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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

Carbamoylmethylphosphoryl Compounds: Ch-Acidity and Basicity

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To cite this Article Matrosov, E. I., Matveeva, A. G., Nesterova, N. P., Tere-khova, M. I., Petrov, E. S., Kabachnik, M. I. and Nesmeyanov, A. N.(1990) 'Carbamoylmethylphosphoryl Compounds: Ch-Acidity and Basicity', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 353

To link to this Article: DOI: 10.1080/10426509008040882 URL: http://dx.doi.org/10.1080/10426509008040882

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CARBAMOYLMETHYLPHOSPHORYL COMPOUNDS: CH-ACIDITY AND BASICITY

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Carbamoylmethylphosphoryl compounds (CMP) are used as neutral bifunctional extractants. However, little is known about acid-base properties of these compounds. We have studied CH-acidity and basicity of selected CMP, $RR'P(0)CH_2C(0)NEt_2$ with R,R'=Alk, Alk_2N , Ar, AlkO, and also H-complexes of CMP with HNO_3 .

Equilibrium acidities (pK's) are determined in Me₂SO by overlapping indicator method. We have found acidity constants for CMP to be in the range of 22,4-25,7 pK units. The correlations between these pK's and $\Sigma \sigma^p$ -constants of substituents at the phosphorus atom, and $\Sigma \sigma_{CH_2}$ -constants of substituents at the central carbon atom have been obtained. The structure of carbanions are discussed using the data of IR and UV-spectroscopy.

Protonation of CMP has been studied by potentiometric titration with perchloric acid in MeNO $_2$. Basicity constants of CMP in the range of 3,1 to 7,0 are reported. There is a correlation between pK(MeNO $_2$) and $\Sigma \sigma^p$ -constants. The structure of protonated salts has been established by X-ray analysis and IR spectra.

The interaction of CMP with ${\rm HNO_3}$ in ${\rm CCl_4}$ has been investigated by termometric titration and IR-spectra. The formation of molecular complexes proceeds via two steps; the first one is the coordination of ${\rm HNO_3}$ to P=O group, and the second one is the coordination of ${\rm HNO_3}$ to C=O groups.