Concurrent Primary and Secondary Deuterium Kinetic Isotope Effects
in Anilinolysis of O-Aryl Methyl Phosphonochloridothioates

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Experimental

(a) Substrates. The starting material, methyl phosphonothioic dichloride, phenols and triethylamine were G.R. grade and were used without further purification. Aryl methyl phosphonochloridothioates were prepared by reacting methyl phosphonothioic dichloride with phenols for 2 hrs in the presence of triethylamine in methylene chloride on an ice bath. Triethylamine hydrochloride salt was separated by filtration. The remaining product was treated with ether and water for workup. After workup, anhydrous MgSO$_4$ was added, and the solvent was evaporated under reduced pressure after filtration. The substrates were identified by TLC, IR, $^1$H NMR, $^{13}$C NMR, $^{31}$P NMR, GC-MS and elemental analysis. The physical constants after column chromatography (silica gel/ethyl acetate + n-hexane) were as follows.

4-Methoxyphenyl methyl phosphonochloridothioate: liquid; IR (neat) 3006 (C-H, aromatic), 2833 (C-H, aliphatic), 1595, 1502, 1443, 1405 (POC$_6$H$_4$), 1301 (P-CH$_3$), 840 cm$^{-1}$ (P=S); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.89 (d, $J$ = 8.8 Hz, 2H, phenyl), 7.18 (d, $J$ = 8.8Hz, 4H, phenyl), 3.79 (s, 3H, OCH$_3$), 2.50 and 2.46 (two s, 3H, P-CH$_3$-H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.34, 142.89, 122.28, 114.48, (C=C, phenyl), 55.58 (OCH$_3$), 50.64 and 29.64 (P-CH$_3$); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 99.50 (s, 1P, P=S); m/z 236 (M$^+$); Anal. Calcd for C$_8$H$_{10}$O$_2$PSCl: C, 40.6, H, 4.3. Found: C, 40.8; H, 4.5.
4-Methylphenyl methyl phosphonochloridothioate: liquid; IR (neat) 3028 (C-H, aromatic), 2919 (C-H, aliphatic), 1611, 1508, 1405, 1204 (POC₆H₄), 1301 (P-CH₃), 824 cm⁻¹ (P=S); ¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, J = 7.2 Hz, 2H, phenyl), 7.14 (d, J = 7.2 Hz, 2H, phenyl), 2.47 and 2.51 (two s, 3H, P-CH₃-H), 2.35 (s, 3H, CH₃-H); ¹³C NMR (100 MHz, CDCl₃) δ 121.26, 121.37, 130.23, 130.27 (C=C, phenyl), 31.37 and 29.36 (P-CH₃), 20.39 (CH₃); ³¹P NMR (162 MHz, CDCl₃) δ 98.65 (s, 1P, P=S); m/z 220 (M⁺); Anal. Calcd for C₈H₁₀OPSCl: C, 43.6; H, 4.6. Found: C, 43.5; H, 4.4.

Phenyl methyl phosphonochloridothioate: liquid; IR (neat) 3001 (C-H, aromatic), 2925 (C-H, aliphatic), 1595, 1486, 1404, 1160 (POC₆H₄), 1307 (P-CH₃), 737 cm⁻¹ (P=S); ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, J = 9.2 Hz, 2H, phenyl), 7.28 (t, J = 9.2 Hz, 3H, phenyl), 2.57 and 2.50 (two s, 3H, P-CH₃-H); ¹³C NMR (100 MHz, CDCl₃) δ 149.54, 129.56, 126.04, 125.35, 121.50, (C=C, aromatic), 30.91 and 29.90 (P-CH₃); ³¹P NMR (162 MHz, CDCl₃) δ 98.21 (s, 1P, P=S); m/z 206 (M⁺); Anal. Calcd for C₇H₈OPSCl: C, 40.7; H, 3.9. Found: C, 40.5; H, 3.8.

