

THE KINETICS OF THE ALKALINE HYDROLYSIS OF ARYL DIPHENYLPHOSPHINOTHIOATES;  
THE SIGNIFICANCE FOR THE MECHANISM OF DISPLACEMENT AT PHOSPHORUS.

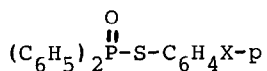
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Summary:

The rate of hydrolysis of aryl phosphinothioates, the most reactive phosphinates yet studied, correlates with Hammett's  $\sigma$  values suggesting that formation of a pentacoordinate intermediate is the rate-determining step.

There are two proposals in the literature for the mechanism of hydrolysis of acyclic phosphorus esters: i) direct displacement,  $S_N2(P)^{2a}$ , and ii) displacement through an intermediate<sup>2b</sup>. A useful manner in which to study this problem is to examine the effect of the leaving group on the reaction rate. A number of studies have been carried out on aryl phosphinates<sup>3-15</sup>, however, aryl phosphinothioate hydrolysis has not yet been investigated. A mechanism involving direct displacement should give rise to an appreciable rate difference between the phosphinates and phosphinothioates because of the differences in basicity of the leaving groups and the rates of reaction in the two systems should correlate with Hammett's  $\sigma^-$  values. For a reaction proceeding via an intermediate the rate-determining step for both substrates should be formation of the intermediate because the leaving groups are less basic than  $HO^-$  and this should lead to a relatively small difference in rate between the two systems and a correlation of the rates with Hammett's  $\sigma$  values. Accordingly we have studied the hydrolysis reactions of esters Ia-h at 25°C in a 20% methanol-80% carbonate buffer solution at an ionic strength of 0.056 M. The second-order rate constants, kinetic wavelength and the melting points of the esters are given in Table 1.



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Ia	X = NO <sub>2</sub>	Ie	X = NHC(O)CH <sub>3</sub>
Ib	X = Br	If	X = H
Ic	X = Cl	Ig	X = CH <sub>3</sub>
Id	X = F	Ih	X = OCH <sub>3</sub>

Table 1. Melting Points, Second-order Rate Constants and Kinetic Wavelength for the Compounds Ia-h.

Compound <sup>a</sup>	m.p. °C	$k \text{ M}^{-1} \text{ sec}^{-1}$ <sup>b</sup>	Kinetic Wavelength nm
Ia	121-23	31.3	420
Ib	112-13	4.93	280
Ic	111-12 (111) <sup>c</sup>	4.52	280
Id	106-07	2.84	280
Ie	168-69	2.54	300
If	89-91 (90-91) <sup>c</sup>	1.86	280
Ig	112-14 (112-13) <sup>c</sup>	1.34	280
Ih	140-42	0.91	295

<sup>a</sup>The esters give characteristic infrared and nmr spectra. All unreported esters give good elemental analyses except the p-NO<sub>2</sub> compound which was shown to contain, upon chromatographic analysis, a small amount of diphenylphosphinic acid. The lability of the ester made it impossible to purify it further. The acid impurity was shown to have no effect on the kinetic determination.

<sup>b</sup>The average of several runs at 25°C in 20% methanol-80% carbonate buffer; pH = 11.4

<sup>c</sup>H. Schindlbaeur and W. Prikoszovich, *Monatsh. Chem.*, **99**, 1792 (1968).

