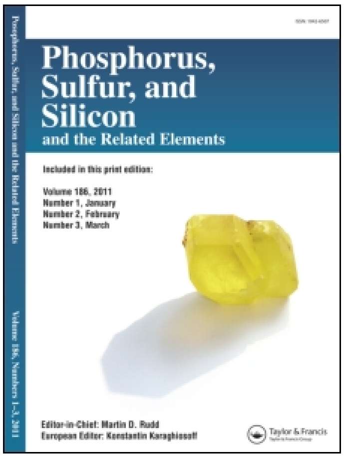


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ON THE INTERACTION BETWEEN DIALKYL PHOSPHITES AND AMINE HYDROCHLORIDES

K. Troev[a]; E. Tashev[a]; G. Borisov[a]
[a] Central Laboratory on Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria

To cite this Article Troev, K. , Tashev, E. and Borisov, G.(1981) 'ON THE INTERACTION BETWEEN DIALKYL PHOSPHITES AND AMINE HYDROCHLORIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 11: 3, 363 — 367

To link to this Article: DOI: 10.1080/03086648108077436

URL: http://dx.doi.org/10.1080/03086648108077436

Phosphorus and Sulfur, 1981, Vol. 11, pp. 363–367
0308-664X/81/1103-0363/$06.50/0

ON THE INTERACTION BETWEEN DIALKYL PHOSPHITES AND AMINE HYDROCHLORIDES

K. TROEV, E. TASHEV and G. BORISOV

Central Laboratory on Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

(*Received April 1, 1981; in final form May 11, 1981*)

The interaction between dialkyl phosphites and amine hydrochlorides is examined. It is found that an alkyl halide is evolved and an ammonium monoalkyl phosphonate, i.e. $(R)_3NH^+O^-P(H)(O)(OR)$, is formed.

INTRODUCTION

The transesterification rate of acid phosphonates has been found to increase at higher hydroxyl group nucleophilicities[1,2,3] and higher basicity of the medium.[4] The study of the interaction between dialkyl phosphites and triethanolamine hydrochloride was interesting with the view of elucidating the influence of nucleophilicity and basicity on the process of transesterification. Triethanolamine hydrochloride in contrast to triethanolamine would not increase the basicity of the reaction system and would thus permit an evaluation of the influence of basicity on the process of transesterification to be carried out. An examination of this interaction should also provide a possibility of better understanding the exothermal effect observed on the interaction between dialkyl phosphites and amino alcohols. Trialkyl phosphites are known to react readily with hydrochlorides of weakly basic amines such as aniline (pKa = 4.58).[5] The hydrochlorides, used in the present case are of strongly basic amines. This could permit to observe a difference in the interactions of dialkyl and trialkyl phosphites. K. A. Petrov and co-workers[6] have shown that the hydrochlorides of dialkylamino alkylphosphonic acids on heating evolve alkyl halides and form the internal salt of the dialkylamino alkylphosphonic acid monoester.

EXPERIMENTAL

Starting material: dimethyl phosphite (Fluka), $n_D^{20} = 1.4020$; diethyl phosphite (Fluka), $n_D^{20} = 1.4078$; diisopropyl phosphite (Fluka), $n_D^{20} = 1.4082$; dibutyl phosphite (Fluka), $n_D^{20} = 1{,}4248$; diphenyl phosphite was obtained as described;[7] triphenyl phosphite (Fluka), $n_D^{20} = 1{,}5585$; triethyl phosphite (Fluka), $n_D^{20} = 1.4130$; triethanolamine hydrochloride m.p. 178–179°C; diethylamine hydrochloride m.p. 227–229°C; triethylamine hydrochloride m.p. 256–259°C and pyridine.hydrochloride m.p. 139–143°C.

Interaction between dialkyl phosphite and triethanolamine hydrochloride.

Triethanolamine hydrochloride (7.94 g, 0.043 mole) and dimethyl phosphite (9.40 g, 0.086 mole) are placed in a three-necked flask provided with a capillary argon inlet, thermometer and condensor. The methanol evolved is collected in a graduated receiver placed in an ice bath; in a second receiver cooled with liquid nitrogen is collected the methyl chloride. Methanol evolution begins at about 102–105°C and at 122°C the reaction mixture turns homogeneous. Heating is maintained at 140–145°C for 2 hrs during which interval of time are collected 2.1 ml of methanol and 2.2 g of methyl chloride.

The interaction between diethyl phosphite and triethanolamine hydrochloride (mole ratio 2:1) conducted under the same conditions led to the evolution of ethanol that began at 108°C. After 2 hrs 3.0 ml of ethanol and 2.5 g of ethyl chloride were collected.

Interaction between dibutyl phosphite and diethylamine hydrochloride

Diethylamine hydrochloride (11.9 g, 0,108 mole) and dibutyl phosphite (38.8 g, 0.20 mole) are reacted in an analogous manner at 130°C.

