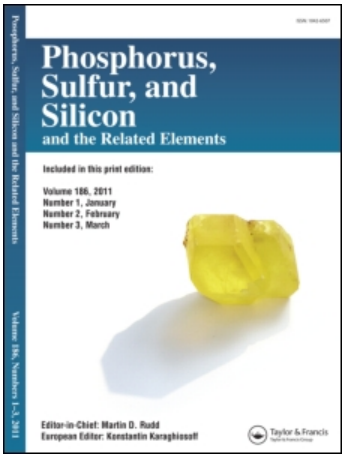

Phosphorus, Sulfur, and Silicon and the Related Elements

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

Carbamoylmethylphosphoryl Compounds: Ch-Acidity and Basicity

E. I. Matrosov[a]; A. G. Matveeva[a]; N. P. Nesterova[a]; M. I. Tere-khova[b]; E. S. Petrov[b]; M. I. Kabachnik[a]; A. N. Nesmeyanov[a]

[a] Institute of Organo-Element Compounds, Academy of Science of the USSR, Moscow, USSR [b] L.Ya. Karpov Physico-Chemical Institute, Moscow, USSR

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

Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, p. 353
Reprints available directly from the publisher
Photocopying permitted by license only

CARBAMOYLMETHYLPHOSPHORYL COMPOUNDS: CH-ACIDITY AND BASICITY

E.I.MATROSOV, A.G.MATVEEVA, N.P.NESTEROVA, M.I.TEREKHOVA[a], E.S.PETROV[a], and M.I.KABACHNIK
A.N.Nesmeyanov Institute of Organo-Element Compounds, Academy of Science of the USSR, Vavilov Str. 28, Moscow 117334, USSR
[a]L.Ya.Karpov Physico-Chemical Institute, Obuch Str. 10, Moscow 103062, USSR

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, $RR'P(O)CH_2C(O)NEt_2$ with R,R' = Alk, Alk_2N, Ar, AlkO, and also H-complexes of CMP with HNO_3.

Equilibrium acidities (pK's) are determined in Me_2SO 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 HNO_3 in 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 HNO_3 to P=O group, and the second one is the coordination of HNO_3 to C=O groups.