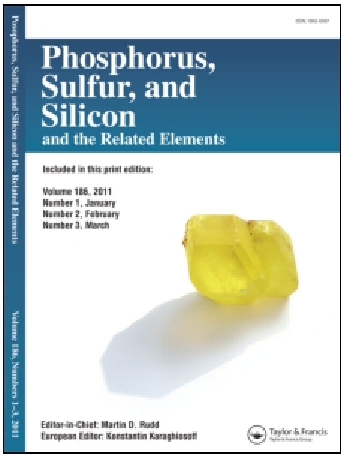


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

KINETIC INVESTIGATION OF THE REACTION BETWEEN DIALKYL PHOSPHITES AND AMINE HYDROCHLORIDES

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

To cite this Article Troev, K. , Tashev, E. and Borisov, G.(1982) 'KINETIC INVESTIGATION OF THE REACTION BETWEEN DIALKYL PHOSPHITES AND AMINE HYDROCHLORIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 13: 3, 359 — 362

To link to this Article: DOI: 10.1080/03086648208081197

URL: http://dx.doi.org/10.1080/03086648208081197

Phosphorus and Sulfur, 1982, Vol. 13, pp. 359–362
0308-664X/82/1303-0359/$06.50/0

KINETIC INVESTIGATION OF THE REACTION BETWEEN DIALKYL PHOSPHITES AND AMINE HYDROCHLORIDES

K. TROEV, E. TASHEV and G. BORISOV

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

(*Received April 6, 1982; in final form May 25, 1982*)

The kinetics of the reaction between dialkyl phosphites and amine hydrochlorides is reported. It is shown that the reaction is bimolecular and its rate depends on the type of alkyl group of the alkoxyl function of the dialkyl phosphite, as well as on the basicity of the amine.

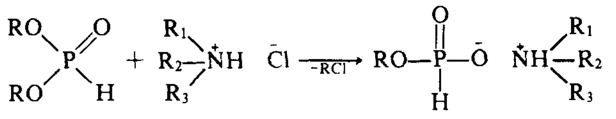
I. INTRODUCTION

It was established earlier[1] that amine salts of the monoalkyl esters of phosphorous acid, $(R_1)_3\overset{+}{N}H\bar{O}P(O)\ (H)\ (OR_2)$ are obtained from the reaction between dialkyl phosphites and amine hydrochlorides.

The aim of this paper is to study the mechanism of this reaction as well as the effect of the type of alkyl in the alkoxyl groups of the dialkyl phosphites and the basicity of the amine on the reaction rate.

II. RESULTS AND DISCUSSION

The reaction between dialkyl phosphites and amine hydrochlorides proceeds according to the following scheme:



Two possible mechanisms have been proposed for this reaction.[1] According to the first, the formation of amine salts of the monoalkylesters of the phosphorous acid III proceeds through a stage of dissociation of the amine hydrochloride II to amine and HCl, which subsequently dealkylates the dialkyl phosphite I to monoester according to the known reaction scheme.[2] Then the monoester forms the salt III with the amine. According to the second mechanism, the formation of the amine salt III occurs by the direct reaction between I and II.

In order to find out which of these two mechanisms is operative, we carried out kinetic investigations of the reaction between dialkyl esters of phosphorous acid and the hydrochlorides of diethylamine and pyridine. The experiments, consisting in heating at 110°C of 0.365 mole/l solutions of diethylamine hydrochloride or pyridine hydrochloride in dimethylformamide revealed that the concentration of the chloride ions in the solution remains constant, implying that under the conditions of the reaction, the amine hydrochlorides do not dissociate to amine and HCl. The

TABLE I

Kinetic data for the reactions between dialkyl phosphites and amine hydrochlorides

