanism for the transfer of the thiophinoyl group from aryl dimethylphosphinothioate esters to oxyanionic nucleophiles in aqueous solution. Authors calculated $\beta_{Nu}$ and $\beta_{lg}$ by using Linear Free Energy Relationship (LFER)-Brönsted-type correlations. The linear plot obtained giving $\beta_{Nu}$= 0.47 which was indicative of concerted mechanism. This value was compared to $\beta_{Nu}$ = 0.41 for the hydrolysis of the oxygenanalogue which proceeds through concerted mechanism.

In a report Lee et al. [3] studied the anilinolyses of the phosphonochloridothioates, the nucleophilic substitution reactions of *O*-methyl, *O*-propyland*O*-isopropylphenyl phosphonochloridothioates with anilines ($XC_6H_4NH_2$) and deuterated anilines ($XC_6H_4ND_2$) in acetonitrile (MeCN) at 55.0 ± 0.1°C are investigated kinetically based on the selectivity parameters, steric effects of the two ligands on the rates and deuterium kinetic isotope effects (DKIEs). This work was done to gain further information on the anilinolyses of the phosphonochloridothioates depending upon the two ligands. The kinetic results of this work were compared with those of *O*-ethyl [Ph(EtO)P(=S)Cl] [4a], Y-*O*-aryl [$Ph(YC_6H_4O)P(=S)Cl$] [4b] and Y-*S*-aryl [$Ph(YC_6H_4S)P(=S)Cl$] [4c] phenyl phosphonochloridothioates.

A concerted mechanism was proposed based on the negative $\rho_{XY}$ [= –0.38and –0.31] values for the anilinolysesreactions of Y-*O*-aryl [$Ph(YC_6H_4O)P(=S)Cl$] and Y-*S*-aryl [$Ph(YC_6H_4S)P(=S)Cl$] phenyl phosphonochloridothioates. A concerted mechanism was also proposed for the anilinolysisof O-ethyl [Ph(EtO)P(=S)Cl]phenyl phosphonochloridothioates based on the Brönstedcoefficient [$\beta_{X(H)}$ = 1.23]. In this work, a concerted mechanism was proposed based on the Brönsted coefficient [$\beta_{X(H)}$ = 1.26, 1.04 and 1.10 comparable with $\beta_{X(H)}$ = 1.23, $\beta_{X(H)}$ = 1.22-1.33 and $\beta_{X(H)}$ = 1.21-1.25]. The relatively large Brönsted coefficients ($\beta_{X(H)}$ = 1.04-1.33) were typical for the anilinolyses of the phosphonochloridothioates even though the reactions proceed through a concerted $S_N2$ mechanism. The Deuterium Kinetic Isotope Effect (DKIEs) have provided a useful means to determine the TS structures in the nucleophilic substitution reactions, and how the reactants, especially through changes in substituents, alter the TS structures. By Incorporatingdeuteriumin the nucleophile gets an advantage in that the α-DKIEs reflect only the degree of bond formation. When partialdeprotonation of the aniline occurs in a rate-limiting step by hydrogen bonding, the $k_H/k_D$ values are greater than unity, primary normal ($k_H/k_D$> 1.0). The greater the extent of the hydrogen bond, the value of $k_H/k_D$ becomes greater. In contrast, the DKIEs can only be secondary inverse ($k_H/k_D$<1.0) in a normal $S_N2$ reaction, since the N–H(D) vibrational frequencies invariably increase upon going to the TS because of an increase in steric congestion in the bond-making process. The greater the degree of the steric congestion in the TS, the value of $k_H/k_D$ becomes smaller. The DKIEs of ($k_H/k_D$ = 1.08-1.17) and ($k_H/k_D$ = 1.02-1.48) are primary normal while those ($k_H/k_D$ = 0.63-0.99) and ($k_H/k_D$ = 0.65-0.98) are secondary inverse. Both the primary and inverse secondary kinetic isotope effects were obtained in this work. The DKIEs of ($k_H/k_D$ = 0.93-1.28) and ($k_H/k_D$ = 0.44-1.34) are both secondary inverse and primary normal. The $k_H/k_D$ values of andincrease as the aniline becomes less basic (symbol of ↓), but those increase for other substrates as the aniline becomes more basic (symbol of ↑). The authors cannot find the consistent correlations between the $\beta_X$ values and DKIEs, between the $\beta_X$ values and variation trends of DKIEs, between the DKIEs and two ligands, or between the reaction mechanism and variation trends of DKIEs. The attacking direction of aniline nucleophile can be semiquantitatively divided into three groups based on the magnitudes of the $k_H/k_D$ values: (i) predominant backside attack inline-type TSb when $k_H/k_D$< 1; (ii) the fraction of the frontside attack hydrogen bonded, four-center-type TSfis greater than that of backside attack TSb when 1.0 <$k_H/k_D$< 1.1: (iii) predominant front-side attack TSf when $k_H/k_D$> 1.1.