3-Chlorophenyl methyl phosphonochloridothioate: liquid; IR (neat) 3095 (C-H, aromatic), 2920 (C-H, aliphatic), 1592, 1487, 1410, 1200 (POC₆H₄), 1301 (P-CH₃), 843 cm⁻¹ (P=S); ¹H NMR (400 MHz, CDCl₃) δ 7.18–7.32 (m, 3H, phenyl), 7.35 (s, 1H, phenyl), 2.58 and 2.50 (two s, 3H, P-CH₃-H); ¹³C NMR (100 MHz, CDCl₃) δ 135.12, 129.85, 129.81, 123.08, 122.97, 118.12 (C=C, aromatic), 31.40 and 29.40 (P-CH₃); ³¹P NMR (162 MHz, CDCl₃) δ 98.30 (s, 1P, P=S); m/z 241 (M⁺); Anal. Calcd for C₇H₇OPSCl₂: C, 34.9; H, 2.9. Found: C, 34.7; H, 2.8.
**4-Cyanophenyl methyl phosphonochloridothioate:** liquid; IR (neat) 3103 (C-H, aromatic), 2920 (C-H, aliphatic), 2229 (C≡N) 1604, 1495, 1410, 1231 (POC₆H₄), 1301 (P-CH₃), 851 cm⁻¹ (P=S); ¹H NMR (400 MHz, CDCl₃) δ 7.69–7.72 (d, J = 8.8 Hz, 2H, phenyl), 7.38–7.40 (d, J = 8.8 Hz, 2H, phenyl), 2.53 and 2.56 (two s, 3H, P-CH₃-H); ¹³C NMR (100 MHz, CDCl₃) δ 152.60, 133.91, 122.63, 117.95 (C=C, aromatic), 110.14 (C≡N), 30.95 and 29.95 (P-CH₃); ³¹P NMR (162 MHz, CDCl₃) δ 97.97 (s, 1P, P=S); m/z 232 (M⁺); Anal. Calcd for C₈H₇NOPSCl: C, 41.5; H, 3.1; N 6.1. Found: C, 41.7; H, 3.2; N 6.2.
(b) Product analysis. 4-Methylphenyl methyl phosphonochloridothioate was reacted with excess 4-methoxy aniline for more than 15 half lives at 55.0 °C in acetonitrile. The 4-methoxy aniline hydrochloride salt was separated by filtration. Acetonitrile was evaporated under reduced pressure. The remaining product was isolated with ether by a workup process and dried over anhydrous MgSO₄. The product was isolated by evaporating the solvent under reduced pressure after filtration. The physical constants after column chromatography (silica gel/ethyl acetate + n-hexane) were:

\[(\text{CH}_3)(4\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{P(=S)}\text{NH-C}_6\text{H}_4\text{-4-CH}_3\text{O}: \text{yellowish solid; mp 96–98 °C; IR (nujol) 2943 (C-H, aromatic), 2826 (C-H, aliphatic), 1508, 1459, 1383 (POC}_6\text{H}_4, 1286 (P-CH}_3, 780 \text{cm}^{-1} \text{(P=S); } ^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.06 (s, 4H, phenyl), 7.01 (d, } J = 9.2 \text{ Hz, 2H, phenyl), 6.83 (d, } J = 8.8 \text{ Hz, 2H, phenyl), 5.15 (1H, d, } J = 9.2 \text{ Hz, NH-H), 3.76 (s, 3H, OCH}_3\text{-H), 2.27 (s, 3H, CH}_3\text{-H), 2.04 and 2.00 (two s, 3H, P-CH}_3\text{-H); } ^1\text{C NMR (100 MHz, CDCl}_3) \delta 155.84, 147.94, 134.76, 132.78, 129.99, 121.18, 114.93 (C=C, aromatic), 55.53 (OCH}_3, 20.78 and 20.40 (P-CH}_3, 19.34 (CH}_3; ^3\text{P NMR (162 MHz, CDCl}_3) \delta 82.66 (s, 1P, P=S); m/z 307 (M^+); Anal. Calcd for C}_{15}\text{H}_{18}\text{NO}_2\text{PS: C, 58.62; H, 5.90; N, 4.56. Found: C, 58.39; H, 6.03; N, 4.46.} \]
$^1$H NMR spectra

(a) $^1$H NMR spectrum for 4-cyanophenyl methyl phosphonochloridothioate:
$^{13}$C NMR spectrum for 4-cyanophenyl methyl phosphonochloridothioate:
(b) $^1$H NMR spectrum for (CH$_3$)(4-CH$_3$C$_6$H$_4$O)P(=S)NH-C$_6$H$_4$-4-CH$_3$O:
$^{13}$C NMR spectrum for $(\text{CH}_3)(4-\text{CH}_3\text{C}_6\text{H}_4\text{O})\text{P}(=\text{S})\text{NH-C}_6\text{H}_4-4-\text{CH}_3\text{O}$:
$^3$P NMR spectrum for (CH$_3$)(4-CH$_3$C$_6$H$_4$O)P(=S)NH-C$_6$H$_4$-4-CH$_3$O:
**Figure S1.** The Hammett plots of $\log k_{H(D)}$ vs $\sigma_X$ for the reactions of Y-O-aryl methyl phosphonochloridothioates with XC₆H₄NH₂ (1) and XC₆H₄ND₂ (2) in MeCN at 55.0 °C.

**Figure S2.** The Hammett plots of $\log k_{H(D)}$ vs $\sigma_Y$ for the reactions of Y-O-aryl methyl phosphonochloridothioates with XC₆H₄NH₂ (1) and XC₆H₄ND₂ (2) in MeCN at 55.0 °C.
References


