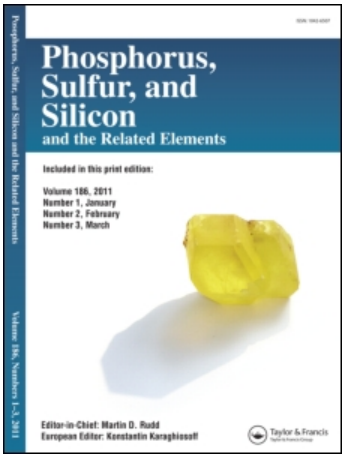

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ON RUPTURE OF THE P-E BOND IN REACTIONS OF ACIDIC DERIVATIVES OF TRIVALENT PHOSPHORUS

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Abstract The reactions of P(III) acid derivatives of the P-E type (where E=N, O, S) occuring with the rupture of the P-E bond were studied and classified. The basic types of such reactions have been concluded to be acid catalyzed.

Rupture of the P-E bond by different nucleophilic and electrophilic agents should be considered as one of the fundamental properties of the P(III)-E acidic derivatives where E is a heteroatom with a lone electron pair (N,O,S). Numerous phosphorylation reactions of organic compounds are based on this property. Among these are the reactions of substitution or addition occuring with preservation or with alteration of the phosphorus atom coordination. These reactions can be classified according to the type of reagents into substitution reactions with the proton containing reagents, the substitution reactions with aprotic electrophilic reagents and addition reactions with insertion of unsaturated fragment into the P-E bond.

$$>P-ER + HX \longrightarrow >PX + REH$$

$$>P-ER + AX \longrightarrow >PX + REA$$

$$>P-ER + >C=X \longrightarrow >P-X-\overset{ER}{\overset{|}{C}}< \xrightarrow{X=O} >P-\overset{O}{\overset{\|}{\underset{|}{C}}}-ER<$$

The systematic study of these reactions has led us to the conclusion, that the acidic catalysis is characteristic of the reactions occurring with the rupture of the P-E bond. Some examples of such acid catalysis have been mentioned earlier[1-3]. In the course of our subsequent study the examples of the acid catalysis have been found practically for all the basic types of the transformations occuring with the rupture of the P-E bond. Besides, on

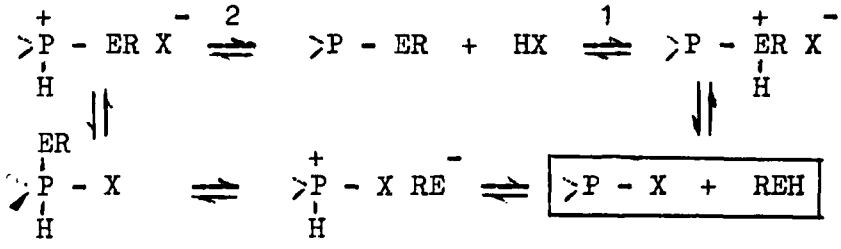
the basis of the concept of acid catalysis new types of such reactions have been found.

The acid catalyst is usually inserted into the reaction mixture together with the initial compounds as admixtures. Elimination of them presents certain difficulties and requires special methods. Thus the system is usually three-component. In general two variants are possible. When the initial compounds react readily the presence of acid does not influence the reaction direction, thus usually leading to the P-E bond preservation. However, if the rate of the reaction of at least one of the compounds in the presence of acid is higher or comparable with the rate of interaction of the initial compounds, the alteration of the direction towards the P-E bond rupture is observed. Solution of the problem of acid catalysis should be to our mind considered in two aspects. The first problem concerns the fact of acid catalysis itself, the second relates to its mechanism. Acid catalysis should be considered as a general feature for the reactions under investigation, whereas the mechanism of catalysis may be different and it should be studied specially in each case. Catalytic action of acids was confirmed as follows. Under the above conditions but in the absence of catalysts the described conversions slow down or cease completely. Addition of acid resumes the reactions with the P-E rupture, the latter significantly accelerated with the increase of the catalyst content.

Acid catalysis was established in the alcoholysis, aminolysis, thiolysis, hydrolysis reactions of amides[3-6], esters[7] of P(III) acids. Discussing reactions with the proton containing reagents, it should be kept in mind that besides the reactions catalyzed by acids, there is a group of purely nucleophilic substitution reactions catalyzed by bases occurring with the rupture of the P-E bond: e.g. cases when the entering grous are more basic than eliminating ones. No acid catalysis is required in reactions if the protondonors possess strong acidic function.

