Kinetics of Phosphine Hydroxymethylation with Formaldehyde

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Abstract—The kinetics of phosphine hydroxymethylation with formaldehyde is studied. In the absence of a catalyst, phosphine reacts slowly with formaldehyde under normal conditions. Taken separately, amines, hydrochloric acid, and nickel chloride have a low catalytic activity, but the addition of a primary aliphatic amine to nickel chloride effectively increases the hydroxymethylation rate. A probable reaction mechanism is suggested.

The reaction between PH_3 and CH_2O in the presence of transition metal salts (primarily Pt, Pd, and Ni chlorides) affords tris(hydroxymethyl)phosphine (THMP)

$$PH_3 + 3CH_2O \longrightarrow P(CH_2OH)_3, \qquad (I)$$
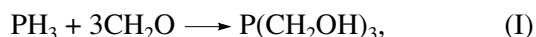
which is a valuable intermediate for the synthesis of polymers, with increased fire resistance [1–4].

There are only a few systematic studies on this reaction. The main difficulty in carrying out this reaction is the low catalytic activity of the known catalysts and, as a consequence, an insufficiently high yield of the desired product [2, 4].

In the present work, we studied the kinetics of phosphine hydroxymethylation with aqueous formaldehyde in the presence of nickel chloride activated with primary aliphatic amines.

EXPERIMENTAL

The kinetics of reaction (I) was studied by a volumetric method under unsteady-state conditions in a closed system. The system consisted of a vigorously shaken isothermal catalytic reactor and a precalibrated gas burette filled with a necessary concentration of phosphine. Concentrated PH_3 and PH_3–Ar gas mixtures were used. Phosphine was prepared by the sulfuric acid decomposition of Zn_3P_2 and was analyzed on an LKhM-8 MD chromatograph equipped with a thermal conductivity detector and a steel column (length 2 m, diameter 3 mm, Porapak Q packing) at 373 K in a helium flow (12 ml/min). The chromatograph was calibrated against iodometric phosphine concentration data.

Kinetic studies were performed as follows. Phosphine from the gas burette was passed through a 150-ml reactor filled with an aqueous solution of formaldehyde, the system was sealed, the phosphine content of the gas mixture was determined, and the catalyst and

activator were added. The volume of absorbed PH_3 was continuously determined while shaking the reactor.

In order to change the reaction from diffusion (mass-transfer) to kinetic control, the number of rockings of the catalytic shaker was set to be 170 per minute. This critical value for the overall rate of the process to be determined by chemical reaction (kinetic control) was determined experimentally. The deviation of the reaction rate thus measured from the average value is at most 5%, in agreement with published data [4].

A filter paper impregnated with a 1% solution of $AgNO_3$ was used as a phosphine leakage indicator in sealing tests [4]. The PH_3 concentration in the liquid phase was determined by standard procedures [5–8].

After the water and unreacted CH_2O were distilled off under reduced pressure, the reaction products were characterized by elemental analysis [9]; refractive index (n_d^{20}) measurements; IR spectroscopy; and ^{31}P, ^{13}C, and ^1H NMR [10–14]. NMR spectra were recorded on a Bruker WP-80 spectrometer operating at 31.44 MHz (^{31}P) or 20.55 MHz (^{13}C). The solvent was D_2O. The ^{31}P NMR spectra, referenced to an external standard (85% H_3PO_4), contained signals with chemical shifts of 24.6 ppm characteristic of THMP. The ^{13}C NMR spectra exhibited signals with chemical shifts of 57.6 and 54.0 ppm from the carbon atoms of the methylene groups of organophosphorus compounds. The ^1H NMR spectra contained two signals at 4.8 and 4.2 ppm, indicating the presence of methylene and hydroxyl hydrogen atoms. IR spectra were recorded on a Specord IP-75 spectrophotometer. Intense absorption bands characteristic of the O–H (3190 cm^{-1}), C–O (1004 cm^{-1}), and C–H (2795 cm^{-1}) bonds were observed. The absorption bands of the P–H and C=O bonds were absent.

