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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

The Structure of Adducts of Phosphoryl Compounds with Nitric Acid

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To cite this Article Matrosov, E. I., Kabachnik, M. I. and Nesmeyanov, A. N.(1987) 'The Structure of Adducts of Phosphoryl Compounds with Nitric Acid', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 3, 708

To link to this Article: DOI: 10.1080/03086648708079202

URL: http://dx.doi.org/10.1080/03086648708079202

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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 HNO₃ has been studied by means of IR spectra, thermometric titration and X-ray diffraction.

The X-ray analysis has been performed for adduct Ph₃PO·HNO₃ (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:

$$Ph_3PO_1 \cdots H : O_4 > N-O_2$$
 $O_1 \cdots O_4 = 2,51(2)$
 $O_1 \cdots O_3 = 3.04(2)$
 $O_1 \cdots O_3 = 3.04(2)$

The properties of (I) are strongly dependent of the medium. Thus, if (I) is solved in CCl_4 , the V_{PO} bond is displaced towards the high frequencies by $IOOcm^{-I}$. 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 $CHCl_3$:

Ph₃PO·HNO₃+ Ph₄P⁺Br == Ph₄P⁺NO₃ + Ph₃POH⁺Br = Ph₃PO + HBr |

The stable liquid adducts (RO)₃PO·HNO₃H₂O (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.