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Quantum-Chemical Calculations of Thermodynamic Parameters of the Synthesis of Tris(hydroxymethyl)phosphine

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Abstract—Thermodynamic characteristics of the process of tris(hydroxymethyl)phosphine synthesis are calculated by the Hartree–Fock–Roothaan method in the basises LANL2DZ and 6-31G. From the calculated data degrees of accumulation are found of the target product that correlate with experimental data. This fact can be taken into account at the choice of conditions for producing tris(hydroxymethyl)phosphine.

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Tris(hydroxymethyl)phosphine is a valuable organophosphorus compound that can find practical application for creation of polymeric materials with reduced combustibility [1–4] and also at development of modern effective antimicrobial means [5]. Synthesis of tris(hydroxymethyl)phosphine is carried out by the reaction of phosphine with formaldehyde along the reaction (1):

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

This process was performed under various conditions: in the gas or liquid phase, with catalysts of different nature and in different amounts, at alternative temperatures and pressures [6–12]. However, for the examination of the process under pilot plant conditions certain additional data are required, including quantitative characteristics describing thermodynamics of this reaction. In published sources there are no data concerning thermodynamics of the process of the tris(hydroxymethyl)phosphine synthesis.

The purpose of our work was evaluating thermodynamic characteristics of the synthesis of tris(hydroxymethyl)phosphine in the gas phase on the ground of quantum-chemical calculations.

The actual physicochemical processes in the synthesis of tris(hydroxymethyl)phosphine are too complicated, and the problems cannot be solved only by experimental methods. Therefore we analized them using nonempirical quantum-chemical calculations by the Hartree–Fock–Roothaan method in the basises LANL2DZ and 6-31G [13, 14].

A significant advantage of the quantum-chemical nonempirical calculations is the possibility of evaluating from the frequency characteristics the main thermodynamic properties of molecules, the enthalpy and entropy of formation [15]. Thus, their variations and hence Gibbs energy for the examined reaction might be estimated.

Noteworthy that in the course of the reaction the reaction mixture composition depends on the number of moles of reacting substances, therefore we carried out calculations for stoichiometric ratio of reagents. The results of calculations of thermodynamic characteristics and equilibrium constants of reaction (1) listed in Table 1 show that within the whole examined temperature range (200 to 450 K) this reaction is exothermic and its enthalpy weakly depends on the temperature. The reaction entropy is negative, and close values are obtained regardless the used basis, and it weakly depends on the reaction temperature. The system is in equilibrium at approximately 400 K (calculation in LANL2DZ basis) or at 350 K (6-31G). As far as the change in the Gibbs energy in the reaction at these temperaturesis is close to zero, then, in correspondence with the Le Chatelier principle, further increase in temperature should shift equilibrium to the

Table 1. Thermodynamic functions (ΔH, ΔS, and ΔG) and equilibrium constants (K_{eq}) for the reaction of tris(hydroxymethyl)-phosphine synthesis (calculations in LANL2DZ and 6-31G basises)

Temperature, K	LANL2DZ				6-31G			
	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}	ΔG, kJ mol^{-1}	K_{eq}	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}	ΔG, kJ mol^{-1}	K_{eq}
200	199.1	486.9	–102	3.6×10^{26}	168.7	489.1	–70.9	3.3×10^{18}
250	199.6	489.6	–77.2	1.4×10^{16}	169.3	491.8	–46.3	4.8×10^{9}
300	199.7	489.9	–52.7	1.5×10^{9}	169.3	491.8	–21.7	6.0×10^{3}
350	199.2	488.3	–28.3	1.7×10^{4}	168.8	490.4	+2.9	0.37
400	198.4	489.1	–3.93	3.26	163.8	488.1	27.3	2.7×10^{-4}
450	197.4	483.4	+20.2	4.6×10^{-3}	172.8	490.0	47.7	2.9×10^{-6}

side of the initial components. The calculation of equilibrium constants was carried out with the equation of van't Hoff's isotherm $\ln K_{eq} = -G^0_T/RT$ in the temperature range 200–450 K. It is seen from the results of calculation that equilibrium constants K_{eq} decrease with the rising temperature.

For effective use of raw material it is desirable to perform the technological process under the conditions of maximum conversion of the parent substances. Therefore from practical viewpoint it is important to reveal the effect of various factors, temperature and pressure first of all, on the equilibrium in the system.