The molar-ratio spectrophotometric method (SF-46 instrument) was used to elucidate the character of interaction between the components of the system [15].

RESULTS AND DISCUSSION

The addition of PH_3 to CH_2O (reaction (I)), which produces THMP, is unusual. Classical theoretical chemistry predicts the existence of two reaction mechanisms, namely, nucleophilic and electrophilic. The reaction with phosphine cannot be assigned exactly to this or another type. This can be explained by the chemical properties of PH_3 itself [10, 16], which is called a "problematic" nucleophilic reagent, such as P–H acids. At the same time, phosphine cannot be viewed as an electrophilic reagent. This is the reason why it is difficult to find a catalyst for the reaction examined.

In the absence of a catalyst, reaction (I) occurs only under severe conditions, such as an elevated PH_3 pressure (40 atm) and a high temperature (373 K) [1, 2]. If the system does not contain any catalyst or contains an organic base (N,N,N^1,N^1-tetramethylethylenediamine), formaldehyde absorbs phosphine at 293 K very slowly. Raising the acidity of the CH_2O–PH_3–H_2O system by adding HCl up to a concentration of 0.44 mol/l accelerates the reaction. However, phosphonium salts rather than THMP are the final products in reactions catalyzed by protonic acids [2].

The rate of phosphine absorption by aqueous CH_2O is a decreasing function of reaction time (Fig. 1), and the reaction rate is described by the first-order equation

$$w = k_{app}V, \qquad (1)$$

where V is the current volume of PH_3 and k_{app} is the apparent rate constant. The k_{app} values determined graphically from the linear anamorphoses $\ln V - t$ (t is the reaction time) are given in Table 1.

When 0.022 mol/l of unsubstituted ethylenediamine (En) is introduced into the CH_2O–PH_3–H_2O system, the reaction rate increases noticeably (Fig. 1, curve 3), although the En concentration is one order of magni-
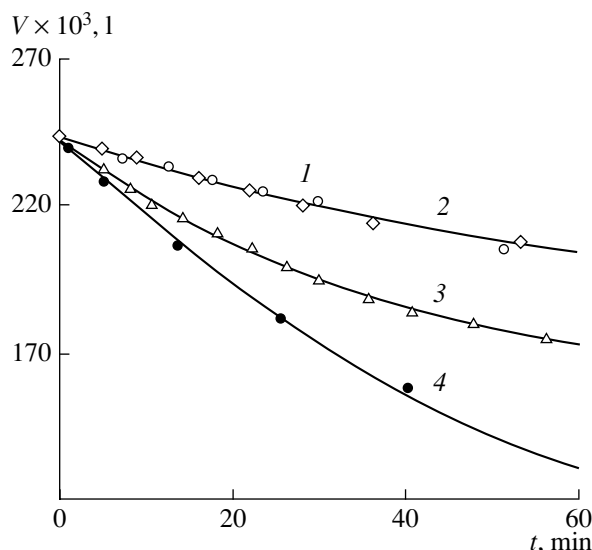

Fig. 1. Kinetics of phosphine hydroxymethylation with formaldehyde (1) in the absence of a catalyst and in the presence of (2) 0.22 mol/l N,N,N^1,N^1-tetramethylethylenediamine, (3) 0.022 mol/l ethylenediamine, and (4) 0.44 mol/l HCl. Reaction conditions: 293 K, P_{PH_3} = 0.92×10^5 Pa, $[CH_2O] = 2.71$ mol/l.

tude lower than the concentration of N,N,N^1,N^1-tetramethylethylenediamine (see Table 1). It turned out, unexpectedly, that the introduction of En into the CH_2O–PH_3–$NiCl_2$–H_2O system containing nickel chloride markedly increased the reaction rate (w_{max}) and the amount of absorbed phosphine (x) (Table 1) [17]. Since ethylenediamine was found to activate the $NiCl_2$ catalyst, the main attention in our further investigation was given to its influence on the mechanism of the reaction.

