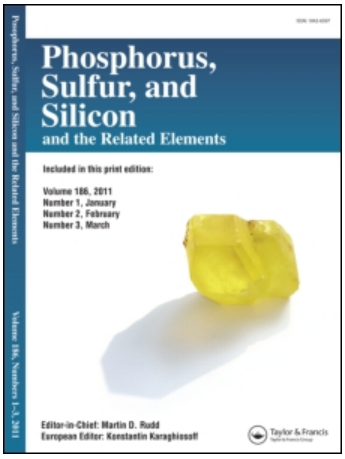

Phosphorus, Sulfur, and Silicon and the Related Elements

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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 pKa values in different media has been found. For all series of acids a linear relationship between pKa 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:

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

pKa 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 solvatation.

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