Lee et al. [5] reported further systematic information into the reactivity and mechanism depending on the variation of the two ligands, $R_1O$ and $R_2O$, where $R_1$ and $R_2$ are alkyl and/or phenyl (aryl). For example, $R_1$=$R_2$=Bu in following reaction system.

The second-order rate constants ($k_2$) with unsubstitutedpyridine ($C_5H_5N$) at 35.0°C, natural bond order (NBO)charges at the reaction center P atom in the substrate in the gas phase [B3LYP/6-311+G(d,p) level of theory], [6] summations of the Taft's steric constants [$\Sigma E_S = E_S(R_1) + E_S(R_2)$] of the two ligands, [7] Brönsted coefficients ($\beta_X$), crossinteractionconstants (CICs; ρXY), [8] and variation trends ofthe free energy relationships with X for the pyridinolyses ofsix $(R_1O)(R_2O)P(=S)Cl$-type chlorothiophosphates in MeCNare summarized in following Table 1.

The numbering of the substrates follows the sequence of the size of the two ligands, $R_1O$ and $R_2O$. The sequence of the pyridinolysis rates of the substrates is roughlyinversely proportional to the size of the two ligands ($R_1O$ and $R_2O$). The free energy relationships with X for the pyridinolyses of **1-6** are all biphasic concave upwards while those for theanilinolyses of **1-6** are all linear [1c, 3, 4]. The nonlinear free energycorrelations of biphasic concave upward plots with X in thenucleophiles were rationalized by a change in the attacking direction of the nucleophile from a backside with less basicpyridines to a frontside attack with more basic pyridines. A concerted $S_N2$ mechanism is proposed with a change of the attackingdirection of the X-pyridine from a frontside attack with the strongly basic pyridines to a backside attack with the weakly basic pyridines.

**Table 1.** Summary of the Second-Order Rate Constats ($k_2$ with $C_5H_5N$ at 35.0°C, NBO Charges at the Raction center P Atom, Summations of the Taft's Constants ($\Sigma Es$) of the Two Ligands, Brönsted Coefficient (βx), CICs (ρxy), and Variation Trends of Free Energy Relationships with X for the Pyridinolyses of 1-6 in MeCN

| Substrate | $k_2\times10^{3}$[a] | Charges at P | $-\sum E_S$[d] | $\beta_X$ | $\rho_{XY}$ | Trend |
|---|---|---|---|---|---|---|
| **1:** $(MeO)_2P(=S)Cl$ | 1.54[b] | 1.687 | 0 | 1.09/0.20[e] | – | V[g] |
| **2:** $(EtO)_2P(=S)Cl$ | 1.19[b] | 1.701 | 0.14 | 1.02/0.29[e] | – | V |
| **3:** $(PrO)_2P(=S)Cl$ | 1.16 | 1.723 | 0.72 | 1.08/0.31[e] | – | V |
| **4:** $(BuO)_2P(=S)Cl$ | 1.01 | 1.703 | 0.78 | 1.26/0.31[e] | – | V |
| **5:** (EtO) $(YC_6H_4O)P(=S)Cl$ | 0.137[c] | 1.687[c] | 2.55[c] | 2.31-2.33/0.45-0.47[e] | 0/0/0/0[f] | V |
| **6:** (PhO)$(YC_6H_4O)P(=S)Cl$ | 0.333[c] | 1.661[c] | 4.96[c] | 1.36-1.50/0.23/0.48[e] | 2.42/5.14/−1.02/−0.04[f] | V |