In a series of experiments on the effect of different amines on the catalytic activity of nickel chloride, we found that the V–t curves are linear and the reaction rate is low and is described by Eq. (1) in the presence of

Table 1. Hydroxymethylation of phosphine with formaldehyde in the presence of different catalytic systems at 293 K

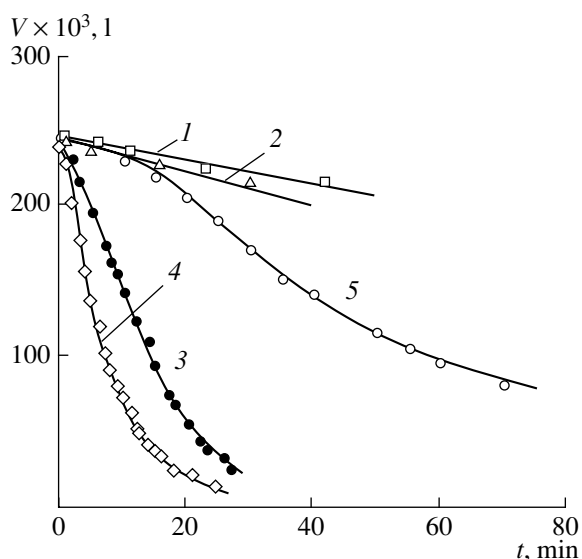| Reaction system	Concentration, mol/l			t, min	$w_{max} \times 10^3$, mol l^{-1} min^{-1}	$k_{app} \times 10^3$, min^{-1}	PH_3 conversion, %
	HCl	En	$NiCl_2$				
PH_3–CH_2O	–	–	–	60	5.5	3.2	16
PH_3–CH_2O–HCl	0.44	–	–	90	18	10.5	58
PH_3–CH_2O–TEn*	–	22×10^{-2}	–	72	7	3.2	21
PH_3–CH_2O–En	–	2.2×10^{-2}		54	18	–	28
PH_3–CH_2O–$NiCl_2$	–	–	2.56×10^{-3}	60	15	–	60
				90			75
PH_3–CH_2O–$NiCl_2$–En	–	1.1×10^{-2}	2.56×10^{-3}	10	110	–	70
				31			96

* TEn = N,N,N^1,N^1-tetramethylethylenediamine.

Fig. 2. Kinetics of phosphine hydroxymethylation with formaldehyde in the presence of (*1*) 1×10^{-2} mol/l $(C_2H_5)_3N$, (*2*) 0.96×10^{-2} mol/l $(C_2H_5)_2NH$, (*3*) 1.06×10^{-2} mol/l $(C_2H_5)NH_2$, and (*4*) 1.09×10^{-2} mol/l $C_2H_4(NH_2)_2$ and (*5*) in the absence of an amine. Reaction conditions: 293 K; P_{PH_3} = 0.92×10^5 (*1, 2*), 0.91×10^5 (*3*) 0.89×10^5 Pa (*4, 5*); $[CH_2O]$ = 2.71 mol/l, $[NiCl_2]$ = 0.256×10^{-2} mol/l.

diethylamine or triethylamine (Fig. 2, curves *1, 2*). The corresponding reaction rate constants (k_{app}) in the presence of a secondary or tertiary amine found from the $\ln V$–t linear anamorphoses are presented in Table 2.

In the absence of an amine or in the presence of a primary aliphatic amine, the V–t curves are S-shaped (Fig. 2, curves *3–5*) and indicate an induction period after which the reaction rate increases significantly. A possible explanation for this shape of the curves can be the autocatalytic acceleration of the reaction [18].

Indeed, when the desired product (THMP) (0.9×10^{-2} mol/l) was introduced into the original CH_2O–PH_3–$NiCl_2$–En–H_2O reaction system, the initial rate increased and the induction period decreased.

