

LETTERS TO THE EDITOR

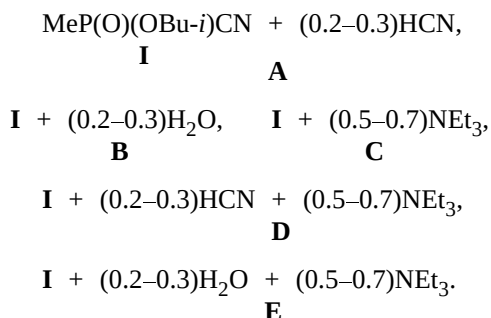
Cyanide Exchange between Isobutyl Methylphosphonocyanidate and Hydrogen Cyanide in the Presence of Amines

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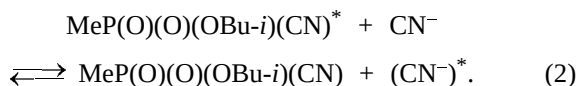
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Previously we reported on fluoride exchange between phosphorus acid difluorides and hydrogen fluoride in the presence of amines [1]. It was shown that the actual exchanging species are fluoride ions formed by deprotonation of hydrogen fluoride with amines. It was interesting to evaluate to what extent such exchange reactions are general. For this purpose, we recorded the ^{13}C NMR spectra of isobutyl methylphosphonocyanidate **I**, binary systems **A–C**, and ternary systems **D** and **E**.



In going from **I** to binary systems **A–C**, the spectral characteristics of **I** vary insignificantly. The spectrum of system **E**, in contrast to **B**, contains an HCN signal (δ_{C} 111 ppm) of the same intensity as in the spectrum of system **D**. This suggests that compound **I** underwent hydrolysis. In the spectrum of systems **D** and **E**, the doublet of the P–CN group of **I**, compared to the spectra of systems **A–C**, is broadened (signal width 3.1 ± 0.2 Hz). The width of the other signals of **I** remains constant and does not exceed 1 Hz. The HCN signal in the spectra of systems **D** and **E** is also broadened and shifted downfield by 1 ppm relative to system **B**. The observed trends suggest the occurrence of cyanide exchange in systems **D** and **E** between hydrogen cyanide and phosphonate **I**, initiated with triethylamine. On the whole, by analogy with data of [1], the following scheme of exchange in systems **D** and **E** can be proposed:



The role of the amine, as in the case of fluoride exchange [1, 2], apparently consists in “generation” of cyanide ions.

It is difficult to determine accurately the rate of cyanide exchange from the shape of the lines of the P–CN doublet in the ^{13}C NMR spectrum, because the line shape is influenced by two factors: exchange between two states with different chemical shifts and suppression of the ^{13}C – ^{31}P coupling in the molecule of **I**. An approximate estimation can be made using a simple formula (3) [3] for slow exchange:

$$w^* - w = 1/\pi\tau. \quad (3)$$

Here w is the linewidth in the absence of exchange (Hz); w^* , linewidth under the conditions of exchange (Hz); and τ , mean lifetime of the cyano group in the molecule of **I** between the exchange events (s). The calculations give $\tau \sim 0.1$ s. Note that alkyl alkylphosphonofluoridates RP(O)(OR)F do not enter into fluoride exchange similar to reaction (2) [1]. This may be due to considerably higher reactivity of phosphorus acid cyanides compared to fluorides in nucleophilic substitution at the P atom.

Our results in combination with data from [1] suggest that the exchange processes similar to cyanide [Eq. (2)] and fluoride [1] exchange are common reactions of a wide range of phosphorus acid halides and pseudohalides.

Isobutyl methylphosphonocyanidate I. ^{13}C NMR

spectrum, δ_C , ppm: 116.6 d (PCN, $^1J_{PC}$ 107.9 Hz), 16.4 d (CH_3P , $^1J_{PC}$ 123.2 Hz), 73.7 d ($P-OCH_3$, $^3J_{PC}$ 8.5 Hz), 28.9 d (CH , $^3J_{PC}$ 6.8 Hz), 18.4 s (CH_2). ^{31}P NMR spectrum: δ_P 12.7 ppm.

The ^{13}C and ^{31}P NMR spectra were recorded on a Varian FT-80A spectrometer (80 MHz, neat samples) relative to external TMS and 85% H_3PO_4 .

REFERENCES

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2. Morozik, Yu.I. and Vasil'ev, N.G., *Zh. Obshch. Khim.*, 1992, vol. 62, no. 6, p. 1201.
3. Piets, L.H. and Anderson, W.A., *J. Chem. Phys.*, 1959, vol. 30, no. 4, p. 899.