ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 6, pp. 1111–1119. © Pleiades Publishing, Ltd., 2011.
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Mechanism of Noncatalytic Synthesis of Tris(hydroxymethyl)phosphine. Nonempirical Quantum-Chemical Approach

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Received June 3, 2010

Abstract—The gas-phase reaction of the synthesis of tris(hydroxymethyl)phosphine from phosphine and formaldehyde was studied using a calculation scheme based on the density functional theory with hybrid exchange-correlation functional B3LYP in the 6-311++G** basis. The reaction was shown to proceed with the participation of unstable intermediates containing three-membered ring. The transformation into final products includes opening of the three-membered ring and intramolecular proton transfer. The results can be useful at selecting catalysts and for explaining the mechanism of the catalytic reaction of tris(hydroxymethyl)phosphine synthesis.

DOI: 10.1134/S1070363211060065

The elucidation of mechanism, especially of the features of limiting stage, provides information of the probable pathways of the chemical reactions and allows developing methods for optimizing conditions of its implementation. The theoretical model calculations give an opportunity to find out the details and estimate contribution of some interactions into the reaction mechanism.

The investigation of the mechanism of reactions of phosphines that have been adequately studied experimentally is of particular interest. The specificity of the structure of phosphines predetermines a possibility to form a large number of different functionalized organic compounds based on them, which may find practical application in various fields [1–4].

Tris(hydroxymethyl)phosphine is a representative of the phosphines that can be used to produce chemically, hydrolytically, and thermally resistant polymer materials with low combustibility [2, 5–7]. It can be obtained in a sufficiently high yield under rigid conditions without a catalyst at a temperature of 353–373 K and a pressure of 40 MPa, or under relatively mild conditions in the presence of catalysts (the salts of transition metals like Pt, Pd, and Ni, commonly chlorides) by the following reaction (1) [8–10].

$$PH_3 + 3CH_2O \rightarrow P(CH_2OH)_3. \quad (1)$$

We have improved the method of synthesis of this substance using the nickel(II) chloride complexes with primary amines as catalysts. We have studied the reaction kinetics and suggested a possible reaction mechanism [11–15]. However, to establish some details of the mechanism it seems logical to clarify the nature and patterns of the noncatalytic reaction taking into account the energy and structural parameters of the whole sequence of elementary acts. In this connection, the purpose of this work was a quantum-chemical study of the mechanism of noncatalytic synthesis of tris(hydroxymethyl)phosphine from phosphine and formaldehyde.

The mechanism of this reaction is commonly considered to be based on the established notions of nucleophilic addition at the carbonyl group [16], that assumes the initial addition of the nucleophile with the formation of an intermediate with tetrahedral carbon atom. The future direction of the reaction depends on the nature of transformations of this intermediate. It was suggested [17, 18] that in the absence of a catalyst the reaction (1) passed through the formation of a phosphine–formaldehyde intermediate (complex) as a bipolar ion, which was afterwards converted into hydroxymethylphosphine [reaction (2)], and then bis-(hydroxymethyl)phosphine [reaction (3)] and tris-

(hydroxymethyl)phosphine [reaction (4)] were formed along the similar scheme.

$$PH_3 + CH_2O \rightarrow [H_3P^+CH_2O^-] \rightarrow H_2PCH_2OH, \quad (2)$$

$$H_2PCH_2OH + CH_2O \rightarrow [HOCH_2(H_2)P^+CH_2O^-] \rightarrow HP(CH_2OH)_2, \quad (3)$$

$$HP(CH_2OH)_2 + CH_2O \rightarrow [(HOCH_2)_2(H)P^+CH_2O^-] \rightarrow P(CH_2OH)_3. \quad (4)$$

According to [19], the limiting step is the first stage of the synthesis of tris(hydroxymethyl)phosphine [reaction (2)], the second and third stages [reactions (3) and (4)] are fast and do not affect the kinetics of the process. To date, however, this view has not been confirmed.

It should be noted that the methyl- and dimethylphosphines react with formaldehyde easier than unsubstituted phosphine, which is consistent with the increasing electron-donor properties of the phosphorus atom in the two former compounds, as well as with the increase in the nucleophilic reactivity and basicity in the series [20, 21]: $PH_3 < CH_3PH_2 < (CH_3)_2PH$. According to [17], the pK_a values for PH_3, CH_3PH_2, and $(CH_3)_2PH$ are 14, 3.2, and 3.9, respectively.

