MAPPING TRANSITION STATE STRUCTURES FOR THIOPHOSPHINOYL GROUP TRANSFER BETWEEN OXYANIONIC NUCLEOPHILES IN WATER AND AQUEOUS ETHANOL SOLVENTS

Georgina I. Kalu,[1] Collins I. Ubochi[1] and Ikenna Onyido[2]*
[1]Department of Chemistry, Imo State University, Owerri, Nigeria
[2]Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Nigeria

(Correspondence: Ikenna Onyido, Department of Pure & Industrial Chemistry, Nnamdi Azikiwe University, Awka, Nigeria. E-mail: ikennaonyido@yahoo.com; i.onyido@unizik.edu.ng; Phone +234 806-268-5122)

NEW JOURNAL OF CHEMISTRY

ELECTRONIC SUPPLEMENTARY INFORMATION

Table S1 Pseudo-first-order rate constants for the reaction of 4-nitrophenyl dimethylphosphinothioate with oxygen nucleophiles at 25°C, *I* = 1.0M KCl

A. Solvent: 50% water-50% ethanol (v/v)

1. Nucleophile = HO^- [Substrate] = 5.0×10^{-5}M

10^3[Nucleophile]/M	1.0	2.0	3.0	4.0	5.0
$10^4 k_{obs}/s^{-1}$	2.26	2.62	2.93	3.20	3.38

2. Nucleophile = $CHCl_2CH_2O^-$ [Substrate] = 5.0×10^{-5}M

10^3[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^5 k_{obs}/s^{-1}$	1.48	2.12	2.61	3.47

3. Nucleophile = $CF_3CH_2O^-$ [Substrate] = 5.0×10^{-5}M

10^3[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^5 k_{obs}/s^{-1}$	1.40	1.91	2.48	3.21

4. Nucleophile = $CF_3CF_2CF_2CH_2O$- [Substrate] = 5.0×10^{-5}M

10^3[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^5 k_{obs}/s^{-1}$	1.12	1.36	1.59	1.88

5. Nucleophile = 4-$MePhO^-$ [Substrate] = 5.0×10^{-5}M

10^3[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^6 k_{obs}/s^{-1}$	1.20	1.62	1.85	2.36

6. Nucleophile = PhO^- [Substrate] = 5.0×10^{-5}M

10^3[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^7 k_{obs}/s^{-1}$	9.99	13.1	15.8	20.4

7. Nucleophile = 4-$ClPhO^-$ [Substrate] = 5.0×10^{-5}M

10^3[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^7 k_{obs}/s^{-1}$	6.15	7.90	9.62	1.11

8. Nucleophile = 3-$CNPhO^-$ [Substrate] = 5.0×10^{-5}M

10^3[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^7 k_{obs}/s^{-1}$	3.89	4.96	6.15	7.90

9. Nucleophile = 4-$CNPhO^-$ [Substrate] = 5.0×10^{-5}M

10^3[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^7 k_{obs}$/s^{-1}	1.31	1.64	2.00	2.40

10. Nucleophile = 2,5-Cl_2PhO^- [Substrate] = 5.0 x 10^{-5}M

10^3[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^7 k_{obs}$/s^{-1}	1.02	1.31	1.49	1.92

11. Nucleophile = 2,4,5-Cl_3PhO^- [Substrate] = 5.0 x 10^{-5}M

10^3[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^8 k_{obs}$/s^{-1}	7.99	10.2	12.1	15.0

12. Nucleophile = 2,3,5,6-F_4PhO^- [Substrate] = 5.0 x 10^{-5}M

10^3[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^8 k_{obs}$/s^{-1}	6.96	8.99	9.91	11.6

B. Solvent: 30% water-70% ethanol (v/v)

1. Nucleophile = HO^- [Substrate] = 5.0 x 10^{-5}M

10^2[Nucleophile]/M	1.0	2.0	3.0	4.0	5.0
$10^4 k_{obs}$/s^{-1}	4.48	6.36	8.22	10.1	11.9

2. Nucleophile = $CHCl_2CH_2O^-$ [Substrate] = 5.0 x 10^{-5}M

10^2[Nucleophile]/M	1.0	2.0	3.0	4.0	5.0
$10^4 k_{obs}$/s^{-1}	1.36	1.92	2.47	3.03	3.58

3. Nucleophile = $CF_3CH_2O^-$ [Substrate] = 5.0 x 10^{-5}M

10^2[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^4 k_{obs}$/s^{-1}	1.09	1.58	2.11	2.61

3. Nucleophile = $CF_3CH_2O^-$ [Substrate] = 5.0 x 10^{-5}M

10^2[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^4 k_{obs}$/s^{-1}	1.09	1.58	2.11	2.61

