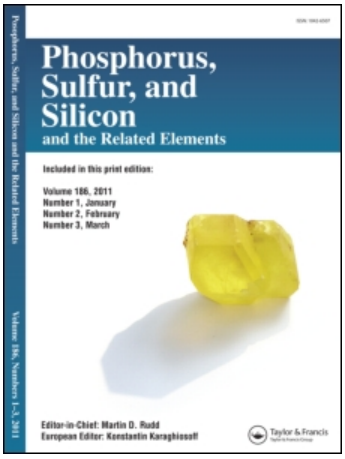

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On the Facile P-C Bond Break

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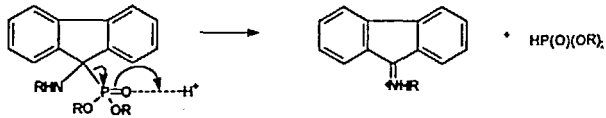
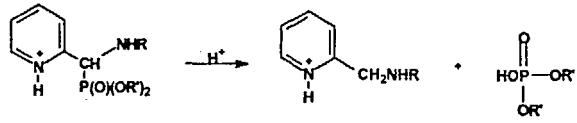
INTRODUCTION

Aminophosphonates as well as hydroxyphosphonates are very frequenly used due to their biological activity. Among them one can find herbicides, pesticides, neuromodulators, HIV protease inhibitors and others.

It is known that they are easily decomposed by fungi and bacteria. The mechanism of their chemical decomposition is not fully known. They are believed to be quite stable in both basic and acidic media. We have notice that 9-fluorene derived aminophophonates were unstable in agueous solution of mineral acids, as well as in alkohol in the presence of Lewis acids (zinc or lantanide chlorides). After 2 hours of refluxing in 20% solution of hydrochloric acid the degree of decomposition was about 10%. On the contrary, 2-fluorenyl-N-phenylaminomethanephosphonic acid derivatives decomposed completely under these conditions within 1 hour yielding carbonyl compound and phosphorous acid. [1]



It was reported recently that 2-pirydyl-aminomethanephosphonic acids undergo decomposition with the formation of phosphate and corresponding amine[2].



These data raised few questions:

-why quite similar compounds behave differently,

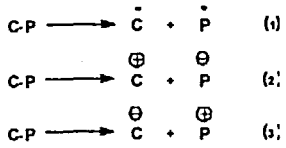
-are these reactions similar to the hydroxyphosphonate decomposition (two alternative ways; phosphonate-phosphate rearrangment vs. retro-Abramov)

-what are the main structural factors which speed up the one path of decomposition and slow down the competitive reactions.

THEORETICAL CALCULATIONS

Decomposition yielding phosphonate should be a result of heterolytic P-C bond break via carbocation like transition state or intermediate. Carbanion like fragment should be

an intermediate in all cases when the phosphoric acid derivatives are reaction products. Thus the presence of electrodonor or electroacceptor groups at carbon adjacent to phosphorus will force the first or the second way of decomposition correspondingly. There is also possibility of homolytic phosphorous-carbon bond breakage. The last one is the common way of the degradation of phosphonates by the microorganisms.



At the begining we try to verify this qualitative considerations by the theoretical calculations. For the model compounds: 1,1 trimethyl-1-aminomethane phosphonate, 1,1 trifluoromethyl-1-aminomethanephosphonate 1,1 trimethyl-1-hydroxymethane phosphonate, 1,1 trifluoromethyl-1-hydroxymethanephosphonate, we have minimized the geometry on the semiempirical level. Then we explored the reaction path by extending the P-C bond length from the optimal value up to the value 10 times longer, with the complete minimization of the rest of the molecule. We have found indeed that in the case of electroaccepting trifluoromethyl group at carbon the negative charge in the transition state is located on the carbon part and positive charge on the phosphorous part of the molecule, whereas the reverse is true for electrodonating methyl groups. We also found that decomposition is more facile for aminophosphonic acid derivatives than for hydroxy ones. The difference in the energy of the transition state is greater when they decompose to phosphorous acid. If amine is in the form of ammonium ion decomposition to phosphorous acid is higher energy process.

DECOMPOSITION OF AMINOPHOSPHONATES

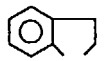
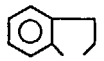
Kinetic studies

We have synthesized several compounds of various structure and measured their rate of decomposition in acidic medium. The data are collected in the Table 1

As can be seen from the Table, the N-aryl aminophosphonates are very unstable when refluxed in the water solution of hydrochloric acid, decomposing to phosphorous acid whereas decomposition of N-alkil derivatives after 24 hrs accounts for only few percent. These experimental data satisfactory corelate with the calculations showing that for such decomposition unprotonated nitrogen atom is required. For the less basic aromatic amino group the concentration of free base is greater and thus the decomposition is faster.