The experimental measurement of the rates of reactions (2)–(4) and establishing the presence of various intermediates is rather difficult. Transition states cannot be observed directly, because they are unstable. Therefore we performed the quantum-chemical calculations to reveal geometric parameters of phosphines, intermediates, and transition states, as well as energy and activation parameters of the stages of tris-(hydroxymethyl)phosphine synthesis.

While performing this task, we preferred to use the method of calculation, which reflects well the geometric parameters of phosphine and methyl-, dimethyl- and trimethylphosphine molecules for which the respective experimental values are known [22]. We used a high-level calculation scheme based on the density functional theory [23] with hybrid exchange-correlation potential of Becke–Lee–Yang–Parr [24, 25] in the valence-split basis of atomic orbitals, represented as a linear combination of Gaussian functions with adding the polarization and diffuse orbitals (the scheme DFT/B3LYP/6-311++G** [26]). Note that previously [27, 28] we attempted to investigate the mechanism of this reaction by MNDO-PM3 method, but some details of the mechanism remained unclear.

The comparison of the results of quantum-chemical calculations with the experimental values of geometric parameters of phosphines presented in Table 1 shows their good correlation. At the increase in the number of methyl and hydroxymethyl groups an increase is observed in positive charge on the phosphorus atom, as

Table 1. Atomic charges and geometry of phosphine, methyl-, dimethyl-, and trimethylphosphines

Compound	Charge on phosphorus atom	Charges on hydrogen and carbon atoms and on the functional groups	Geometric parameters	
			bond lengths, Å	bond angles, deg
Experimental values				
PH_3	–	–	1.42 (P–H)	93.4 (HPH)
H_2PCH_3	–	–	1.423 (P–H), 1.858 (P–C)	96.5 (HPC)
$HP(CH_3)_2$	–	–	1.445 (P–H), 1.853 (P–C)	96.5 (HPC), 99.2 (CPC)
$P(CH_3)_3$	–	–	1.844 (P–C)	98.9 (CPC)
Calculated values				
PH_3	0.117	–0.039	1.423 (P–H)	93.524 (HPH), 93.526, 93.532
H_2PCH_3	0.245	–0.602 (C), –0.058 (H), –0.129 (CH_3)	1.424 (P–H), 1.873 (P–C)	93.332 (HPH), 97.615 (HPC)
$HP(CH_3)_2$	0.292	–0.560 (C), –0.081 (H), –0.105, –0.105 (CH_3)	1.425 (P–H), 1.867 (P–C)	96.893 (HPC), 100.333 (CPC)
$P(CH_3)_3$	0.487	–0.588, –0.589, –0.590 (C), –0.163, –0.162, –0.162 (CH_3)	1.863 (P–C)	99.429 (CPC), 99.475, 99.521

Table 2. Energy characteristics and phosphorus chemical shifts of phosphines

Compound	Energy of LUMO , eV	ΔE [a], eV	Activation energy, kJ mol^{-1}	Chemical shift, δ_P, ppm	
				experiment	calculation
Phosphine					
PH_3	–7.593	5.852	40.58	238, 240, 241	238.47
Methylphosphines					
CH_3–PH_2	–6.962	5.221	22.93	163.5	163.41
$(CH_3)_2$–PH	–6.512	4.770	9.62	98.5, 99.5	98.94
$(CH_3)_3$–P	–6.184	4.443	–	62.61	62.06
Hydroxymetylphosphines					
$HOCH_2$–PH_2	–7.230	5.489	–	–	137.24
$(HOCH_2)_2$–PH	–6.855	5.114	–	–	43.0
$(HOCH_2)_3$–P	–6.551	4.810	–	31	27.9

[a] Energy difference of phosphine HOMO and formaldehyde LUMO.

well as an increase in the bond angles in the substituted phosphines. The increasing positive charge on the phosphorus atom with increasing number of substituents can be explained by the effect of "positive charge," whose nature has been discussed earlier [29]. The bond angles in the phosphines are determined by the nature of hybridization of the phosphorus atom bonding orbitals [25].