Being convinced that the reaction is autocatalytic, we used known procedures [18, 19] proposed for reactions of this type to determine kinetic constants. The plots of the rate of phosphine absorption by an aqueous solution of CH_2O versus conversion at different amounts of absorbed (reacted) phosphine were constructed (Fig. 3a). Let us assume that the hydroxymethylation reaction proceeds as follows. At the initial moment, when the concentration of the product (THMP) is close to zero, the reaction in the presence of nickel chloride proceeds at a low rate comparable with the reaction rate without a catalyst. The presence of an extremum in the plots in Fig. 3a indicates that the appearance of THMP in the system accelerates the reaction. Tertiary phosphines are known to play the key role in homogeneous catalytic processes using transition metals, determining the activity and selectivity of the catalytic system [20, 21]. Therefore, it is quite probable that a catalytically active tris(hydroxymethyl)phosphine complex of nickel chloride or a [THMP–Ni^{2+}–amine] complex is formed during the induction period in the ascending branch of the w–x plots. The reaction rate reaches its highest value and then decreases because of a decrease in the amount of starting reactants.

The experimental data obtained indicate that the rate of reaction (I) is described by an autocatalysis equation (taking into account the noncatalytic reaction rate) [18]:

$$w = k_{app,noncat}[CH_2O^*] + k_{app,cat}[CH_2O^*][THMP^*], \quad (2)$$

where $[CH_2O^*]$ and $[THMP^*]$ are the current concentrations of formaldehyde and tris(hydroxymethyl)phosphine, and $k_{app,noncat}$ and $k_{app,cat}$ are the apparent rate constants of the noncatalytic (min^{-1}) and cat-

Table 2. Hydroxymethylation of phosphine with formaldehyde ($[CH_2O]$ = 2.71 mol/l) in the presence of different amines and 0.256×10^{-2} mol/l $NiCl_2$

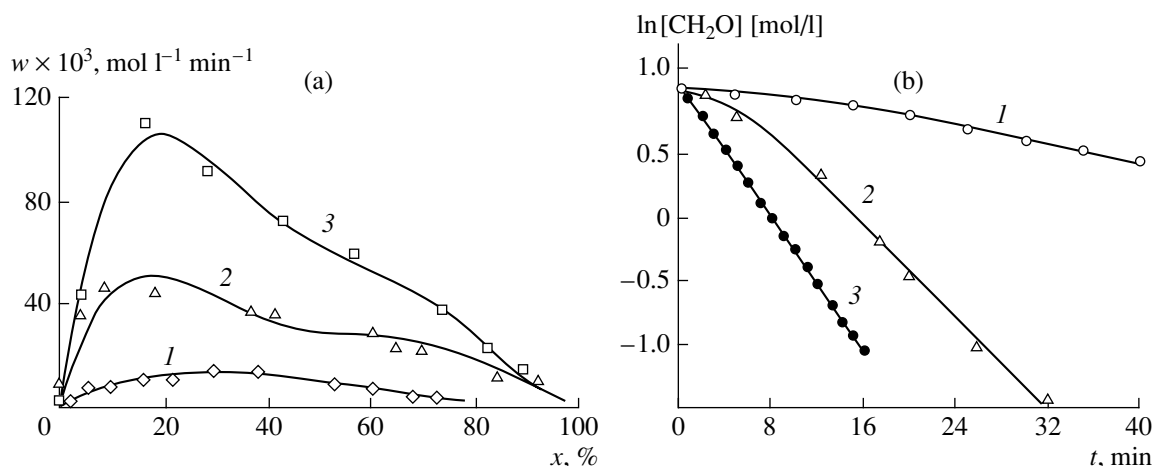| Activator	Activator concentration $\times 10^2$, mol/l	$w_{max} \times 10^3$, mol l^{-1} min^{-1}	$k_{app,cat} \times 10^3$, l mol^{-1} min^{-1}	$k_{app} \times 10^3$, l mol^{-1} min^{-1}	x, %
No catalyst and activator	0	5.5	–	3.7	6.5
No activator	0	15	1.1	–	75
NH_3	1.44	37	5.2	–	75
CH_3NH_2	1.12	48	7.7	–	91
$C_2H_5NH_2$	1.06	51	8.5	–	93
En	1.09	110	13.6	–	96
$(C_2H_5)_2NH$	0.96	7	–	5.3	8.1
$(CH_3)_3N$	1.08	2.4	–	2.5	3.3
$(C_2H_5)_3N$	1.07	3	–	3.3	4.1