The degree of accumulation of tris(hydroxymethyl)-phosphine in reaction (1) we calculated by solving an equation expressed via mole fractions and connecting the degree of accumulation with the pressure in the system and with the equilibrium constant [16]:

$$x + t\sqrt[4]{x} - 1 = 0,\ t = \sqrt[4]{(9.48P_0^3)/(K_{eq}P_{total}^3)},$$

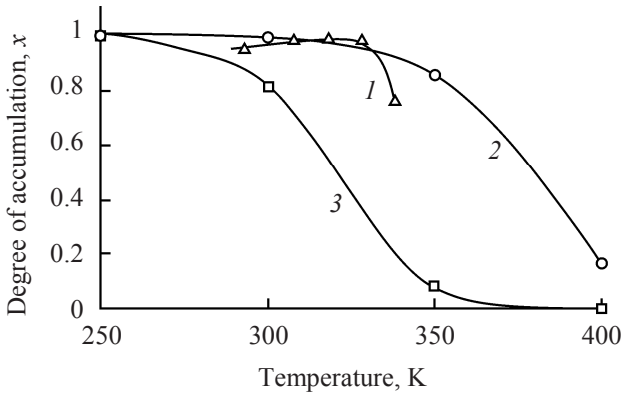

Fig. 1. Plots of degree of tris(hydroxymethyl)phosphine accumulation vs. reaction temperature for reaction (1): (*1*) experimental observations, (*2*) calculations in LANL2DZ basis, and (*3*) calculations in 6-31 G basis.

where x is the degree of accumulation of tris(hydroxymethyl)phosphine; K_{eq} is the equilibrium constant; P_0 is ambient pressure (1.01325×10^5 Pa), P_{total} is total pressure.

The dependence of tris(hydroxymethyl)phosphine accumulation on the reaction (1) temperature is shown in Fig. 1. The most appropriate temperature of the process is 300 K (6-31G) or 300–350 K (LANL2DZ). Increasing temperature above these values leads to a decrease in the degree of accumulation of the target substance. Note that the calculations with LANL2DZ basis led to the dependence of tris(hydroxymethyl) phosphine accumulation on temperature that fit the best to the experimental observations, 293–328 K [11].

In the course of reaction (1) according to data [1] three steps are clearly seen corresponding to consecutive replacement of hydrogen atoms of phosphine by hydroxymethyl groups [reactions (2)–(4)]:

$$PH_3 + CH_2O \rightarrow H_2PCH_2OH, \quad (2)$$

$$H_2PCH_2OH + CH_2O \rightarrow HP(CH_2OH)_2, \quad (3)$$

$$HP(CH_2OH)_2 + CH_2O \rightarrow P(CH_2OH)_3. \quad (4)$$

Therefore there is no doubts that each of these reactions contributes to the energetics of reaction (1). It is seen from the data listed in Table 2 that the enthalpy and entropy of reactions (2)–(4) are negative, weakly depend on temperature, and their values decrease at the successive hydrogen replacement in the phosphine by hydroxymethyl group in the following sequence of reactions 2 → 3 → 4. Noteworthy that maximum changes in enthalpy and entropy occur at the 2 → 3 transition. From the values of Gibbs energy it is presumable that reaction (2) is allowed thermodynamically up to 350 K, and reactions (3) and (4) up to approximately 400 K. The values of equilibrium constants K_{eq} grow with the degree of hydrogen

Table 2. Thermodynamic functions (ΔH, ΔS, and ΔG) and equilibrium constants (K_{eq}) for the reaction of the synthesis of hydroxymethylphosphines (2)–(4) (calculations in LANL2DZ basis)

Temperature, K	$PH_3 + CH_2O \rightarrow H_2PCH_2OH$				$H_2PCH_2OH + CH_2O \rightarrow HP(CH_2OH)_2$				$HP(CH_2OH)_2 + CH_2O \rightarrow P(CH_2OH)_3$			
	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}	ΔG, kJ mol^{-1}	K_{eq}	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}	ΔG, kJ mol^{-1}	K_{eq}	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}	ΔG, kJ mol^{-1}	K_{eq}
200	59.50	157.4	–27.9	2.0×10^7	66.95	163.3	–34.3	8.9×10^8	72.61	166.3	–39.4	2×10^{10}
250	59.98	159.6	–20.1	1.6×10^4	67.13	164.1	–26.1	2.8×10^5	72.61	166.0	–31.1	3.1×10^6
300	60.21	160.4	–12.1	1.3×10^2	67.13	164.1	–17.9	1.3×10^3	72.32	165.4	–22.7	9.0×10^3
350	60.23	160.5	–4.06	4.0	66.99	163.7	–9.71	2.8×10	71.98	164.2	–14.5	147
400	60.08	160.1	+3.9	0.31	66.71	162.9	–1.55	1.60	71.56	163.0	–6.36	6.8
450	59.97	159.4	11.80	0.04	66.33	162.0	+6.6	0.17	71.06	161.9	+1.8	0.63

replacement in phosphine in the course of reactions (2) → (3) → (4) and fall when temperature increases.

