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On the Protonation Behavior of Several Simple Thiophosphate Anions

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ON THE PROTONATION BEHAVIOR OF SEVERAL SIMPLE THIOPHOSPHATE ANIONS

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Stepwise protonation constants of several thiomonophosphate anions, that is, $\text{PS}_n\text{O}(4-n)^{3-}$ ($n = 1-4$), have been determined (Table I). Since the rate of substitution of sulfur in thiomonophosphate anions for oxygen atom belonging to water molecule is fast, it is difficult to measure the protonation constants of these anions with conventional methods, so ^{31}P NMR has been employed in this study. The successive protonation constants decrease with an increase in the number of sulfur atoms bound to center phosphorus atom. It has been revealed that the logarithms of the stabilities of the proton complexes of thiomonophosphate anions decreases “linearly” with an increase in the number of sulfur atoms which constitute the anions.

TABLE I Protonation Constants and Intrinsic Chemical Shift Values for Thiophosphate Anions (No Salt Added, $22 \pm 1^\circ\text{C}$)

	$\text{HnPSO}_3(3-n)^-$	$\text{HnPS}_2\text{O}_2(3-n)^-$	$\text{HnPS}_3\text{O}(3-n)^-$	$\text{HnPS}_4(3-n)^-$
$\log K_1$	10.12 ± 0.02	8.37 ± 0.03	7.55 ± 0.05	6.19 ± 0.04
$\log K_2$	5.25 ± 0.01	3.90 ± 0.01	3.35 ± 0.03	2.82 ± 0.03
$\log K_3$	0.99 ± 0.01	—	—	—
$\delta_{\text{L}}^{3-}/\text{ppm}$	30.83 ± 0.03	60.78 ± 0.06	85.25 ± 0.07	109.74 ± 0.02
$\delta_{\text{HL}}^{2-}/\text{ppm}$	35.35 ± 0.03	69.36 ± 0.08	91.96 ± 0.13	106.17 ± 0.05
$\delta_{\text{H}_2\text{L}}/\text{ppm}$	44.75 ± 0.03	89.79 ± 0.11	101.77 ± 0.13	100.18 ± 0.09
$\delta_{\text{H}_3\text{L}}^0/\text{ppm}$	54.71 ± 0.05	—	—	—

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