After the evolution of the theoretical amount of butyl chloride the reaction product diethylammonium salt of monobutyl phosphonate is dissolved in dry ethanol and recrystallized from a mixture of acetone and ethanol. M.p. 127-128°C. Yield 17 g, 75%.

$C_8H_{22}O_3NP$ calc.: N, % 6.63; P, % 14.68
found: N, % 7.02; P, % 14.92

Interaction between diethyl phosphite and diethylamine hydrochloride

Diethylamine hydrochloride (8.1 g, 0.074 mole) and diethyl phosphite (43.3 g, 0.313 mole) are reacted as described at 130°C. The reaction mixture is then repeatedly extracted with petroleum ether or dry diethyl ether. 8.3 g (62%) diethylammonium salt of monoethyl phosphonate.

$C_6H_{18}O_3NP$ calc.: N, % 7,60; P. % 16.94
found: N, % 7,28; P. % 16,34

Interaction between dibutyl phosphite and triethylamine hydrochloride

Triethylamine hydrochloride (13.35 g, 0.097 mole) and dibutyl phosphite (29.95 g, 0.145 mole) are heated at 145°C. The reaction product is the triethylammonium salt of monobutyl phosphonate. Yield 19,7 g, 85%.

$C_{10}H_{26}O_3NP$ calc.: N, % 5,85; P, % 12.97
found: N, % 5.52; P, % 12,26

Interaction between dibutyl phosphite and pyridine hydrochloride

Pyridine hydrochloride (28,7 g, 0,248 mole) and dibutyl phosphite (72.1 g, 0.372 mole) are heated at 130°C. The product obtained is the pyridinium salt of monobutyl phosphonate. Yield 28 g, 52%.

$C_9H_{16}O_3NP$ calc.: N, % 6.45; P, % 14,28
found: N, % 6.12; P, % 13.98

Interaction between diisopropyl phosphite and diethylamine hydrochloride.

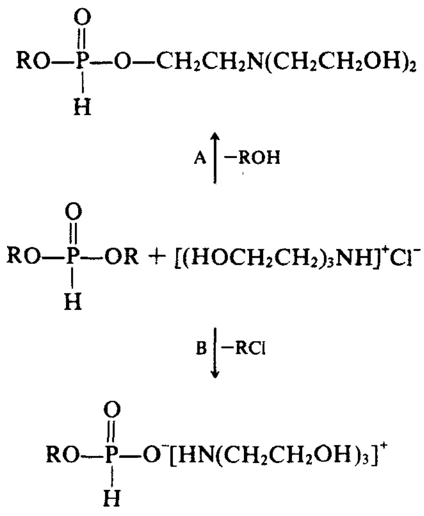
Diethylamine hydrochloride (8,45 g, 0,077 mole) and diisopropyl phosphite (22,57 g, 0.135 mole) are heated at 135°C. The product obtained is the diethylammonium salt of monoisopropyl phosphonate. Yield 10 g, 67%.

$C_7H_{20}O_3NP$ calc.: N, % 7,11; P, % 15,73
found: N, % 6,98; P, % 15.11

RESULTS AND DISCUSSION

The experimental data indicated that the transesterification of dimethyl phosphite with triethanolamine hydrochloride proceeds at 102–105°C i.e. by 14 to 17° higher than the transesterification with triethanolamine.[4] The rate of the process was not determined because it was found that simultaneously to the transesterification reaction a volatile gas was evolved. Nevertheless transesterification between dimethyl phosphite and triethanolamine hydrochloride can be considered to proceed at a considerably lower rate than with triethanolamine, since in the former case about 30% of the methanol is evolved within 2 hrs while using triethanolamine at the same molar ratio affords 30% of the methanol within the first few minutes (2–3 min.). This difference in the observed reaction rates as well as the absence of an exothermal effect can solely be ascribed to the difference in the pH of the reaction medium and to the lack of a free base when the hydrochloride of triethanolamine was employed.

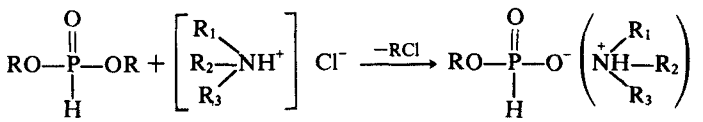
With the aid of infrared spectroscopy and gas-chromatography it was found that the gas evolved in the transesterification of dimethyl phosphite with triethanolamine hydrochloride was methyl chloride, while in the case of diethyl phosphite the gas was ethyl chloride. These results indicate that the interaction between dialkyl phosphites and triethanolamine hydrochloride proceeds in the following two ways:



Reaction route B, that is the interaction between dialkyl phosphites and amine hydrochlorides, has not been described in the literature so far.

In order to obtain and isolate defined products formed according to route B we carried out interactions between dibutyl, diethyl and diisopropyl phosphite and the hydrochlorides of diethyl and triethylamine and pyridine. In these cases transesterification and formation of oligomers is precluded.

