

**THIOPHOSPHINOYL TRANSFER FROM ARYL
DIMETHYLPHOSPHINOTHIOATE ESTERS TO ANIONIC OXYGEN
NUCLEOPHILES: THE EFFECT OF SOLVENT POLARITY ON THE TRANSITION
STATE[†]**

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Electronic Supplementary Information

Table S1

Pseudo-First-Order Rate Constants (k_{obs}/s^{-1}) for the Reaction of 4-Nitrophenyl Dimethylphosphinates (**3a**)^a with Oxyanionic Nucleophiles in 70% Water-30% Ethanol (v/v) at 25°C^b

A.	Nucleophile = HO ⁻ 10 ⁴ [HO ⁻]/M 10 ⁴ k_{obs}/s^{-1}	5.0 2.60	10.0 3.10	20.0 3.80	30.0 4.74	40.0 5.64	50.0 6.39
B.	Nucleophile = CHCl ₂ CH ₂ O ⁻ 10 ⁴ [CHCl ₂ CH ₂ O ⁻]/M 10 ⁵ k_{obs}/s^{-1}	5.0 3.04	10.0 6.03	20.0 12.5	30.0 18.3	40.0 24.4	50.0 30.0
C.	Nucleophile = CF ₃ CH ₂ O ⁻ 10 ⁴ [CF ₃ CH ₂ O ⁻]/M 10 ⁵ k_{obs}/s^{-1}	5.0 2.05	10.0 4.27	20.0 8.55	30.0 13.1	40.0 16.6	50.0 21.5
D.	Nucleophile = CF ₃ (CF ₂) ₂ CH ₂ O ⁻ 10 ⁴ [CF ₃ (CF ₂) ₂ CH ₂ O ⁻]/M 10 ⁵ k_{obs}/s^{-1}	5.0 1.46	10.0 2.55	20.0 5.07	30.0 7.63	40.0 10.1	50.0 12.8
E.	Nucleophile = 4-MeOPhO ⁻ 10 ⁴ [4-MeOPhO ⁻]/M 10 ⁷ k_{obs}/s^{-1}	5.0 6.15	10.0 15.4	20.0 27.7	30.0 43.1	40.0 55.4	50.0 70.8
F.	Nucleophile = PhO ⁻ 10 ⁴ [PhO ⁻]/M 10 ⁷ k_{obs}/s^{-1}	5.0 6.15	10.0 12.3	20.0 24.6	30.0 36.9	40.0 49.2	50.0 61.5
G.	Nucleophile = 4-ClPhO ⁻ 10 ⁴ [4-ClPhO ⁻]/M 10 ⁷ k_{obs}/s^{-1}	5.0 5.54	10.0 9.22	20.0 19.4	30.0 30.8	40.0 40.0	50.0 52.3
H.	Nucleophile = 3-CNPhO ⁻ 10 ⁴ [3-CNPhO ⁻]/M 10 ⁷ k_{obs}/s^{-1}	5.0 1.76	10.0 1.85	20.0 5.54	30.0 7.39	40.0 9.22	50.0 12.3
I.	Nucleophile = 4-CNPhO ⁻ 10 ⁴ [4-CNPhO ⁻]/M 10 ⁸ k_{obs}/s^{-1}	5.0 8.79	10.0 17.6	20.0 44.0	30.0 61.5	40.0 73.9	50.0 92.2
J.	Nucleophile = 2,5-Cl ₂ PhO ⁻ 10 ⁴ [2,5-Cl ₂ PhO ⁻]/M 10 ⁸ k_{obs}/s^{-1}	5.0 7.68	10.0 15.4	20.0 30.7	30.0 44.0	40.0 61.5	50.0 70.3
K.	Nucleophile = 2,4,5-Cl ₃ PhO ⁻ 10 ⁴ [2,4,5-Cl ₃ PhO ⁻]/M 10 ⁸ k_{obs}/s^{-1}	5.0 5.13	10.0 7.18	20.0 16.7	30.0 23.0	40.0 30.8	50.0 38.4
L.	Nucleophile = 2,3,5,6-F ₄ PhO ⁻ 10 ⁴ [2,3,5,6-F ₄ PhO ⁻]/M 10 ⁸ k_{obs}/s^{-1}	5.0 3.62	10.0 5.13	20.0 11.2	30.0 16.7	40.0 23.0	50.0 30.8

^a[Substrate] generally in the range of 3.0-5.0 x 10⁻⁵M. ^bReactions were carried out at ionic strength, *I* = 1.0M (KCl).