It has been found [24, 25] that the increase in the number of substituents at the phosphorus atom in the phosphines leads to an increase in their reactivity in the reaction with formaldehyde. This is qualitatively confirmed by the data of ^{31}P NMR spectroscopy (Table 2), since the chemical shift reflects the degree of shielding of the phosphorus nucleus and provides an important information on the nature of hybridization of valence orbitals. A significant chemical shift of phosphorus atom in phosphine is defined by the fact that the bonds between phosphorus and hydrogen atoms have *p*-character and are almost pure $p\sigma$(P)–$s\sigma$(H) bonds [30–32]. The lone electron pair of the phosphorus atom occupies spherically symmetric 3*s*-orbital that is localized closer to the nucleus compared with 3*p*-orbitals, so there is a strong shielding of the nucleus of phosphorus atom leading to its large chemical shift. As a result of this specific electron configuration, the nucleophilic character of the molecule is not very large, and therefore the phosphine reactivity is rather low. In passing from phosphine to the methyl and hydroxymethylphosphines, the degree of screening is reduced and their reactivity as nucleophilic agents increases significantly. Thus, using ^{31}P NMR spectroscopy we for the first time confirmed that the rate-limiting step of the synthesis of tris(hydroxymethyl)phosphine is the first stage [reaction (2)], which results in the formation of hydroxymethylphosphine. The NMR spectra were analyzed using the program ACDLabs 6 [33].

Since the reaction of aldehydes with nucleophilic reagents is likely to proceed under the orbital control [34, 35], a special attention at considering reactivity should be given to the information on the symmetry and the energy of their frontier orbitals. The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting molecules suggest the direction of change in their reactivity with respect to chemical transformations. LUMO of formaldehyde is the π^*-antibonding orbital localized on the carbonyl fragment (>C=O) whose experimentally found energy is 0.86 eV [36]. The phosphine HOMO is predominantly of 3*s*-character [30]. From the results listed in Table 2 it follows that with increasing extent of substitution of hydrogen in phosphine by methyl or hydroxymethyl groups the HOMO energy increases and the difference between the energies of the HOMO of the phosphine and