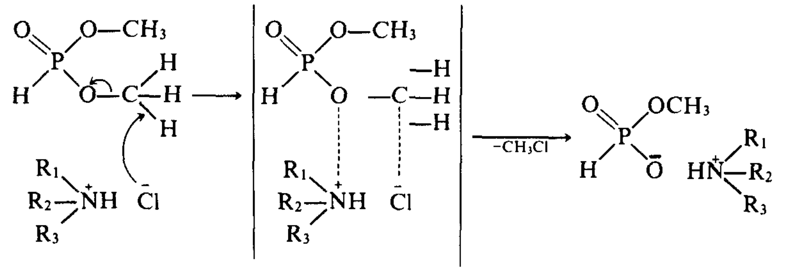
Starting compounds		$[A_o]$ amine·HCl mole/L.	$[B_o]$ phosphorus cpd. mole/L.	Initial rate W_o mole·L.$^{-1}$·s^{-1}.
amine·HCl	phosphorus cpd.			
diethylamine hydrochloride	dimethyl phosphite	0.365	0.189	$1.2 \cdot 10^{-3}$
diethylamine hydrochloride	dimethyl phosphite	0.367	0.368	$2.03 \cdot 10^{-3}$
diethylamine hydrochloride	dimethyl phosphite	0.365	0.738	$4.02 \cdot 10^{-3}$
diethylamine hydrochloride	dimethyl phosphite	0.183	0.367	$1.18 \cdot 10^{-3}$
diethylamine hydrochloride	dimethyl phosphite	0.531	0.367	$2.95 \cdot 10^{-3}$
diethylamine hydrochloride	dibutyl phosphite	0.367	0.368	no reaction
diethylamine hydrochloride	diisopropyl phosphite	0.367	0.368	no reaction
pyridine hydrochloride	dimethyl phosphite	0.369	0.376	$3.51 \cdot 10^{-3}$
pyridine hydrochloride	dibutyl phosphite	0.368	0.367	$2.04 \cdot 10^{-3}$
pyridine hydrochloride	diisopropyl phosphite	0.370	0.371	no reaction

$$W_o = \frac{dx}{dt} = k \cdot A_o^x \cdot B_o^y$$

results of these two experiments demonstrated that the first of the possible reaction paths discussed above is to be discarded.

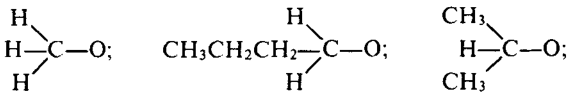
The kinetic investigations of the reaction between dimethyl phosphite and diethylamine hydrochloride showed that (Table I) the rate depends on the concentrations of both reagents. The reaction order with respect to dimethyl phosphite is unity and the rate constant is 0.017 mole·l^{-1}·s^{-1}.[3] The same reaction order and rate constants were found with respect to diethylamine hydrochloride.

The present results demonstrate that the reaction between dialkyl phosphites and amine hydrochlorides is a second-order bimolecular nucleophilic substitution, apparently proceeding according to the following scheme:



As seen from the proposed scheme, the reaction rate should depend on the type of radical in the alkoxyl group of the dialkyl phosphite as well as on the basicity of the amine.

The experiments performed to explore this effect revealed that upon the substitution of the methyl by butyl or isopropyl groups, the reaction does not take place at all at 110°C. It takes place, however, at higher temperatures: at 125°C with dibutyl phosphite and at 135°C with diisopropyl phosphite. It was found further that the rate of the reaction between dibutyl phosphite and pyridine hydrochloride is one order of magnitude lower (Table I). At 110°C there is no interaction between pyridine hydrochloride and diisopropyl phosphite. The lack of reactivity between dibutyl phosphite and diisopropyl phosphite with diethylamine hydrochloride and pyridine hydrochloride as well as the strong decrease of the reaction rate between dibutyl phosphite and pyridine hydrochloride is related to the great influence of the substituents at the carbon atom. If we consider the functions

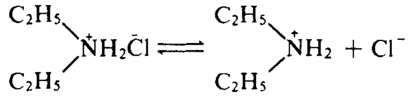


and compare the values of the partial positive charge of the carbon atom directly attached to oxygen, we find that it decreases in the order methyl > butyl > isopropyl which is due to the inductive effect of the substituents. The retarded reaction with the butyl ester of phosphorous acid and the lack of reaction with the isopropyl ester is not associated solely with the inductive effect of the substituents, but also with the increase in the number of alkyl groups screening the carbon atom, implying some steric hindrance, which is strongest with the isopropyl group.