[a]Second-order rate constant with unsubstituted pyridine (X=H) at 35$^0$C. [b]Extrapolated value in the Arrhenius plot. [c]The value with Y = H. [d]Note that the value of $\sum E_S$ is not '$E_S(R_1O) + E_S(R_2O)$' but '$E_S(R_1) + E_S(R_2)$' because of a lack of data of $E_S(R_iO)$. [e]Strongly basic/weakly basic pyridines. [f]Stronger nucleophiles and weaker electrophiles/ weaker nucleophiles and weaker electrophiles/ Stronger nucleophiles and stronger electrophiles/ weaker nucleophiles and stronger electrophiles. [g]The symbol of V indicates biphasic concave upward free energy correlation with a break point for the substituent X variations in the nucleophiles.

Um et al. [9] reported the mechanism of aminolyses of aryl diphenylphosphinothioates. Authors reported that reactions of 2,4-dinitrophenyl diphenylthioate with alicyclic secondary amines result in a good linear Brönsted type plot with $\beta_{nuc}$ = 0.52, implying the reactions proceed through a concerted mechanism. The $\beta_{nuc}$ value determined for the reactions of 2,4-dinitrophenyl diphenylphosphinothioate is slightly larger than that reported for the corresponding reactions of 2,4-dinitrophenyl diphenylphosphinate ($\beta_{nuc}$= 0.38), suggesting that reactions of 2,4-dinitrophenyl diphenylphosphinothioate proceed through a tighter transition state (TS) than that of dinitrophenylphosphinate.

### 2.2. Stepwise Mechanism

Harger et al. [10] reported that the reactions between thiophosphinyl and thiophosphonyl chlorides and $R_2NH$ proceed through stepwise mechanism forming thiophosphene intermediates. Authors reported that the substitution rates increased by factors of 80 and $>10^3$ respectively when the reactions of $ArCH_2P(S)(Ph)Cl$ and $ArCH_2P(S)(NMe_2Cl)$ with $Et_2NH$, changing $ArCH_2$ from benzyl to 4-nitrobenzyl were studied. Authors proposed the formation of intermediate by elimination-addition mechanism based on following grounds. Authors observed that in the course of reactions the ability reduced markedly to discriminate between competing $Et_2NH$ and $Me_2NH$ nucleophiles. When the substrates reacted with $Et_2ND$, the nitrobenzyl substrates gave deuterium containing products in the benzylic methylene group.

Lee et al. reported [11] the kinetic studies on the reactions of ethyl methyl and ethyl propyl chlorothiophosphates with X-pyridines have been carried out in acetonitrile at 35.0°C. The substituent effects of the nucleophiles upon the pyridinolysis rates correlate with those for a typical nucleophilic substitution reaction where the stronger nucleophile leads to a faster rate with a positive charge development at the nucleophilic N atom in the transition state (TS). However, both the Hammett (log $k_2$*vs.*$\sigma_X$) and Brönsted [log $k_2$*vs.*p*K*a(X)] plots were biphasic concave upwards with a break point at X = H) and 3-Ph, respectively. The rate of X = H is slightly faster than that of X = 3-Ph. The magnitudes of $\rho_X$ [= −7.27 and −6.96] and $\beta_X$ [= 1.50, 1.44] with strongly basic pyridines are 3-4 times larger than those [$\rho_X$ = –2.54, –2.16; $\beta_X$ = 0.43, 0.36] with weakly basic pyridines.