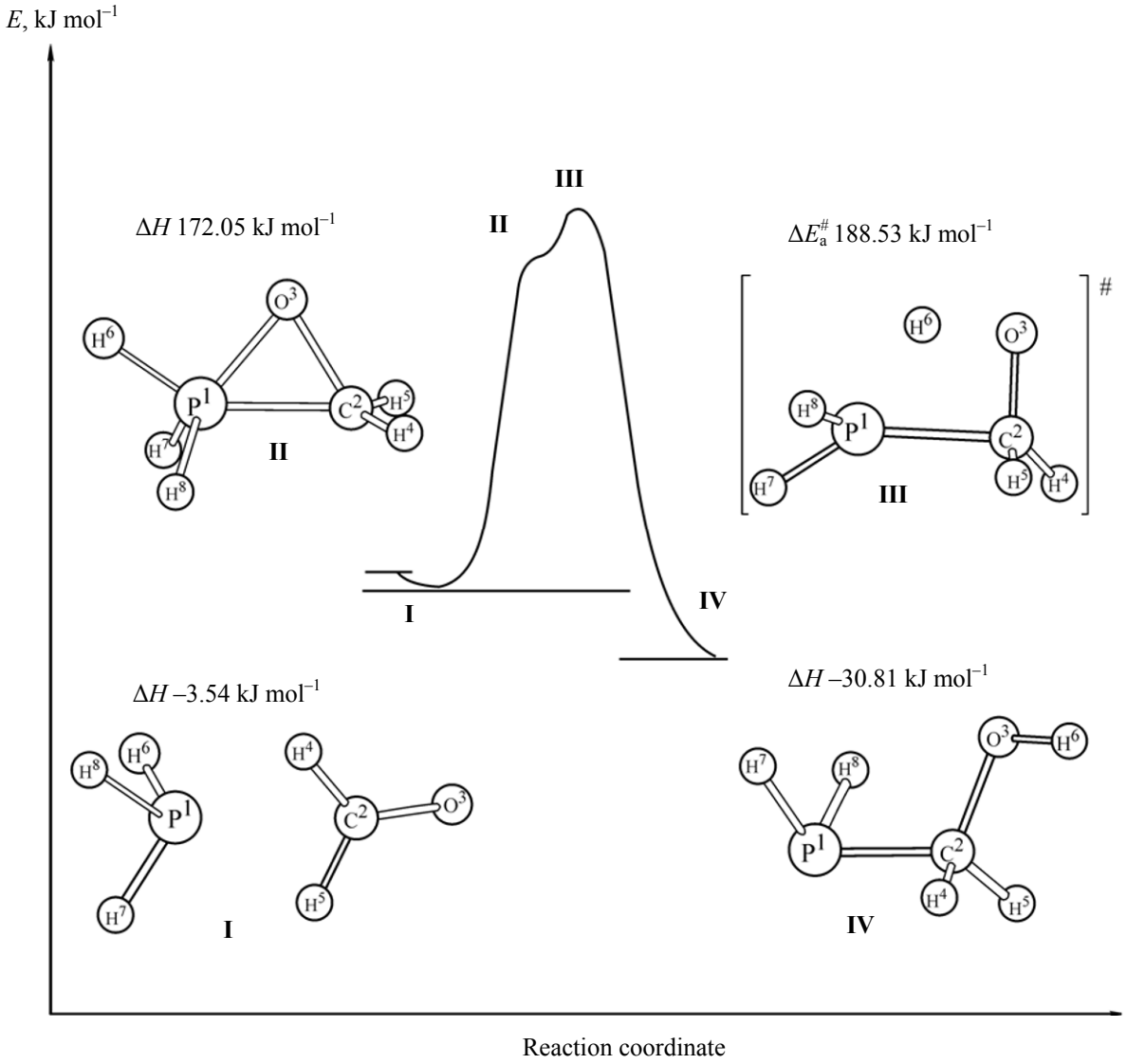

Fig. 1. Intermediate structures and schematic profile of the first step [reaction (2)] in the synthesis of hydroxymethylphosphine: (**I**) phosphine–formaldehyde complex, (**II**) intermediate, (**III**) transition state, (**IV**) hydroxymethylphosphine. For each structure atomic charges, bond length, Å, and bond angles, deg, are indicated in Table 3.

LUMO of formaldehyde decreases causing increased reactivity of substituted phosphines in the reaction with formaldehyde.

It was shown in [19] that the rate equation of reaction (1) is of the first order with respect to both phosphine and formaldehyde. On the other hand, it is known that all the reactions whose stoichiometric equation contains four or more particles of reagents certainly occur sequentially [37], so we can agree with the view stated in [21, 22] that reaction (1) proceeds consecutively.

Our calculations confirmed that the reaction under study actually has three stages. The mechanism of each stage involves the formation of phosphine–formaldehyde complex converting into an unstable intermediate which through a transition state transforms into the final product (Figs. 1–3).

Formaldehyde and phosphine have little affinity to each other and therefore they form unstable phosphine–formaldehyde complexes **I**, **V**, and **IX** with a low exothermic effect.

The intermediate compounds **II**, **VI**, and **X** formed in every stage include a three-membered ring in their structure with full-fledged P–C and P–O bonds. A possibility of such structures to exist has been shown