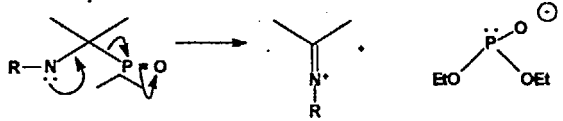
The steric factors could also prevent the protonation of nitrogen. Aliphatic benhydryl nitrogen atom is not protonated and thus the N-substituted ester does not survive the hydrolysis (example 8 in Table 1). The removal of N-benzhydryl group make this compound completely stable (example 9).

Table 1 Diethyl aminomethanephosponate decomposition (column 4-6 contains the molar ratio of not decomposed product: phosphorous acid derivatives:phosphoric acid derivatives) R',R''-substituent at carbon and nitrogen.

	R'	R"	1h	6h	24h
1	*2*	*3*	*4*	*5*	*6*
1	Ph	CH_2Ph	100:0:0	100:0:0	95:5:0
2	Ph	Ph	32:68:0	0:100:0	0:100:0
3	2Py	Ph	78:0:22	25:0:75	0:0:100
4	Ph	2Py	100:0:0	100:0:0	100:0:0
5	o-NO_2	Ph	-	4:36:60	-
6	o-NO_2	CH_2Ph	100:0:0	100:0:0	100:0:6
7	p- Br	Ph	58:42:0	34:66:0	6:93:1
8		$(Ph)_2CH_2$	28:72:0	28:72:0	28:72:0
9		H	100:0:0	100:0:0	100:0:0

Mechanism of decomposition

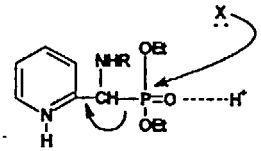
Based on the calculations and experimental results we propose the following mechanism of decomposition.



Acidic enviroment help the phosphorous atom to become more positive due to hydrogen bonding. On the other hand the protonation of nitrogen prevents the P-C bond breakage since the lone nitrogen pair is necessary for carbocation stabilisation. Consequently, there is some optimal pH region when the decomposition has the maximal rate[5]

Changing the nature of the substituents on the carbon side of the P-C bond towards more elektroacceptory moiety, like nitro, bromo or pirydyl (the last after protonation becomes strong elektroacceptor) makes this kind of decomposition less likely or completely blocked since the carbocation is not well stabilised. This, in turn, helps the formation of carboanion like transition state and another posibility of decomposition becomes possible. P-C bond breaks in such a way that lone pair, from P-C bond, stays with carbon part of molecule resulting in phosphoric acid derivative formation.

It is not clear if it is unimolecular bond breakage, like it was reported in the literature or is it nucleophilic substitution at phosphorus atom



. Our preliminary calculations suggest that bimolecular substitution is the lower energy process. The fact that diesters decompose to diethyl esters of phosphoric acid suggest that path via metaphosphate is also not important. The dependence of the reaction rate on the steric factors of substituents at nitrogen seems to sugget the bimolecular nucleophilic substitution at phosphorus atom.

It is worth to note that in less acidic conditions (e.g. acetic acid) when the pirydyl aminophosphonate are not completely protonated 2-pirydyl-N-phenylaminomethane phosphonates decompose more or less equally in both directions yielding both phosphorous or phosphoric acid derivatives

DECOMPOSITION OF HYDROXYPHOSPHONATES

Decomposition of hydroxyphosphonates is to some extend similar to this observed for aminophosphonates. The reaction of these compounds proceeds, however, mainly in a basic conditions. In this case also two alternative paths are observed: toward phosphorous (retro-Abramov) or phosphoric (phophonate-phosphate rearrangement) acid derivatives.

The stronger electronoacceptor character of substituents at carbon atom adjacent to phosphorus the faster the decomposition and the greater the ratio of rearrangement with respect to retro-Abramow. This conclusion is based on the kinetic studies on a series of intentionally designed compounds and calculations on a semiempirical and ab initio levels.[6] The measurement of the reaction rate, ethalpy and entropy of these reactions, allows us to state that rearrangement reaction is intramolecular, as was earlier reported in the literature. The negative entropy for the rearrangement suggests that transition state is highly organised (probably three membered ring). Entropy close to zero for the retro -Abramow suggests that the reaction is not unimolecular. The changes of the reaction rates for rearrangement and retro Abramow by the same factor (three order of magnitude) for sterically hindered hydroxyphosphonates confirms that both reactions may proceed via the same transition state or intermediate

ACKNOWLEDGMENTS

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