The reaction follows the scheme:



$$\mathrm{RO{-}\overset{O}{\underset{H}{P}}{-}OR} + \left[\mathrm{R_1R_2R_3NH^+}\right]\mathrm{Cl^-} \xrightarrow{-\mathrm{RCl}} \mathrm{RO{-}\overset{O}{\underset{H}{P}}{-}O^-}\left(\overset{+}{\mathrm{N}}\mathrm{H{-}R_1R_2R_3}\right)$$

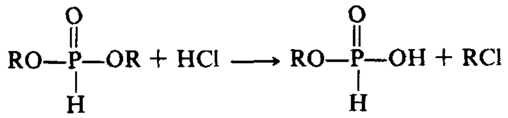
The following two mechanisms appear likely:

The alkyl halide is formed probably according to the stages:

a) the hydrochloride dissociates to amine and hydrogen chloride:

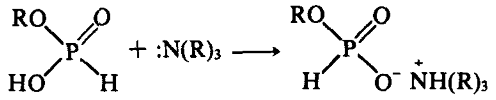
$$\overset{+}{\mathrm{N}}\mathrm{H(R)_3\,Cl^-} \longrightarrow \mathrm{:N(R)_3 + HCl}$$

b) the hydrogen chloride effects the dealkylation of dialkyl phosphites:



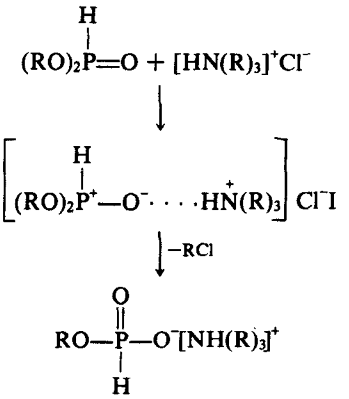
$$RO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}-OR + HCl \longrightarrow RO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}-OH + RCl$$

c) the monoalkyl phosphonate forms a salt with the amine



The hydrochloride dissociation stage is supported by experimental data. The experiments indicated that the interaction proceeds most rapidly and at the lowest temperatures with pyridine hydrochloride. It can be assumed that the latter loses hydrogen chloride more easily than the other two hydrochlorides on the basis of the pKa values of the triethylammonium-(pKa 10.67), diethylammonium-(pKa 11.04) and pyridinium-(pKa 5.21) ions at 25°C.

The evolution of the alkylhalides was found to proceed as a non-exothermal process, while the dealkylation of the dialkyl phosphites by means of hydrogen chloride is known to be exothermal.[9] On these reasons we assume the dealkylation to take place directly via a dialkyl phosphite and hydrochloride interaction. The reaction center can be considered to be the phosphoryl oxygen atom:



The positively charged $[H\overset{+}{N}(R)_3]$-group acts probably as an electrophile with respect to the phosphoryl oxygen and thus facilitating the formation of the alkyl halide.

Trialkyl- and triaryl phosphites were treated with diethylamine hydrochloride with the view to checking the correctness of the assumed schemes. It was found that no interaction took place between the esters and the hydrochloride (the reaction mixture was heated at 153°C the boiling point of triethyl phosphite).

If the dealkylation of the trialkyl phosphites[5] and the dialkyl phosphites is assumed to proceed under the influence of hydrogen chloride the dealkylation of dialkyl phosphites by the hydrochlorides of such strong bases as diethylamine and triethylamine remains unclear. According to the obtained experimental results the presence of dialkyl phosphite in the reaction mixture is essential probably either facilitating hydrogen chloride dissociation or interaction via the phosphoryloxygen atom with the hydrochlorides of the strongly basic amines.

REFERENCES

1. V. P. Vassil'eva and G. G. Lykhina, *Izv. Tomskovo Polyt. Instituta*, **258**, 83 (1976).
2. A. N. Pudovik and G. I. Efstaf'ev, *Vysokomol. Soed.*, **6**, 2139 (1964).
3. B. E. Ivanov and V. F. Zheltuhin, *Uspekhi Khimii*, **39**, 5, 773 (1970).
4. K. Troev, E. Tashev and G. Borisov, in press.
5. E. E. Nifant'ev, *Khimia Phosphororganicheskikh Soed.*, Izd Moskovskogo Universiteta, 1974, p. 14.
6. K. A. Petrov, F. L. Maklyaev and N. K. Blizniuk, *Zhurnal Obshchey Khimii*, **29**, 558 (1959).
7. F. N. Walsh, *J. Am. Chem. Soc.*, **81**, 3023 (1959).
8. D. D. Perrin, "Dissociation constants in organic bases in aqueous solution," London, 1965, p. 31, p. 70.
9. C. H. Campbell and D. H. Chadwick, *J. Am. Chem. Soc.*, **77**, 3379 (1955).