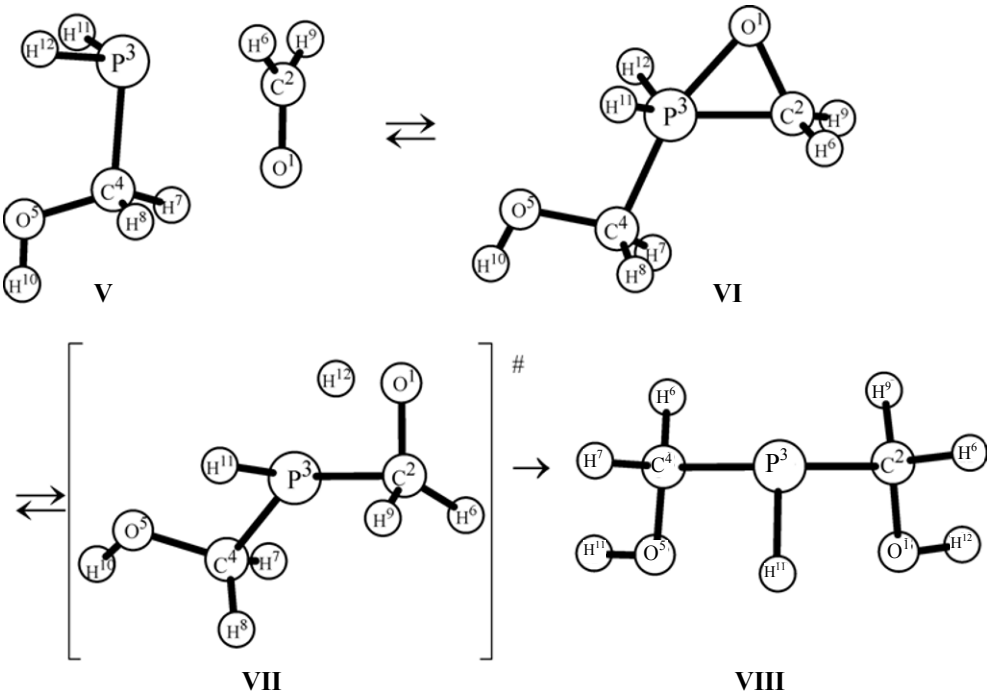

Fig. 2. Mechanism of the second stage (reaction 3) in the synthesis of bis(hydroxymethyl)phosphine: (**V**) hydroxymethylphosphine–formaldehyde complex, ΔH = –0.93 kJ mol^{-1}, (**VI**) intermediate, ΔH = 132.66 kJ mol^{-1}, (**VII**) transition state, $\Delta E_a^{\#}$ = 176.64 kJ mol^{-1}, (**VIII**) bis(hydroxymethyl)phosphine, ΔH = – 38.05 kJ mol^{-1}. For each structure atomic charges, bond lengths, Å, and bond angles, deg, are indicated in Table 5.

in [38] when studying the reactions of phosphites with carbonyl compounds. Note that formation of these intermediates occurs without a significant activation energy, which is associated apparently with a consecutive change in the hybridization of the phosphorus atom from p^3 to sp^3 and further sp^3d state [39].

The intermediates are capable of ready opening of the three-membered ring and of further transfer of proton from the phosphorus atom to the oxygen atom, to form the final products of each stage: hydroxymethylphosphine **IV**, bis(hydroxymethyl)phosphine **VIII**, and tris(hydroxymethyl)phosphine **XII** through the transition states **III**, **VII**, and **XI**, respectively.

The intermediate in every stage requires less energy for back transformation into the original phosphine–formaldehyde complex along the reverse reaction than to turn into final products through the transition state. Therefore, the reaction of the intermediate formation is reversible. The calculated activation energy of direct reactions (2)–(4) for **I**, **II** and **III** are 188.53, 176.64, and 174.39, and of the reverse reactions, 219.34, 214.69, and 204.89 kJ mol^{-1}, respectively. Note that a significantly greater values of the activation energy of reverse reaction compared to the direct reactions evidence in favor of the irreversibility of the reactions (2)–(4), and hence the overall reaction (1). The rate-limiting step is the reaction (2). All three stages proceed with the heat evolution.

To characterize the reaction mechanism of the synthesis of tris(hydroxymethyl)phosphine it is interesting to consider the data on the change in the entropy of the separate steps in the stages (2)–(4) presented in Table 6.

Since each stage is a bimolecular reaction combining molecules, the overall entropy decreases already at the formation of the phosphine–formaldehyde complex existing as one unit. The difference between the values of the entropy of the initial compounds and the resulting complexes is close to the corresponding values for bimolecular formation of a bond, which falls to the range from –84 to –126 J mol^{-1} K^{-1} [40].

The next step of the formation of the intermediates (three-membered ring) causes a further decrease in the total entropy, which is consistent with the results of [40] indicating a change in entropy in the range 21–63 J mol^{-1} K^{-1} at the ring closure.