The degree of accumulation of hydroxymethylphosphines in the intermediate reactions (2)–(4) was found by solving equation expressed via mole fractions of components that connects the degree of accumulation with the pressure in the system and the equilibrium constant [16]:

$$x^2 - (2 + t)x + 1 = 0,$$

where x is the degree of accumulation of hydroxymethylphosphines; K_{eq} is equilibrium constant; P_0 is ambient pressure; P_{total} is total pressure.

The plots of hydroxymethylphosphine accumulation in reactions (2)–(4) versus temperature are shown in Fig. 2. The degree of accumulation is seen to grow in the sequence of the consecutive reactions 2 → 3 → 4. Nonetheless, in each step an increase in the temperature of reaction leads to decrease in the degree of accumulation. Addition of formaldehyde proceeds most difficultly in reaction (2), and probably this step is the limiting one in the series of consecutive reactions of the synthesis of tris(hydroxymethyl)phosphine. Moreover, hydroxymethylphosphine and bis(hydroxymethyl)phosphine formed in reactions (2) and (3), respectively, are more reactive than the parent phosphine and undergo further reaction with formaldehyde more effectively.

A special feature of the tris(hydroxymethyl)phosphine synthesis by liquid phase condensation of phosphine with formaldehyde is the establishment of a dynamic equilibrium between the reactive liquid phase and the gas phase. Thus, the yield of the target product depends considerably on the process tem-perature and pressure [11]. Therefore the data obtained for the pressure ranges 0.1–3 and 0.1–0.02 MPa are very important for the development of the processing.

The results of calculations of thermodynamic characteristics and equilibrium constants of reaction (1) when it is carried out at the pressure 0.1–3 MPa are listed in Table 3. These data show that at higher pressure the equilibrium in the system is shifted to the side of the formation of tris(hydroxymethyl)phosphine: the Gibbs energy falls and equilibrium constant grows. The plots of tris(hydroxymethyl)phosphine accumulation versus temperature at the pressure 0.1–3 MPa shown in Fig. 3 indicate that the highest effect on the

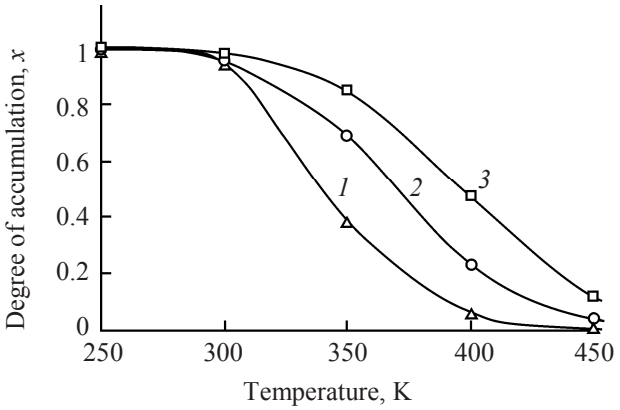

Fig. 2. Plots of degree of accumulation of hydroxymethylphosphines in reactions (2)–(4) vs. temperature: (*1*) accumulation of hydroxymethylphosphine [reaction (2)], (*2*) accumulation of bis(hydroxymethyl)phosphine [reaction (3)], and (*3*) accumulation of tris(hydroxymethyl)phosphine [reaction (4)].

Table 3. Gibbs energy (ΔG) and equilibrium constants (K_{eq}) in reaction of tris(hydroxymethyl)phosphine synthesis (1) at the pressure 0.1–3 MPa (calculation in LANL2DZ basis)

Temperature, K	Pressure, MPa							
	0.1		1		2		3	
	ΔG, kJ mol^{-1}	K_{eq}	ΔG, kJ mol^{-1}	K_{eq}	ΔG, kJ mol^{-1}	K_{eq}	ΔG, kJ mol^{-1}	K_{eq}
200	–101.7	3.6×10^{26}	–113.2	3.6×10^{29}	–116.6	2.8×10^{30}	–118.7	9.8×10^{30}
250	–77.24	1.4×10^{16}	–91.6	1.4×10^{19}	–95.94	1.1×10^{20}	–98.45	3.7×10^{20}
300	–52.68	1.5×10^{9}	–69.99	1.5×10^{12}	–75.19	1.2×10^{13}	–78.20	4.1×10^{13}
350	–28.33	1.7×10^{4}	–48.41	1.7×10^{7}	–54.48	1.4×10^{8}	–57.99	4.5×10^{8}
400	–3.93	3.26	–26.90	3.3×10^{3}	–33.85	2.6×10^{4}	–37.87	8.8×10^{4}
450	+20.17	4.6×10^{-3}	–5.69	4.6	–13.47	36.6	–18.03	1.2×10^{2}

equilibrium shift is attained at the increase in pressure approximately to 1 MPa.