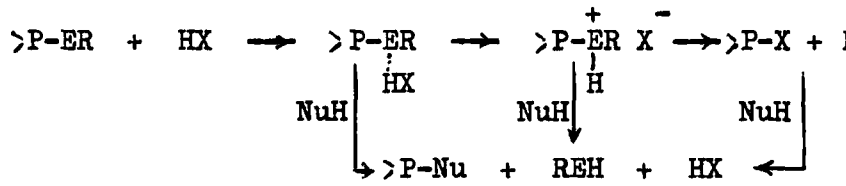
The direction of the ER group substitution in the reactions of amides[4] and thioesters[8] of P(III) acids with acyl halides is also acid catalyzed. Acid catalysis has been found in the exchange reactions at different substituted P(III) atoms[7,9,10]; in the reactions of amidophosphites with esters[4] and acetoxymethylamides[11] of carboxylic acids; in the reactions of thioesters with sulphenyl halides[12]. The addition-insertion reactions of P(III) amides with aldehydes, ketones, isocyanates[4] and thioesters with carbonylic compounds[13] are also catalyzed by acids.

The mechanism of acid catalysis is not quite clear. One of the versions is as follows:



The reaction of ER group substitution may proceed in the E- or P-protonating form. The first direction is preferable for heteroatom with pronounced basic properties (N,O). The second path is more possible for the less basic heteroatom (S). The key elements of the scheme are the products of ER group substitution. If the anhydride derivatives in the initial equilibrium is fixed by the other proton containing compounds the nucleophilic substitution products may be obtained. If REH is fixed by other electrophiles the addition-insertion or electrophilic substitution products are formed. But the acid may as well activate the electrophilic agent, for instance the carbonyl compound.

It is noteworthy that the protophilic contribution of the nucleophilic substitution may occur on the stage of the anhydride derivative as well as at the earlier stages (E-protonating form, H-complex). This depends on the acid strength, the nature of anion, the environment of the phosphorus atom and the nature of the nucleophilic agent.



From the data discussed above it is evident that the acid catalysis is a general feature of the reactions occurring with the P-E bond rupture. The estimated regularities allow one to widen significantly, simplify and improve synthesis on the base of amides, esters, thioesters of P(III) acids, to find out new synthetic routes and new classes of organophosphorus compounds.

REFERENCES

1.A.E.Arbuzov, Selected papers on the chemistry of phosphororganic derivatives. M.: Nauka, 1976, p.204.
2.K.Moedritzer, G.M.Burch, I.R.Van Wezer, H.K.Hofmeister, Inorg.Chem., 1963,p.1152.
3.E.E.Nifantiev, N.L.Ivanova, N.K.Bliznyuk, Zh. Obshch. Khim., 66, p.765(1966).
4.Chem. and appl. of phosphororg. comp. Proceedings of the VI ALL-Union Conference. M.à Nauka, 1981, p.196.
5.E.B.Borisov, N.L.Ivanova, L.K.Vasyanina, E.E.Nifantiev, Zh.Obshch.Khim., 54, p.2141 (1984).
6.E.E.Nifantiev, I.P.Gudkova, I.V.Shilov, Zh.Obshch.Khim., 40, p.1420 (1970).
7.V.A.Al'fonsov, Yu.N.Girfanova, E.S.Batyeva, A.N.Pudovik, Dokl. AN SSSR, 251, p.105 (1980).
8.V.A.Al'fonsov, G.U.Zamaletdinova, E.S.Batyeva, A.N.Pudovik, Izv. AN SSSR, ser. khim., 1982, p.1386
9. M.A.Pudovik, Yu.A.Mikhailov, T.A.Malikh, V.A.Al'fonsov, G.U.Zamaletdinova, E.S.Batyeva, A.N.Pudovik, Zh.Obshch. Khim., 50, p.1677 (1980).
10.O.G.Sinyashin, E.S.Batyeva, A.N.Pudovik, E.N.Ofitserov, Izv. AN SSSR, ser.khim., 1981, p.2133.
11.A.N.Pudovik, E.S.Batyeva, I.S.Nizamov, G.U.Zamaletdinova, V.A.Al'fonsov, Izv. AN SSSR, ser.khim., 1988, p.469.
12.O.G.Sinyashin, Sh.A.Karimullin, E.S.Batyeva, A.N.Pudovik, Zh.Obshch.Khim., 54, p.2463 (1984).
13.V.A.Al'fonsov, I.S.Nisamov, S.A.Kazuba, E.S.Batyeva, A.N.Pudovik, Zh.Obshch.Khim., 58, p.1473 (1988).