4. Nucleophile = $CF_3CH_2O^-$ [Substrate] = 5.0 x 10^{-5}M

10^2[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^5 k_{obs}$/s^{-1}	5.12	7.46	9.77	12.0

5. Nucleophile = 4-$MeOPhO^-$ [Substrate] = 5.0 x 10^{-5}M

10^2[Nucleophile]/M	2.0	3.0	4.0	5.0

$10^6 k_{obs}/s^{-1}$	6.14	11.0	12.9	15.8

6. Nucleophile = PhO^- [Substrate] = 5.0×10^{-5}M

10^2[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^6 k_{obs}/s^{-1}$	5.72	8.59	10.4	12.9

7. Nucleophile = 4-ClPhO^- [Substrate] = 5.0×10^{-5}M

10^2[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^6 k_{obs}/s^{-1}$	5.52	6.74	8.28	9.81

8. Nucleophile = 3-CNPhO^- [Substrate] = 5.0×10^{-5}M

10^2[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^6 k_{obs}/s^{-1}$	5.17	6.43	7.36	8.28

9. Nucleophile = 4-CNPhO^- [Substrate] = 5.0×10^{-5}M

10^2[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^6 k_{obs}/s^{-1}$	4.95	5.30	5.52	5.93

10. Nucleophile = $2,5\text{-Cl}_2\text{PhO}^-$ [Substrate] = 5.0×10^{-5}M

10^2[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^6 k_{obs}/s^{-1}$	4.78	5.07	5.36	5.52

11. Nucleophile = $2,4,5\text{-Cl}_3\text{PhO}^-$ [Substrate] = 5.0×10^{-5}M

10^2[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^6 k_{obs}/s^{-1}$	4.70	4.76	4.90	5.06

12. Nucleophile = $2,3,5,6\text{-F}_4\text{PhO}^-$ [Substrate] = 5.0×10^{-5}M

10^2[Nucleophile]/M	2.0	3.0	4.0	5.0
$10^6 k_{obs}/s^{-1}$	4.66	4.69	4.85	4.90

Table S2 Pseudo-first-order rate constants for the reaction of a series of aryl dimethylphosphinothioate esters with HO^- and PhO^- at 25°C, I = 1.0M KCl

A. Solvent: 50% water-50% ethanol (v/v)

1. Nucleophile: HO^-

Leaving Group	$10^3[HO^-]$/M:	1.0	2.0	3.0	4.0	5.0
4-NO_2PhO^-	$10^5k_{obs}/s^{-1}$	2.26	26.2	29.3	32.0	33.8
4-Cl,3-NO_2PhO^-	$10^5k_{obs}/s^{-1}$		7.40	7.90	8.90	10.4
3-NO_2PhO^-	$10^5k_{obs}/s^{-1}$		4.89	5.35	5.79	6.37
3-CNPhO^-	$10^5k_{obs}/s^{-1}$		4.67	5.00	5.16	2.95
3-ClPhO^-	$10^5k_{obs}/s^{-1}$		3.63	3.78	3.90	4.04

2. Nucleophile: PhO^-

Leaving Group	$10^3[PhO^-]$/M:	2.0	3.0	4.0	5.0
4-NO_2PhO^-	$10^6k_{obs}/s^{-1}$	1.00	1.31	1.58	2.04
4-Cl,3-NO_2PhO^-	$10^7k_{obs}/s^{-1}$	9.03	10.3	11.6	12.8
3-NO_2PhO^-	$10^7k_{obs}/s^{-1}$	8.89	9.40	9.94	10.5
3-CNPhO^-	$10^7k_{obs}/s^{-1}$	8.68	9.07	9.48	9.87

B. Solvent: 30% water-70% ethanol (v/v)

1. Nucleophile: HO^-

Leaving Group	$10^2[HO^-]$/M:	1.0	2.0	3.0	4.0	5.0
4-NO_2PhO^-	$10^2k_{obs}/s^{-1}$	1.41	1.44	1.46	1.47	1.50
4-Cl,3-NO_2PhO^-	$10^3k_{obs}/s^{-1}$		1.42	1.51	1.57	1.64
3-NO_2PhO^-	$10^3k_{obs}/s^{-1}$		1.34	1.37	1.40	1.43
3-CNPhO^-	$10^3k_{obs}/s^{-1}$		1.02	1.05	1.06	1.10
3-ClPhO^-	$10^4k_{obs}/s^{-1}$		8.64	8.72	8.81	8.90

2. Nucleophile: PhO^-

Leaving Group	$10^2[PhO^-]$/M:	2.0	3.0	4.0	5.0
4-NO_2PhO^-	$10^6k_{obs}/s^{-1}$	5.72	8.59	10.4	12.9
4-Cl,3-NO_2PhO^-	$10^6k_{obs}/s^{-1}$	5.62	6.67	7.72	8.77
3-NO_2PhO^-	$10^6k_{obs}/s^{-1}$	5.49	5.99	6.53	7.02
3-CNPhO^-	$10^6k_{obs}/s^{-1}$	5.38	5.70	6.03	6.35

Table S3 Parameters (slope, intercept, and *R*) extracted from the plots of log k_{nuc} *versus* $1/\varepsilon$ of the solvents shown in Fig. 5 for HO- and PhO- for the reaction of **3a** with various oxygen nucleophiles in water and three water-ethanol mixtures at 25°C.