The rates of hydrolysis of esters Ia-h correlate with Hammett's  $\sigma$  and not  $\sigma^-$  values. The  $\rho$  value obtained is 1.46 ( $r = 0.997$ ). All other phosphinates and phosphinothionates which have been studied under alkaline hydrolysis conditions, with the exception of aryl dimethylphosphinates<sup>6</sup>, also give better correlations with  $\sigma$  values (Table 2). Although it is not possible to compare the  $\rho$  values for the aryl phosphinates and phosphinothionates in the same solvent, it appears that the latter series has a slightly lower  $\rho$  value (1.46 in 20% methanol) than the phosphinates (1.55 in 10% dioxane<sup>4</sup> or 1.566 in 20% ethanol<sup>14</sup>). This general trend is also observed with the acetates (series 8 and 9 in Table 2). The ratio of  $\rho_S/\rho_O$  in these series is in agreement with the ratio of the insulating effects of the S and O atoms as calculated from the <sup>13</sup>C-H coupling constants in the methyl group of substituted anisoles and thioanisoles ( $Z_S/Z_O = 0.90$ )<sup>17</sup>.

Although thiophenols are several powers of ten more acidic than phenols the second-order rate constants for compounds Ia-h are only about 4 times greater than the oxygen analogs<sup>4</sup>. In the case of the acetates the rate difference is also very small with the oxygen compounds having rates less than twice those of the sulfur compounds<sup>15,16</sup>. The similarity of behavior of the phosphinates and the acetates as well as the correlation of their hydrolysis rates with  $\sigma$  and not  $\sigma^-$  strongly suggest that there is no negative charge generated on the leaving group in the rate-determining step. Inasmuch as formation of the intermediate is rate-determining in acetate hydrolysis as supported by

linear free energy data<sup>18,19</sup>, it is reasonable to suggest that formation of a pentacoordinate intermediate would be the rate-limiting step for the hydrolysis of the phosphinates.

Table 2. Hammett Values for the Leaving Group in the Alkaline Hydrolysis of Aryl Phosphinates.

<u>Compound</u>	<u>T°C</u>	<u>Solvent</u>	<u><math>\rho</math></u>	<u><math>\sigma</math> used</u>	<u>Reference</u>
1. (Ph) <sub>2</sub> P(O)OC <sub>6</sub> H <sub>4</sub> X	25	60% acetone	2.20	$\sigma$	3
	25	10% dioxane	1.55	$\sigma$	4
	25	water	1.395	$\sigma^\circ$	14
	25	50% ethanol	1.93	$\sigma^\circ$	14
2. (Ph) <sub>2</sub> P(O)SC <sub>6</sub> H <sub>4</sub> X	25	20% methanol	1.46	$\sigma$	this work
3. (Ph) <sub>2</sub> P(S)OC <sub>6</sub> H <sub>4</sub> X	25	50% ethanol	1.99	$\sigma^\circ$	10
	25	50% ethanol	1.90	$\sigma^\circ$	5
4. (Me) <sub>2</sub> P(O)OC <sub>6</sub> H <sub>4</sub> X	25	10% dioxane	0.93	$\sigma^-$	6
5. (Me) <sub>2</sub> P(S)OC <sub>6</sub> H <sub>4</sub> X	25	water	1.28	$\sigma^\circ$	8,10,11
	25	50% ethanol	1.72	$\sigma^\circ$	8,10,11
6. Ph(Me)P(S)OC <sub>6</sub> H <sub>4</sub> X	25	50% ethanol	1.83	$\sigma^\circ$	10
7. PhC(O)OC <sub>6</sub> H <sub>4</sub> X	30	60% acetone	2.04	$\sigma^\circ$	3
8. MeC(O)OC <sub>6</sub> H <sub>4</sub> X	25	water	0.95	$\sigma^\circ$	15
9. MeC(O)SC <sub>6</sub> H <sub>4</sub> X	25	water	0.79	$\sigma^\circ$	16

The alternative of a direct displacement pathway would require a very early transition state with no (or minimal) phosphorus-leaving group bond breakage. Although it is not possible to determine at which point in the process of breaking a bond the correlation becomes better with  $\sigma^-$  than with  $\sigma$  or, in another way of putting it, the  $r$  value of the Yukawa-Tsuno<sup>20</sup> equation becomes significant, the excellent correlation obtained in these experiments with Hammett's  $\sigma$  values strongly supports no such bond breaking in the transition state.

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