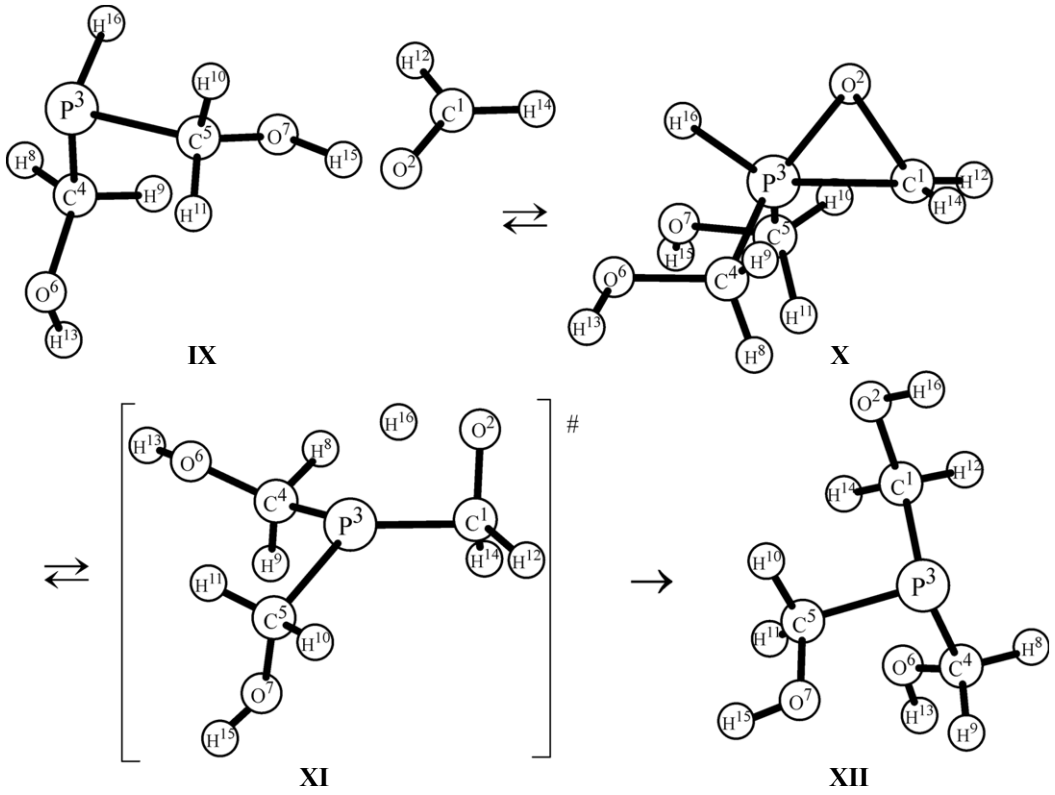

Fig. 3. The mechanism of the third stage [reaction (4)] of the synthesis of tris(hydroxymethyl)phosphine: (**IX**) bis(hydroxymethyl)-phosphine–formaldehyde complex, ΔH = –12.49 kJ mol^{-1}, (**X**) intermediate, ΔH = 141.12 kJ mol^{-1}, (**XI**) transition state, $\Delta E_a^{\#}$ = 174.39 kJ mol^{-1}, (**XII**) tris(hydroxymethyl)phosphine, ΔH = –30.5 kJ mol^{-1}). For each structure atomic charges, bond lengths, Å, and bond angles, deg, are indicated in Table 5.

The change in the entropy of the transition state compared to the initial phosphine–formaldehyde complex in each reaction step is negative, which indicates a certain decrease in the degree of the motion freedom of individual atomic groups at reaching the transition state.

The suggested reaction mechanism reflects adequately the nature of the process of synthesis of tris (hydroxymethyl)phosphine. However, we note that the actual process is much more complicated, mainly due to high sensitivity of the nucleophilic addition to carbonyl group toward the influence of the environ-

Table 3. Atomic charges and geometry characteristics of intermediate structures at the synthesis of hydroxymethylphosphine

Comp. no.	Atomic charges	Bond lengths, Å	Bond angles, deg
I	0.077 (P^1), 0.064 (C^2), 0.09 (H^4), –0.03 (H^7), –0.234 (O^3)	3.978 (P^1–C^2), 1.107 (C^2–H^4), 1.203 (C^2–O^3), 1.422 (P^1–H^7)	122.21 ($H^4C^2O^3$), 115.64 ($H^4C^2H^5$), 93.92 ($H^6P^1H^7$), 93.99 ($H^7P^1H^8$)
II	0.422 (P^1), –0.436 (C^2), 0.159 (H^4), –0.01 (H^7), –0.206 (O^3), –0.077 (H^6)	1.820 (P^1–C^2), 1.530 (C^2–O^3), 1.640 (P^1–O^3), 1.421 (P^1–H^7), 1.445 (P^1–H^6), 2.269 (H^6–O^3)	57.84 ($P^1C^2O^3$), 52.17 ($C^2P^1O^3$), 96.41 ($H^6P^1H^7$), 103.23 ($H^7P^1H^8$), 94.53 ($H^6P^1O^3$), 104.01 ($H^8P^1C^2$)
III	0.244 (P^1), –0.271 (C^2), 0.160 (H^4), –0.06 (H^7), –0.297 (O^3), 0.121 (H^6)	2.080 (P^1–C^2), 1.317 (C^2–O^3), 2.413 (P^1–O^3), 1.445 (P^1–H^7), 1.411 (P^1–H^8), 1.574 (P^1–H^6), 1.442 (H^6–O^3)	87.51 ($P^1C^2O^3$), 96.49 ($H^7P^1H^8$), 145.88 ($H^8P^1C^2$), 65.86 ($H^6P^1C^2$)
IV	0.212 (P^1), –0.480 (C^2), 0.160 (H^4), –0.029 (H^7), –0.297 (O^3), 0.252 (H^6)	1.866 (P^1–C^2), 1.425 (C^2–O^3), 1.422 (P^1–H^7), 0.964 (H^6–O^3), 1.098 (C^2–H^5)	111.76 ($P^1C^2O^3$), 94.18 ($H^7P^1H^8$), 96.31 ($H^8P^1C^2$), 107.62 ($H^4C^2H^5$), 111.50 ($H^5C^2O^3$)

