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Analysis of LFER's Combined with Activation Parameters Assigns a Concerted Mechanism to Alkaline Hydrolysis of X-Substituted Phenyl Diphenylphosphinates

Ik-Hwan Um,^{*} Jeong-Yoon Han and So-Jeong Hwang

Division of Nano Sciences and Department of Chemistry, Ewha Womans University, Seoul 120 – 750, Korea

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Table S1. Kinetic data for alkaline hydrolysis of 3,4-dinitrophenyl diphenylphosphinate (**1a**) in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$k_{\text{obsd}} / \text{s}^{-1}$
1	4.98	0.88
2	9.96	1.78
3	14.9	2.79
4	19.9	3.78
5	24.9	4.85

$k_{\text{OH}^-} = 200 \pm 3 \text{ M}^{-1}\text{s}^{-1}$
corr. coeff. = 0.9996

Table S2. Kinetic data for alkaline hydrolysis of 4-nitrophenyl diphenylphosphinate (**1b**) in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	0.793	1.47
2	1.58	3.18
3	3.13	6.49

4	4.66	9.79
5	6.17	12.9

$k_{\text{OH}^-} = 21.3 \pm 0.1 \text{ M}^{-1}\text{s}^{-1}$
corr. coeff. = 0.9999

Table S3. Kinetic data for alkaline hydrolysis of 4-formylphenyl diphenylphosphinate (**1c**) in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	1.61	1.39
2	3.20	2.77
3	4.76	4.20
4	6.29	5.64
5	7.81	7.01

$k_{\text{OH}^-} = 9.11 \pm 0.07 \text{ M}^{-1}\text{s}^{-1}$
corr. coeff. = 0.9999

Table S4. Kinetic data for alkaline hydrolysis of 4-cyanophenyl diphenylphosphinate (**1d**) in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	1.58	1.97
2	3.13	3.96
3	4.66	6.10
4	6.17	8.09
5	7.65	10.3

$k_{\text{OH}^-} = 13.3 \pm 0.1 \text{ M}^{-1}\text{s}^{-1}$
corr. coeff. = 0.9999

Table S5. Kinetic data for alkaline hydrolysis of 4-acetylphenyl diphenylphosphinate (**1e**) in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	1.58	0.973
2	3.13	1.96
3	4.66	2.98
4	6.17	3.94
5	7.65	4.97

$k_{\text{OH}^-} = 6.57 \pm 0.06 \text{ M}^{-1}\text{s}^{-1}$
 corr. coeff. = 0.9998

Table S7. Kinetic data for alkaline hydrolysis of 3-acetylphenyl diphenylphosphinate (**1g**) in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	1.97	0.599
2	3.90	1.26
3	5.80	1.90
4	7.65	2.60
5	9.48	3.10

$k_{\text{OH}^-} = 3.38 \pm 0.08 \text{ M}^{-1}\text{s}^{-1}$
 corr. coeff. = 0.9990

Table S8. Kinetic data for alkaline hydrolysis of 4-chlorophenyl diphenylphosphinate (**1h**) in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	1.97	0.424
2	3.90	0.949
3	5.80	1.41
4	7.65	1.83
5	9.48	2.27

$k_{\text{OH}^-} = 2.44 \pm 0.05 \text{ M}^{-1}\text{s}^{-1}$
 corr. coeff. = 0.9994

Table S9. Kinetic data for alkaline hydrolysis of phenyl diphenylphosphinate (**1i**) in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	18.1	1.26
2	33.2	2.30
3	45.9	3.19
4	56.9	3.89
5	66.3	4.61

$k_{\text{OH}^-} = 0.690 \pm 0.008 \text{ M}^{-1}\text{s}^{-1}$
 corr. coeff. = 0.9997

Table S10. Kinetic data for alkaline hydrolysis of 3,4-dinitrophenyl diphenylphosphinate (**1a**) in 80 mol % H₂O/20 mol % DMSO at $15.0 \pm 0.1^\circ\text{C}$.

	$10^3 [\text{OH}^-] / \text{M}$	$k_{\text{obsd}} / \text{s}^{-1}$
1	10.2	1.06
2	20.4	2.07
3	30.6	3.28
4	40.8	4.51
5	51.0	5.76

$k_{\text{OH}^-} = 116 \pm 3 \text{ M}^{-1}\text{s}^{-1}$
 corr. coeff. = 0.9992

Table S11. Kinetic data for alkaline hydrolysis of 3,4-dinitrophenyl diphenylphosphinate (**1a**) in 80 mol % H₂O/20 mol % DMSO at $20.0 \pm 0.1^\circ\text{C}$.