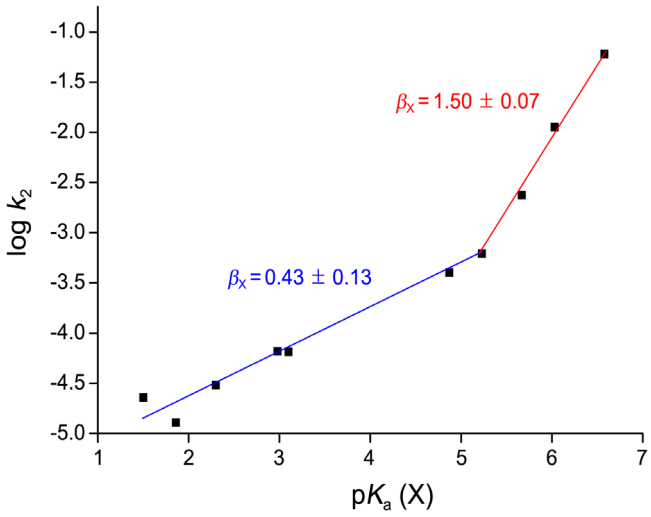



**Figure 3.** Brönsted Plot of the Reactions of Ethyl Methyl Chlorothiophosphate with X-Pyridines in MeCN at 35.0°C

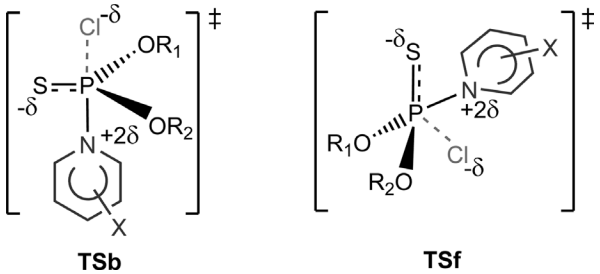



**Figure 4.** Backside Attack TSb and Frontside Attack TSf

Recently Lee et al. [12] reported pyridinolysis of *O*-propyl and *O*-isopropyl phenyl phoshonochloridothioates in acetonitrile at 35.0°C. Authors reported pyridinolysis of *O*-propyl and *O*-isopropyl phenyl

phosphonochloridothioates in acetonitrile (MeCN) at 35.0 ± 0.1°C. Authors reported the reaction mechanism based on the reactivities, selectivity parameters, free energy correlations and reaction mechanisms. Authors interpreted the mechanism as a stepwise with a rate-limiting leaving group departure from the intermediate based on the $\beta_X$ values and biphasic concave upward free energy relationship for both substrates. The biphasic concave upward free energy relationship were rationalized by a front-side nucleophilic attack TSf with more basic pyridines and a backside attack TSb with less basic pyridines for both substrates.

In a very recent paper Lee et al. [13] reported the nucleophilic substitution reactions of Y-aryl methyl and Y-aryl propyl chlorothiophosphates with X-pyridines in acetonitrile (MeCN) at35.0±0.1°C. The number of substrates followthe summation of the Taft steric constants of $R_1$ and $R_2$.

Authors reported, the nucleophilic substitution reactions of Y-aryl methyl and Y-aryl propyl chlorothiophosphates with X-pyridines in acetonitrile at 35.0°C. The Hammett and Brönsted plots with X in the nucleophiles for both substrates exhibit biphasic concave upwards with a break region between X = 3-Me and H. The obtained values of the cross-interaction constants ($\rho_{XY}$) are negative with while positive with despite the same free energy correlations with X for both substrates. A stepwise mechanism with a rate-limitingbond formation was proposed with some substrates, whereas a stepwise mechanism with a rate-limiting leaving group departure from the intermediate was proposed with other substrates based on the sign of ($\rho_{XY}$), negative and positive respectively. A front-side nucleophilic attack ws proposed with strongly basic pyridines based on the considerably great magnitudes of $\rho_X$ and $\beta_X$ values while a backside attack was proposed with weakly basic pyridines based on the relatively small magnitudes of $\rho_X$ and $\beta_X$ for both substrates.

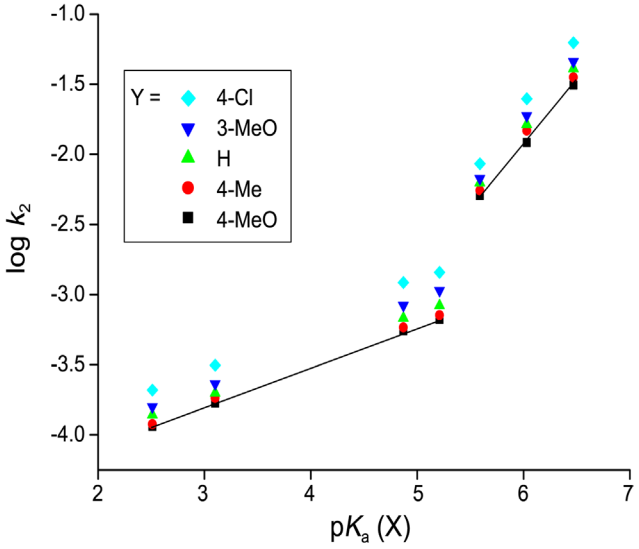
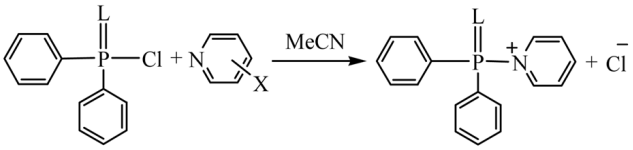



