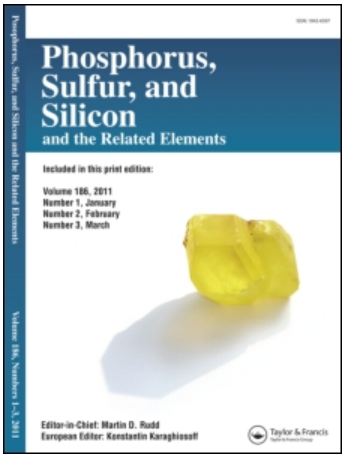

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The Structure of Adducts of Phosphoryl Compounds with Nitric Acid

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The Structure of Adducts of Phosphoryl Compounds with Nitric Acid

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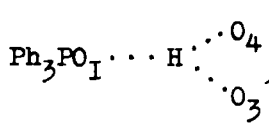
The sctructure of adducts of phosphoryl compounds with HNO_3 has been studied by means of IR spectra, thermometric titration and X-ray diffraction.

The X-ray analysis has been performed for adduct $Ph_3PO \cdot HNO_3$ (I). The molecular complex with strong H-bond has been found in this crystal. The uncommon case of the bifurcated H-bond is realized in this structure:



$O_I \cdots O_4 = 2,51(2)$ Å
$O_I \cdots O_3 = 3.04(2)$ Å

The properties of (I) are strongly dependent of the medium. Thus, if (I) is solved in CCl_4, the ν_{PO} bond is displaced towards the high frequencies by $100 cm^{-1}$. It shows that the H-bond becomes essentially weaker. The behaviour of (I) is associated with strong polarizability of the NO_3 fragment bonds. It explains the anion exchange in $CHCl_3$:

$$Ph_3PO \cdot HNO_3 + Ph_4P^+Br^- \rightleftharpoons Ph_4P^+NO_3^- + Ph_3POH^+Br^- \longrightarrow Ph_3PO + HBr\uparrow$$

The stable liquid adducts $(RO)_3PO \cdot HNO_3 \cdot H_2O$ (II) are formed by the interaction between trialkyl phosphates and nitric acid. The adducts composition do not change by distillation in vacuo. Unlike (I) thier IR spectra are slightly changed with thier medium. The structure of (II) is under discussion.