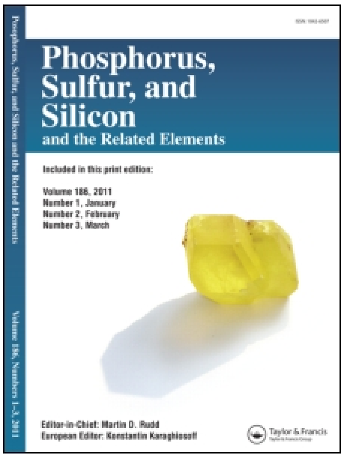

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Structuw-Reactivity Correlation of Phosphonyl Transfer Reactions of Wines with Diphosphonate; Ab Initio Mo and Experimental Studies

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To cite this Article Baba, Y.(1990) 'Structuw-Reactivity Correlation of Phosphonyl Transfer Reactions of Wines with Diphosphonate; Ab Initio Mo and Experimental Studies', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 225

To link to this Article: DOI: 10.1080/10426509008040759
URL: http://dx.doi.org/10.1080/10426509008040759

Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, p. 225
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STRUCTURE-REACTIVITY CORRELATION OF PHOSPHONYL TRANSFER REACTIONS OF AMINES WITH DIPHOSPHONATE; AB INITIO MO AND EXPERIMENTAL STUDIES

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The present author investigated the structure-reactivity correlation in the reactions of amines with P-O-P bridged phosphonylating agent **1**, diphosphonate.

$$H\text{-}\overset{O}{\underset{O^-}{P}}\text{-}O\text{-}\overset{O}{\underset{O^-}{P}}\text{-}H \;\; \mathbf{1} + RNH_2 \longrightarrow R\overset{H}{N}\text{-}\overset{O}{\underset{O^-}{P}}\text{-}H + {}^-O\text{-}\overset{O}{\underset{O^-}{P}}\text{-}H$$

The rate constants determined by following the rate of disappearance of **1**, for the reactions in an aqueous solution at 30 °C and ionic strength 1.0, are plotted logarithmically against the basicities of the amines in Fig. 1. The plot shows good linearity with β-value of 0.52. Using ab initio computations, the author have also determined the free energies of the reactions. The relationship between computed free energies and basicities of the amines in the gas phase or observed rate constants was discussed. The results are consistent with a concerted reaction mechanism with a single, symmetrical transition state.

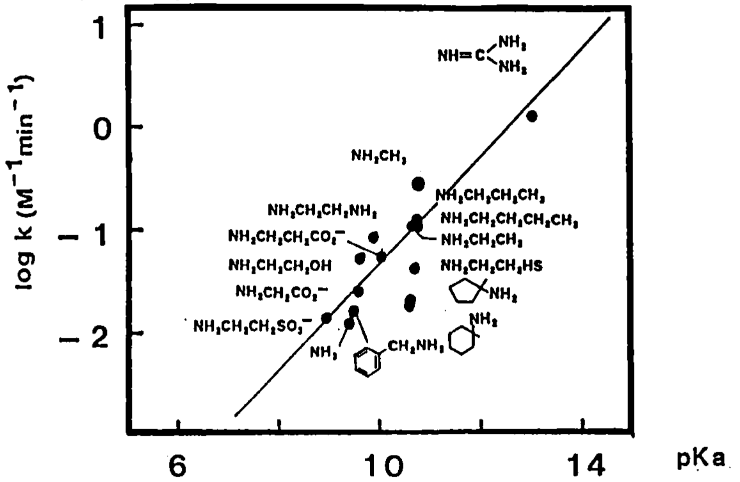

Fig. 1 Brϕnsted-type plot for the reaction of **1** with amines. The pKa and k are statistically corrected.