**Figure 5.** Brönsted Plots with X of the Reactions of Y-Aryl Propyl Chlorothiophosphates with X-Pyridines in MeCN at 35.0°C

## 2.3. Mechanism Change

Guha et al. [14] reported a mechanism change at thiophosphoryl center. Authors reported concurrent primary and secondary deuterium kinetic isotope effects in reaction mechanism change in reactions of O-aryl methyl phosphonochloridothioates with anilines. In the course of reactions the cross-interaction constants were negative ($\rho_{XY(H)}$ = -0.95 and $\rho_{XY(D)}$ = -1.11) for stronger nucleophiles, while positive ($\rho_{XY(H)}$ = +0.77 and $\rho_{XY(D)}$ = +0.21) for weaker nucleophiles. These kinetic results indicate that the mechanism changes from a concerted process involving front side nucleophilicattack for stronger nucleophiles to a stepwise process with a rate limiting leaving group expulsion from the intermediate involving backside attack for weaker nucleophiles. A hydrogen-bonding, four-center-type transition state TS was suggested for a front side attack, while a trigonal bipyramidal pentacoordinate TS was suggested for a backside attack. The unusually small deuterium kinetic isotope effects; as small or equal to 0.4, for weaker nucleophilies seem to be ascribed to serve steric congestion in the Transition State (TS).




L = S at 55.0°C.
X = 4-MeO, 4-Me, 3-Me, H, 3-Ph, 3-MeO, 3-Cl, 3-Ac, 4-Ac,4-CN, 3-CN.

**Figure 6.** Reaction System of Pyridinolysis of Thiophosphinic Chlorides

Lee et al [15] reported "Kinetics and Mechanism of the Pyridinolysis of DiphenylThiophosphinic Chlorides in Acetonitrile". Authors reported that, the kinetic studies of the reactions of diphenylthiophosphinic chlorides with substituted X-pyridines in acetonitrile at 55.0°C. In the case of the pyridinolysis of Diphenyl Thiophosphinic Chlorides, the Hammett and Brönstedplots were biphasic concave upwards with the break point at 3-phenyl pyridine indicating a change in mechanism from a concerted $S_N2(P)$ process with direct back-side nucleophilic attack for less basic nucleophiles (X = 3-CN-3-Ph) to a stepwise process with front-side attack for more basic nucleophiles (X = 4-MeO-3-Ph). The larger magnitudes of $\rho_X$ and $\beta_X$ for stronger nucleophiles are considered to arise from the frontside (equatorial) nucleophilic attack, whereas the smaller values arise from the backside (apical) nucleophilic attack in the TS. The stepwise mechanism with the rate-limiting bond formation was proposed for more basic nucleophiles in the pyridinolysis of above substrate on the basis of greater $\beta_X$ value (1.53). Apparent secondary inverse kinetic isotope effects with deuterated pyridine ($C_5D5_N$), $k_H/k_D < 1$, for the pyridinolysis of Diphenyl Thiophosphinic was interpreted with the more basic properties of d-5 pyridine compared to pyridine.

## 3. Conclusions

Organothiophosphorous compounds are useful in agricultural, pharmaceuticals and Textile chemicals. A significant number of works have been reported on thiophosphoryl (P=S) transfer reactions. Because predicting the effects of replacing the oxygen atom in the phosphoryl group (P=O) with sulfur is necessary. This review article includes summary of results of published papers from 1994-2014. There are two main types of mechanisms at P=S center have been reported in literature: concerted involving displacementat phosphorus through a single pentacoordinate transition state (TS) and stepwise mechanism involving a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate. In some cases mechanistic change from concerted to stepwise or *vice versa* has been reported.

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