It was further established that the reaction rate between dimethyl phosphite and pyridine hydrochloride is 1.7 times as high as that for the same ester with diethylamine hydrochloride. Moreover, in contrast to diethylamine hydrochloride, pyridine hydrochloride reacts with dibutyl phosphite at 110°C.

The difference in the rates of reaction between dialkyl phosphites and amine hydrochlorides could be attributed to the different basicity of the different types of substituents attached to the nitrogen atom.

Under the present reaction conditions, it can be assumed that the amine hydrochloride dissociates according to:



implying that there will be Cl^- ions in the reacting system, which are strongly nucleophilic and will therefore react with the dialkyl phosphites according to the proposed mechanism. If it is assumed that the interaction between dialkyl phosphites and amine hydrochlorides proceeds after the dissociation of the latter, then the present experimental results remain unexplained. This is especially true for the result that diethylamine hydrochloride does not react at all with dibutyl phosphite, whereas pyridine hydrochloride reacts under the same experimental conditions. This implies that the amine hydrochlorides react undissociated, i.e. as ion pairs. Evidence for this assumption is the result that the reaction is bimolecular and proceeds at different rates with diethylamine hydrochloride and pyridine hydrochloride.

The supposition that amine hydrochlorides react undissociated provides an explanation for the difference in the rate of the reaction with the various types of substituents at the nitrogen atom.

Kijima *et al.*[4] have shown in studying the reaction between tetraisopropyl titanite and amine hydrochlorides, that it occurs with aniline hydrochloride ($C_6H_5NH_2 \cdot HCl$), whereas no reaction takes place with diethylamine hydrochloride ($Et_2NH \cdot HCl$). This difference in the reactivity is explained by the steric effects of the substituents at the nitrogen atom. The present experimental results fully agree with these conclusions. As shown, the screening effect of the substituents at the nitrogen atom upon the chlorine atom is different for the two hydrochlorides. The two ethyl groups with their large volume will screen more effectively in comparison with the pyridine ring. This effect presumably accounts for the higher rate of the reaction between dialkyl phosphites and pyridine hydrochloride as compared with diethylamine hydrochloride.

III. EXPERIMENTAL

Starting compounds: dimethyl phosphite, Fluka, $n_D^{20} = 1.4020$; dibutyl phosphite, Fluka, $n_D^{20} = 1.4248$; diisopropyl phosphite, Fluka, $n_D^{20} = 1.4082$; diethylamine hydrochloride, m.p. 228–229°C; pyridine hydrochloride, m.p. 139–143°C; dimethylformamide, purified by vacuum distillation.

Procedures: The solution of 0.189 mole/L dimethyl phosphite and 0.365 mole/L diethylamine hydrochloride in dimethylformamide was heated in a four-neck flask provided with a capillary for argon bubbling, a thermometer and a reflux column. The reaction was carried out at 110°C ± 0.2°C. The reaction rate was determined by the change in concentration of chloride ions in the reaction mixture using the Volhart method during the time interval from the first to the 20th minute. Under these conditions, a series of experiments was carried out at molar ratios indicated in Table I.

REFERENCES

1. K. Troev, E. Tashev, G. Borisov, *Phosphorus and Sulfur*, **11**, 363 (1981).
2. C. H. Campbell, D. H. Chadwick, *J. Am. Chem. Soc.*, **71**, 3379 (1955).
3. K. J. Laidler, *Reaction Kinetics*, Pergamon Press, 1963.
4. I. Kijima, I. Wakashimura, *Kogyo Kagaku Zashi*, **67**, 1, 244 (1964).