The results of calculations in LANL2DZ and 6-31G basises of thermodynamical characteristics and equilibrium constants for reaction (1) carried out at the pressure 0.1–0.02 MPa are listed in Tables 4 and 5. These data reveal the fact of increase in Gibbs energy and decrease in equilibrium constants and in degree of tris(hydroxymethyl)phosphine accumulation at the decrease in the pressure in the examined system. For comparison with experimental observations obtained at 300 K we have drawn the plots of tris(hydroxymethyl) phosphine accumulation degree versus the pressure in the system (Fig. 4). These plots confirm that the results of calculations of the examined process in the pressure range 0.08–0.02 MPa in 6-31G basis are close to the experimental data [11].

Thus we conclude that by means of non-empirical calculations of the thermodynamic caharacteristics ΔH, ΔS and ΔG of reactions (1)–(4) in LANL2DZ and 6-31G basises we found equilibrium constants and degree of accumulation of hydroxymethylphosphine. The results of calculation in LANL2DZ basis turns to be more correct for the pressure ~0.1 MPa, and in 6-31G, for the pressure in the range ~0.08–0.02 MPa. The limiting step in the series of reactions 2–4 is the step of the synthesis of hydroxymethylphosphine (2). At the increase in pressure in the range 0.02–3 MPa the equilibrium is shifted to the side of tris(hydroxymethyl)phosphine formation (decrease in Gibbs energy and increase in equilibrium constant is traced).

The obtained results can be used for the development of conditions for performing industrial processsing of the synthesis of tris(hydroxymethyl)phosphine.

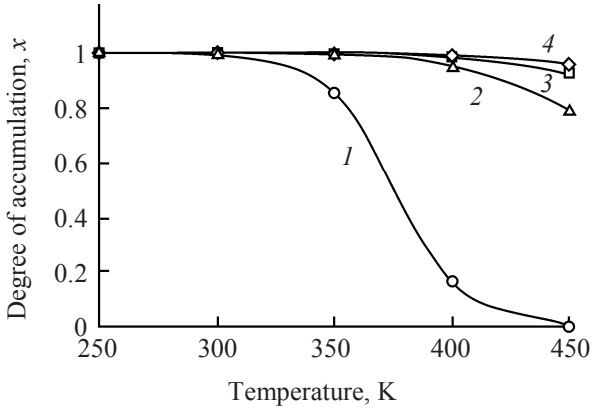

Fig. 3. Plots of tris(hydroxymethyl)phosphine accumulation vs. temperature in reaction (1) at the pressure values 0.1–3 MPa: (*1*) 0,1; (*2*) 1; (*3*) 2; and (*4*) 3.

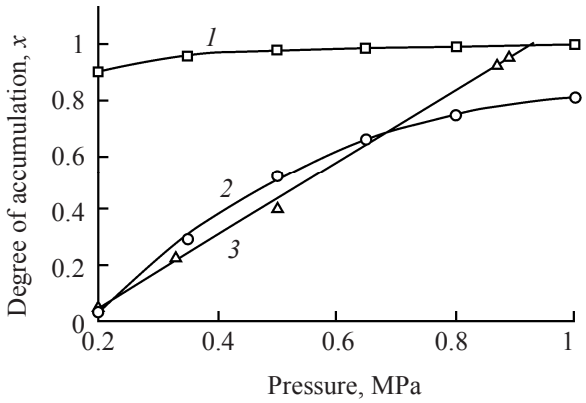

Fig. 4. Plots of tris(hydroxymethyl)phosphine accumulation vs. pressure in reaction (1) at the pressure values 0.1–0.02 MPa at 300 K: (*1*) calculation in LANL2DZ basis; (*2*) calculation in 6-31G basis; and (*3*) experimentasl observations.