Table 4. Atomic charges and geometry characteristics of intermediate structures at the synthesis of bis(hydroxymethyl)phosphine

Comp. no.	Atomic charges	Bond lengths, Å	Bond angles, deg
V	0.155 (P^3), 0.016 (C^2), 0.103 (H^6), –0.22 (O^1), –0.013 (H^{11}), –0.51 (C^4)	3.556 (P^3–C^2), 1.107 (C^2–H^6), 1.204 (C^2–O^1), 1.42 (P^3–H^{11}), 1.863 (P^3–C^4)	122.10 ($H^6C^2O^1$), 115.81 ($H^6C^2H^9$), 94.67 ($H^{11}P^3H^{12}$), 97.05 ($H^{11}P^3C^4$)
VI	0.7 (P^3), –0.471 (C^2), 0.163 (H^6), –0.295 (O^1), –0.007 (H^{11}), –0.55 (C^4)	1.763 (P^3–C^2), 1.094 (C^2–H^6), 1.447 (C^2–O^1), 1.41 (P^3–H^{12}), 1.896 (P^3–C^4), 1.810 (P^3–O^1), 2.355 (O^1–H^{11}, O^1–H^{12})	119.81 ($H^6C^2P^3$), 115.87 ($H^9C^2O^1$), 114.15 ($H^{11}P^3H^{12}$), 116.35 ($C^4P^3C^2$), 67.83 ($P^3C^2O^1$), 47.75 ($O^1P^3C^2$), 111.19 ($H^6C^2H^9$)
VII	0.427 (P^3), –0.344 (C^2), 0.139 (H^6), –0.336 (O^1), –0.019 (H^{11}), –0.45 (C^4), 0.095 (H^{12})	1.968 (P^3–C^2), 1.099 (C^2–H^6), 1.339 (C^2–O^1), 1.54 (P^3–H^{12}), 1.896 (P^3–C^4), 1.51 (H^{12}–O^1), 2.78 (O^1–H^{11})	89.00 ($P^3C^2O^1$), 118.29 ($H^6C^2O^1$), 97.45 ($H^{11}P^3C^4$), 138.15 ($C^4P^3C^2$), 110.99 ($H^6C^2H^9$)
VIII	0.221 (P^3), –0.451 (C^2), –0.448 (C^4), –0.280 (O^1), –0.28 (O^5), –0.02 (H^{11})	1.871 (P^3–C^2), 1.866 (P^3–C^4), 1.428 (C^2–O^1), 1.430 (C^4–O^5), 1.424 (P^3–H^{11})	99.77 ($C^4P^3C^2$), 95.08 ($H^{11}P^3C^4$), 96.11 ($H^{11}P^3C^2$)

Table 5. Atomic charges and geometry characteristics of intermediate structures at the synthesis of tris(hydroxymethyl)phosphine

