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The Influence of the Steric Effect of the Substituents on the Phosphorus Acids Dissociation

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THE INFLUENCE OF THE STERIC EFFECT OF THE SUBSTITUENTS ON THE PHOSPHORUS ACIDS DISSOCIATION

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The dissociation processes of a series of phosphoric, phosphonic, and phosphinic acids have been studied by the modified method of potentiometry in water and water-ethanol media at 25°C. The influence of substituents on the acidic properties of these compounds has been investigated. As a measure of the substituents steric effects the R_S constants, calculated on the basis of frontal steric model (1), have been used. A good linear relationship between pK_a values in different media has been found. For all series of acids a linear relationship between pK_a values and R_S constants of substituents at phosphorus has also been established. In the case of dialkylphosphates in water, for example, such a relationship is expressed by equation:

$$pK_a = (-0.717 \pm 0.028) - (0.556 \pm 0.009) R_S$$
$$N = 7, R = 0.9992, S_0 = 0.011$$

pK_a value rises with the increase of the steric effect of the substituents at phosphorus which may be conditioned by the steric hindrance to the anion solvation.

- (1) V.I.Galkin and R.A.Cherkasov, *Organic Reactivity*, 18, 113, (1981).