Ab initio study of oxaphosphaalkyne P≡C—OH and its isomers

L. V. Ermolaeva* and A. I. Konovalov

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Scientific Center
of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420383 Kazan', Russian Federation.
Fax: +7 (843) 272 2253

An *ab initio* study on HP=C=O → P≡C—OH isomerization has been performed at the 3—21G(d(P)), 4—31G(d(P)) and 6-31G** levels. In contrast to analogous transformation of 1-aza-3-phosphaallene, this process is endothermic in the gas phase. It proceeds *via* a [1,3] *H* shift without an intermediate. The route, including two subsequent [1,2] *H* shifts, leads to phosphinidene.

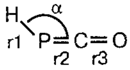
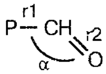
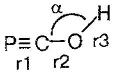
Key words: *ab initio* study, C-substitued phosphaethynes and heterophosphaallenes, isomerization

Low coordination compounds of phosphorus are important reagents in organic and coordination chemistry and have been widely studied during the last decade.[1] Heterosubstituted phosphaalkynes are comparatively less studied, in particular there is still no data on the synthesis of oxaphosphaalkynes. Interest in the heterophosphaalkynes is caused by the fact that, according to experimental and theoretical studies,[2—3] their dimerization or isomerization leads to unexpected products. 1,2,4-Azadiphospholes, a new class of compounds, were obtained as a result of dimerization of azaphosphaalkynes.[2] A theoretical study of P≡C—NH_2 (**1**) → HP=C=NH (**2**) isomerization showed that phosphinidenes and phosphirenes arise together with previously unknown carbenazaphosphirane during the transformation **1** → **2**.[3] Similarly, 1-oxa-phosphaallenes are potential precursors of oxaphosphaalkynes and probably of a series of intermediates with a low coordinated phosphorus atom.

We have made an *ab initio* study of HP=C=O (**3**) → P≡C—OH (**4**) isomerization. Calculations were carried out with the GAMESS program[4] in the standard valent split bases 3-21G,[5] and 4-31G[6] with d-functions on the phosphorous atom, and 6-31G**[7] with complete geometry optimization.

The calculated geometry parameters of isomers **3—5** are given in Table 1, the relative and whole energies of the stable structures are given in Table 2. In Table 3 the data for **1, 3** and phosphaethyne obtained in the 6-31G** basis are given for comparison. In contrast to 1-aza-3-phosphaallene, 1-oxa-3-phosphaallene is more stable than the isomer with the P≡C bond, *i.e.*, the process of **3** → **4** isomerization is endothermic in any basis, although the calculated relative energies of the isomers depend on the basis type (see Table 2). Due to the effect of the donor substituents at the carbon atom, the P≡C bond becomes longer than that in phosphaethyne. The bond is the longest in aminophosphaalkyne, and has an intermediate length in the oxaderivative (see Table 3). The structural data indicate

Table 1. *Ab initio* calculated geometry parameters of 1-oxa-3-phosphaallene isomers

Isomer		3-21G(d(P))	4-31G(d(P))	6-31G**
 **3**	r1	1.690	1.673	1.708
	r2	1.145	1.150	1.127
	r3	1.406	1.412	1.407
	α	89.4	89.5	88.5
 **4**	r1	1.762	1.750	1.801
	r2	1.213	1.219	1.193
	α	135.0	135.9	126.3
 **5**	r1	1.523	1.520	1.527
	r2	1.311	1.310	1.289
	r3	0.969	0.954	0.948
	α	111.5	116.8	115.1

Note. r — bond length (Å); α — bond angles (deg).

Table 2. Whole (au) and relative (in brackets (kcal $mole^{-1}$)) energies of isomers **1—5**

Изомер	3-21G(d(P))	4-31G(d(P))	6-31G**
1	−432.01136* (0.0)	−433.65826* (0.0)	−434.15228 (0.0)
2	−431.99330* (11.3)	−433.63950* (11.8)	−434.14622 (3.8)
3	−451.73506 (0.0)	−453.46348 (0.0)	−454.00206 (0.0)
4	−451.70884 (16.5)	−453.43948 (15.1)	−453.96579 (22.8)
5	−451.64663 (55.5)	−453.38514 (49.2)	−453.920360 (51.3)

* Data see Ref. 3.

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Table 3. Bond lengths (Å) in phosphaalkynes P≡C—X calculated in the 6-31** basis

X	R(P≡C)	R(C—X)
H	1.515	1.063
NH_2	1.538	1.316
OH	1.527	1.289

that p(N)—π*(P≡C) interaction is stronger than p(O)—π*(P≡C) interaction. The endothermic character of the **3** → **4** rearrangement in the gas phase is also indicative of the fact that the oxaderivative is less stabilized by p—π*-interaction.

Thus, no matter which basis is used, the calculations predict a smaller tendency to rearrange into a compound with a one-coordinated phosphorus atom for 1-oxa-3-phosphaallene compared to 1-aza-3-phosphaallene. Unlike the rearrangement of 1-aza-3-phosphaallene, rearrangement **3** → **4** by a [1,3]-*H*-shift does not proceed through the formation of intermediates, because two consequent [1,2]-*H*-shifts can lead only to phosphinidene **5**.

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Polyfluorinated enol acetates

Yu. V. Zeifman,* S. A. Postovoi, and L. S. German

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The synthesis of polyfluorinated enol acetates has been performed by reductive dechlorination of chloropolyfluoroketones with zinc in Ac_2O. Under these conditions, hexafluoroacetone is preferably reduced at the carbonyl group.

Key words: polychlorofluoroketones; reductive dehalogenation; polyfluorinated enol acetates; synthesis; reactivity.

It is known that the reactions of hexafluoroacetone (HFA) with metals occur in multiple ways and result both in dimerization of the ketone into perfluoropinacol and in its reductive defluorination to give pentafluoro-2-propenolates of the respective metals or products of their condensation with the carbonyl precursor.[1] The ratio of the dimerization and defluorination processes depends markedly on the nature of the metal and solvent. In particular, the reaction of HFA with Zn in THF results only in defluorination of the ketone.[1]

It was shown in this study that the reaction of HFA with Zn in Ac_2O also results in reductive defluorination of HFA to Zn enolate, which then undergoes acylation to give pentafluoroisopropenyl acetate (**1**) (for the acylation of other polyfluorinated enolates, *cf.* Refs. 2—4). However, this direction of the reaction is only realized to a small extent, and the yield of compound **1** does not exceed 5 %. The predominant process is reduction of the carbonyl group in HFA resulting in $AcOCH(CF_3)_2$. Perfluoropinacol is not formed in this reaction.

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