Table 4. Gibbs energy (ΔG), equilibrium constants (K_{eq}) and degree of accumulation (x) of tris(hydroxymethyl)phosphine in reaction (1) at the pressure 0.1–0.02 MPa (calculation in LANL2DZ basis)

Pressure, MPa	Parameter	Temperature, K				
		200	250	300	350	400
0.02	ΔG, kJ mol^{-1}	–93.6	–67.2	–40.7	–14.3	12.1
	K_{eq}	2.9×10^{24}	1.1×10^{14}	1.2×10^{7}	1.34×10^{2}	2.6×10^{-2}
	x	0.9999	0.9982	0.9028	0.0806	2.2×10^{-5}
0.035	ΔG, kJ mol^{-1}	–96.4	–70.7	–44.9	–19.2	6.5
	K_{eq}	1.5×10^{25}	5.8×10^{14}	6.6×10^{7}	7.21×10^{2}	0.14
	x	0.9999	0.9992	0.9576	0.4062	6.3×10^{-4}
0.05	ΔG, kJ mol^{-1}	–98.2	–72.9	–47.6	–22.3	2.97
	K_{eq}	4.5×10^{25}	1.74×10^{15}	1.9×10^{8}	2.1×10^{3}	0.41
	x	0.9999	0.9995	0.9750	0.6143	5.3×10^{-3}
0.065	ΔG, kJ mol^{-1}	–99.5	–74.6	–49.50	–24.60	0.3
	K_{eq}	9.9×10^{25}	3.78×10^{15}	4.39×10^{8}	4.63×10^{3}	0.91
	x	0.9999	0.9997	0.9833	0.7285	0.0239
0.08	ΔG, kJ mol^{-1}	–101.0	–76.7	–51.1	–26.4	–1.72
	K_{eq}	1.8×10^{26}	1.0×10^{16}	7.99×10^{8}	8.6×10^{3}	1.68
	x	0.9999	0.9998	0.9877	0.7964	0.0680
0.1	ΔG, kJ mol^{-1}	–102.0	–77.2	–52.7	–28.3	–3.93
	K_{eq}	3.6×10^{26}	1.4×10^{16}	1.5×10^{9}	1.7×10^{4}	3.26
	x	0.9999	0.9998	0.9911	0.8523	0.1660

Table 5. Gibbs energy (ΔG), equilibrium constants (K_{eq}) and degree of accumulation (x) of tris(hydroxymethyl)phosphine in reaction (1) at the pressure 0.1–0.02 MPa (calculation in 6-31G basis)

Pressure, MPa	Parameter	Temperature, K				
		200	250	300	350	400
0.02	ΔG, kJ mol^{-1}	–62.83	–36.29	–9.68	16.89	43.36
	K_{eq}	2.57×10^{16}	3.8×10^{7}	48.53	3.0×10^{-3}	2.2×10^{-6}
	x	0.9995	0.9268	3.5×10^{-2}	2.9×10^{-6}	9.5×10^{-7}
0.035	ΔG, kJ mol^{-1}	–65.63	–39.78	–13.87	12.00	37.77
	K_{eq}	1.4×10^{17}	2.0×10^{8}	2.6×10^{2}	0.016	1.2×10^{-5}
	x	0.9998	0.9680	0.2930	7.2×10^{-5}	9.5×10^{-7}
0.05	ΔG, kJ mol^{-1}	–67.40	–42.00	–16.54	8.89	34.21
	K_{eq}	4×10^{17}	5.97×10^{8}	7.6×10^{2}	0.047	3.4×10^{-5}
	x	0.9998	0.9812	0.5215	6.2×10^{-4}	9.5×10^{-7}
0.065	ΔG, kJ mol^{-1}	–68.71	–43.64	–18.50	6.59	31.59
	K_{eq}	1.1×10^{18}	1.3×10^{9}	1.67×10^{3}	0.104	7.5×10^{-5}
	x	0.9999	0.9873	0.6582	2.97×10^{-3}	2.86×10^{-6}
0.08	ΔG, kJ mol^{-1}	–69.75	–44.93	–20.05	4.79	29.52
	K_{eq}	1.65×10^{18}	2.45×10^{9}	3.1×10^{3}	0.193	1.4×10^{-4}
	x	0.9999	0.9907	0.7422	1.0×10^{-2}	6.7×10^{-6}
0.1	ΔG, kJ mol^{-1}	–70.88	–46.32	–21.71	2.85	27.28
	K_{eq}	3.3×10^{18}	4.8×10^{9}	6.0×10^{3}	0.37	2.7×10^{-4}
	x	0.9999	0.9933	0.8108	3.4×10^{-2}	2.8×10^{-5}

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