Table S2

Pseudo-First-Order Rate Constants (k_{obs}/s^{-1}) for the Reactions of Substituted Aryl Dimethylphosphinates (**3a-g**)^a with HO⁻ and PhO⁻ as Nucleophiles in 70% Water-30% Ethanol (v/v) at 25°C^b

A. Nucleophile = HO⁻							
1.	Substrate = 3a ; leaving group = 4-NO ₂ PhO ⁻						
	10 ⁴ [HO ⁻]/M	5.0	10.0	20.0	30.0	40.0	50.0
	10 ⁴ k_{obs}/s^{-1}	2.60	3.10	3.80	4.74	5.64	6.39
2.	Substrate = 3b ; leaving group = 4-Cl,3-NO ₂ PhO ⁻						
	10 ⁴ [HO ⁻]/M	20.0	30.0	40.0	50.0		
	10 ⁴ k_{obs}/s^{-1}	1.18	1.74	2.11	2.48		
3.	Substrate = 3c ; leaving group = 3-NO ₂ PhO ⁻						
	10 ⁴ [HO ⁻]/M	20.0	30.0	40.0	50.0		
	10 ⁵ k_{obs}/s^{-1}	8.89	11.2	13.1	24.1		
4.	Substrate = 3d ; leaving group = 3-CNPhO ⁻						
	10 ⁴ [HO ⁻]/M	20.0	30.0	40.0	50.0		
	10 ⁵ k_{obs}/s^{-1}	6.84	8.14	9.59	10.3		
5.	Substrate = 3e ; leaving group = 3-ClPhO ⁻						
	10 ⁴ [HO ⁻]/M	20.0	30.0	40.0	50.0		
	10 ⁵ k_{obs}/s^{-1}	6.21	6.93	7.61	8.77		
6.	Substrate = 3f ; leaving group = 4-ClPhO ⁻						
	10 ⁴ [HO ⁻]/M	20.0	30.0	40.0	50.0		
	10 ⁵ k_{obs}/s^{-1}	4.95	5.58	5.99	5.65		
7.	Substrate = 3g ; leaving group = PhO ⁻						
	10 ⁴ [HO ⁻]/M	20.0	30.0	40.0	50.0		
	10 ⁵ k_{obs}/s^{-1}	3.47	3.58	3.63	3.68		
B. Nucleophile = PhO⁻							
1.	Substrate = 3a ; leaving group = 4-NO ₂ PhO ⁻						
	10 ⁴ [PhO ⁻]/M	5.0	10.0	20.0	30.0	40.0	50.0
	10 ⁷ k_{obs}/s^{-1}	6.15	12.3	24.6	36.9	49.2	61.5
2.	Substrate = 3b ; leaving group = 4-Cl,3-NO ₂ PhO ⁻						
	10 ⁴ [PhO ⁻]/M	20.0	30.0	40.0	50.0		
	10 ⁷ k_{obs}/s^{-1}	8.25	12.4	16.5	20.6		
3.	Substrate = 3c ; leaving group = 3-NO ₂ PhO ⁻						
	10 ⁴ [PhO ⁻]/M	20.0	30.0	40.0	50.0		
	10 ⁷ k_{obs}/s^{-1}	3.23	4.85	6.47	8.07		
4.	Substrate = 3d ; leaving group = 3-CNPhO ⁻						
	10 ⁴ [PhO ⁻]/M	20.0	30.0	40.0	50.0		
	10 ⁷ k_{obs}/s^{-1}	2.64	3.96	5.27	6.60		
5.	Substrate = 3e ; leaving group = 3-ClPhO ⁻						
	10 ⁴ [PhO ⁻]/M	20.0	30.0	40.0	50.0		
	10 ⁷ k_{obs}/s^{-1}	1.34	2.00	2.67	3.34		
6.	Substrate = 3f ; leaving group = 4-ClPhO ⁻						
	10 ⁴ [PhO ⁻]/M	20.0	30.0	40.0	50.0		
	10 ⁸ k_{obs}/s^{-1}	7.25	7.78	15.6	16.8		

^a[Substrate] generally in the range of 3.0-5.0 x 10⁻⁵M. ^bReactions were carried out at ionic strength, *I* = 1.0M (KCl).