	$10^3 [\text{OH}^-] / \text{M}$	$k_{\text{obsd}} / \text{s}^{-1}$
1	5.10	0.700
2	10.2	1.45
3	15.3	2.24
4	20.4	3.01
5	25.5	3.82

$k_{\text{OH}^-} = 153 \pm 1 \text{ M}^{-1}\text{s}^{-1}$
 corr. coeff. = 0.9999

Table S12. Kinetic data for alkaline hydrolysis of 3,4-dinitrophenyl diphenylphosphinate (**1a**) in 80 mol % H₂O/20 mol % DMSO at 35.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$k_{\text{obsd}} / \text{s}^{-1}$
1	2.50	0.765
2	4.99	1.61
3	7.49	2.45
4	9.98	3.33
5	12.5	4.17

$$k_{\text{OH}^-} = 341 \pm 1 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{corr. coeff.} = 0.9999$$

Table S13. Kinetic data for alkaline hydrolysis of 3,4-dinitrophenyl diphenylphosphinate (**1a**) in 80 mol % H₂O/20 mol % DMSO at 45.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$k_{\text{obsd}} / \text{s}^{-1}$
1	2.00	1.44
2	4.00	2.59
3	6.00	3.60
4	8.00	4.79
5	10.0	5.77

$$k_{\text{OH}^-} = 543 \pm 9 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{corr. coeff.} = 0.9996$$

Table S14. Kinetic data for alkaline hydrolysis of 4-nitrophenyl diphenylphosphinate (**1b**) in 80 mol % H₂O/20 mol % DMSO at 15.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	0.793	0.762
2	1.58	1.78
3	3.13	3.54
4	4.66	5.31
5	6.17	7.21

$$k_{\text{OH}^-} = 11.9 \pm 0.1 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{corr. coeff.} = 0.9998$$

Table S15. Kinetic data for alkaline hydrolysis of 4-nitrophenyl diphenylphosphinate (**1b**) in 80 mol % H₂O/20 mol % DMSO at 20.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	0.793	1.11
2	1.58	2.39
3	3.13	4.78
4	4.66	7.47
5	6.17	9.79

$$k_{\text{OH}^-} = 16.2 \pm 0.2 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{corr. coeff.} = 0.9997$$

Table S16. Kinetic data for alkaline hydrolysis of 4-nitrophenyl diphenylphosphinate (**1b**) in 80 mol % H₂O/20 mol % DMSO at 35.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	0.793	2.74
2	1.58	5.42
3	2.36	8.54
4	3.13	11.4
5	3.90	14.7

$$k_{\text{OH}^-} = 38.5 \pm 0.8 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{corr. coeff.} = 0.9993$$

Table S17. Kinetic data for alkaline hydrolysis of 4-nitrophenyl diphenylphosphinate (**1b**) in 80 mol % H₂O/20 mol % DMSO at 45.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	0.793	4.46
2	1.58	9.61
3	2.36	15.3
4	3.13	20.0
5	3.90	24.7

$$k_{\text{OH}^-} = 65.5 \pm 1.3 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{corr. coeff.} = 0.9994$$

Table S18. Kinetic data for alkaline hydrolysis of phenyl diphenylphosphinate (**1i**) in 80 mol % H₂O/20 mol % DMSO at 15.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	18.4	0.620
2	33.7	1.17
3	46.6	1.59
4	57.7	1.94
5	67.3	2.33

$$k_{\text{OH}^-} = 0.344 \pm 0.007 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{corr. coeff.} = 0.9993$$

Table S19. Kinetic data for alkaline hydrolysis of phenyl diphenylphosphinate (**1i**) in 80 mol % H₂O/20 mol % DMSO at 20.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	18.4	0.904
2	33.7	1.66
3	46.6	2.27
4	57.7	2.77
5	67.3	3.24

$$k_{\text{OH}^-} = 0.475 \pm 0.004 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{corr. coeff.} = 0.9998$$

Table S20. Kinetic data for alkaline hydrolysis of phenyl diphenylphosphinate (**1i**) in 80 mol % H₂O/20 mol % DMSO at 35.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	9.52	1.30
2	18.2	2.31
3	26.1	3.42
4	33.3	4.35
5	40.0	5.16

$$k_{\text{OH}^-} = 1.28 \pm 0.02 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{corr. coeff.} = 0.9995$$

Table S21. Kinetic data for alkaline hydrolysis of phenyl diphenylphosphinate (**1i**) in 80 mol % H₂O/20 mol % DMSO at 45.0 ± 0.1°C.

	$10^3 [\text{OH}^-] / \text{M}$	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
1	9.62	2.26
2	18.4	4.53
3	26.3	6.50
4	33.7	8.26
5	40.4	10.1

$k_{\text{OH}^-} = 2.52 \pm 0.03 \text{ M}^{-1}\text{s}^{-1}$
 corr. coeff. = 0.9998