Comp. no.	Atomic charges	Bond lengths, Å	Bond angles, deg
IX	0.212 (P^3), –0.461 (C^5), –0.453 (C^4), –0.021 (H^{16}), 0.037 (C^1), 0.129 (H^{12}), –0.254 (O^2)	6.099 (P^3–C^1), 1.871 (P^3–C^4), 1.867 (P^3–C^5), 1.425 (P^3–H^{16}), 1.206 (C^1–O^2)	96.14 ($H^{16}P^3C^5$), 94.92 ($H^{16}P^3C^4$), 99.85 ($C^4P^3C^5$), 121.40 ($O^2C^1H^{14}$)
X	0.566 (P^3), –0.485 (C^5), –0.485 (C^4), –0.032 (H^{16}), –0.570 (C^1), 0.167 (H^{12}), –0.096 (O^2)	1.844 (P^3–C^1), 1.859 (P^3–C^4), 1.859 (P^3–C^5), 1.437 (P^3–H^{16}), 1.639 (P^3–O^2), 1.524 (C^1–O^2)	97.14 ($H^{16}P^3C^5$), 97.14 ($H^{16}P^3C^4$), 100.62 ($C^5P^3C^1$), 100.62 ($C^4P^3C^1$), 67.29 ($P^3C^1O^2$), 51.48 ($C^1P^3O^2$), 111.05 ($C^4P^3C^5$), 96.83 ($H^{16}P^3O^2$)
XI	0.486 (P^3), –0.436 (C^5), –0.486 (C^4), 0.1 (H^{16}), –0.440 (C^1), 0.129 (H^{12}), –0.355 (O^2)	1.912 (P^3–C^1), 1.851 (P^3–C^4), 1.885 (P^3–C^5), 1.531 (P^3–H^{16}), 1.548 (O^2–H^{16}), 1.357 (O^2–C^1)	132.89 ($C^5P^3C^1$), 101.04 ($C^5P^3C^4$), 103.24 ($C^4P^3C^1$), 90.83 ($P^3C^1O^2$)
XII	0.35 (P^3), –0.472 (C^5), –0.453 (C^4), 0.243 (H^{16}), –0.532 (C^1), 0.191 (H^{12}), –0.256 (O^2)	1.881 (P^3–C^1), 1.865 (P^3–C^4), 1.868 (P^3–C^5), 1.427 (C^1–O^2), 0.964 (O^2–H^{16})	98.37 ($C^5P^3C^1$), 100.12 ($C^5P^3C^4$), 99.51 ($C^4P^3C^1$)

Table 6. Difference in entropy (J mol^{-1} K^{-1}) in each step of synthesis of tris(hydroxymethyl)phosphine

Process	I step [reaction (2)]	II step [reaction (3)]	III step [reaction (4)]
Formation of phosphine–formaldehyde complex	$\Delta S = S(\mathbf{I}) - S(CH_2O) - S(PH_3) = -103.22$	$\Delta S = S(\mathbf{V}) - S(CH_2O) - S(HOCH_2PH_2) = -82.63$	$\Delta S = S(\mathbf{IX}) - S(CH_2O) - S[HP(HOCH_2)_2] = -90.28$
Formation of intermediates	$\Delta S = S(\mathbf{II}) - S(\mathbf{I}) = -61.75$	$\Delta S = S(\mathbf{VI}) - S(\mathbf{V}) = -77.60$	$\Delta S = S(\mathbf{X}) - S(\mathbf{IX}) = -81.82$
Formation of transition states	$\Delta S^{\#} = S(\mathbf{III}) - S(\mathbf{I}) = -50.44$	$\Delta S^{\#} = S(\mathbf{VII}) - S(\mathbf{V}) = -68.44$	$\Delta S^{\#} = S(\mathbf{XI}) - S(\mathbf{IX}) = -71.12$
Formation of final compounds	$\Delta S = S(\mathbf{IV}) - S(\mathbf{III}) = +0.68$	$\Delta S = S(\mathbf{VIII}) - S(\mathbf{VII}) = -2.18$	$\Delta S = S(\mathbf{XII}) - S(\mathbf{XI}) = +3.57$

ment. Note that the calculated activation energy of the first step of the synthesis exceeds the experimental one, although the basis used for the calculation was, according to [38], tested many times and is known to give the results close to experimental ones. Therefore, we also performed calculations taking into account the presence of the third co-reagent: solvent (water) and/or formaldehyde. It turned out that the processes are

similar and in this case we also have found a significant decrease in activation energy.

In conclusion, we note that using the high-level quantum-chemical calculations we were able to provide a detailed stepwise mechanism for the synthesis of tris(hydroxymethyl)phosphine. Previously it was assumed [21] that the mechanism involves the formation of the intermediate phosphine–formaldehyde complex as a bipolar ion (zwitter-ion) with the $\equiv P^{(+)}–C–O^{(-)}$ frame. Our results do not conform to this view. Also note that on the basis of the quantum-chemical calculations of the reactions of phosphites with aldehydes [38] earlier a similar conclusion has been made that the participation of a zwitter-ions in the reaction schemes involving trivalent phosphorus compounds are unlikely. The information obtained can be useful to explain the mechanism of reaction (1) also in the presence of catalysts.

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