Entry	Nucleophile	-Slope	-Intercept	-R^a
1	HO^-	157	0.24	0.920
2	$CHCl_2CH_2O^-$	244	-0.48	0.816
3	$CF_3CH_2O^-$	530	-5.09	0.999
4	$CF_3CF_2CF_2CH_2O^-$	243	0.45	0.803
5	4-MeOPhO$^-$	157	4.41	0.849
6	PhO^-	174	4.25	0.897
7	4-ClPhO$^-$	202	4.15	0.823
8	3-CNPhO$^-$	88	7.08	0.931
9	4-CNPhO$^-$	179	6.18	0.825
10	2,5-Cl_2PhO$^-$	177	6.46	0.823
11	2,4,5-Cl_3PhO$^-$	194	6.67	0.949
12	2,3,5,6-F_4PhO$^-$	203	6.82	0.918

[a] *R* = correlation coefficient for plots of log k_{nuc} *versus* $1/\varepsilon$ for the reactions of **3a** with various oxygen nucleophiles in water, 70% water-30% ethanol, 50% water-50% ethanol and 30% water-70% ethanol. Only the linear part of the plots (three data points) was utilized in analysis that gave rise to the parameters in this Table.

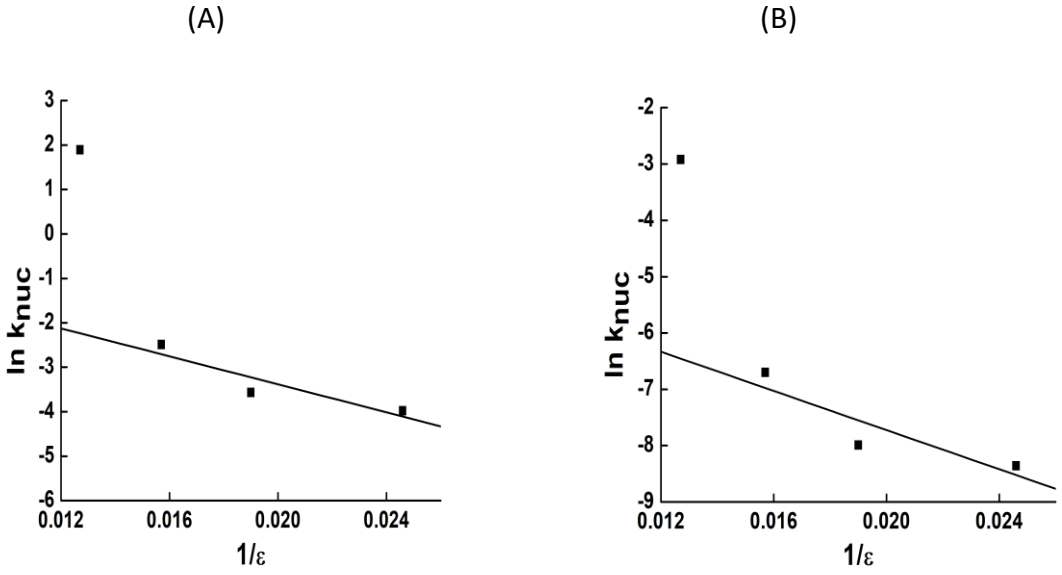

Fig. S1 Plots of (a) log k_{nuc} *versus* $1/\varepsilon$ for the reaction of **3a** with representative oxygen nucleophiles: (A) HO^- and (B) PhO^- in water and water-ethanol mixtures at 25°C. Data point for reaction in 30% water-70% ethanol solvent mixture has been omitted in drawing the regression line due to the curvature of the plots, which indicates the incursion of specific solvation factors in this region of the solvent mixture. The plots for the rest of the nucleophiles studied are not shown but they behaved exactly the same way as the representative plots above. The values of the slopes, intercepts and R obtained from plots for the 12 nucleophiles are shown in Table S3 (ESI). Values of ε used in the plots were taken from G. Akerlof, *J. Am. Chem. Soc.*, 1935, **54**, 4125 and M. Faraji, A. Farajtabar and F. Gharib, *J. Appl. Chem. Res*., 2009, **9**, 7.