Fig. 3. (a) Hydroxymethylation rate versus conversion (*1*) in the absence of amine and in the presence of (*2*) 1.06×10^{-2} mol/l $C_2H_5NH_2$ and (*3*) 1.09×10^{-2} mol/l $NH_2C_2H_4NH_2$. Reaction conditions: 293 K; P_{PH_3} = (*1, 3*) 0.89×10^5 and (*2*) 0.91×10^5 Pa; $[CH_2O]$ = 2.71 mol/l, $[NiCl_2]$ = 0.256×10^{-2} mol/l. (b) Semilogarithmic anamorphoses of the curves in Fig. 3a.

alytic ($l\ mol^{-1}\ min^{-1}$) reactions. The solution of Eq. (2) gives the logarithmic expression [18]

$$\ln[CH_2O^*]$$
$$= \ln \frac{[CH_2O]([CH_2O] + 3k_{app,\,noncat}/k_{app,\,cat})}{3k_{app,\,noncat}/k_{app,\,cat}} \quad (3)$$
$$- 1/3\,k_{app,\,cat}([CH_2O] + 3k_{app,\,noncat}/k_{app,\,cat})t,$$

where $[CH_2O^*]$ and $[CH_2O]$ are the current and initial concentrations of formaldehyde, respectively.

The plot of $\ln[CH_2O^*]$ versus t was used to calculate the apparent rate constants given in Table 2. These plots look like curves turning into straight lines with a negative slope equal to $1/3k_{app,cat}([CH_2O] + 3k_{app,noncat}/k_{app,cat})$ (Fig. 3b) [18].

According to the results presented in Table 2, the nickel catalyst is most efficiently activated by ethylene-diamine, primary amines, and ammonia. Secondary amines weakly affect the nickel catalyst, and tertiary amines suppress the catalytic effect of $NiCl_2$. The phosphine conversion, apparent rate constants, reaction time, and the optimum reactants : catalyst : activator ratios were derived from the plots of the reaction rate versus concentrations of CH_2O, $NiCl_2$, and En (Tables 3–5) [22, 23].

The plots of the reaction rate versus conversion pass through maxima at any PH_3 pressure in the range $(0.33–0.89) \times 10^5$ Pa (Fig. 4). A significant increase in k_{app} and w_{max} (Fig. 5, Table 6) is observed at the PH_3 concentration above 50 vol % in the gas mixture (at pressure above 0.5×10^5 Pa). At a low phosphine concentration, phosphine absorption almost ceases, and the amount of absorbed PH_3 at low conversions does not correspond to the stoichiometry of reaction (I). The substantial effect of the phosphine pressure on the rate of reaction (I) is probably due to the familiar thermodynamic dependence of the equilibrium (complexation) constant on the pressure [24].

The influence of the addition of the desired product on the rate of reaction (I) is illustrated in Table 7. The addition of THMP substantially increases the initial reaction rate, and this fact was taken into account in the optimization of process parameters for the synthesis of tris(hydroxymethyl)phosphine.

Table 3. Effect of the formaldehyde concentration on the rate of the reaction of PH_3 with CH_2O at 293 K, $[NiCl_2] = 0.128 \times 10^{-2}$ mol/l, and $[En] = 1.09 \times 10^{-2}$ mol/l

$[CH_2O]$, mol/l	$P_{PH_3} \times 10^{-5}$, Pa	x, %	$w \times 10^3$, mol l^{-1} min^{-1}		$k_{app} \times 10^3$, $l\ mol^{-1}\ min^{-1}$
			initial	maximum	
0.678	0.82	97	18	44	115
1.356	0.80	94	24	73	77
2.71	0.89	95	37	92	11
5.42	0.80	85	29	110	1
8.14	0.82	49	29	73	0.1

Table 4. Effect of the $NiCl_2$ concentration on the rate of the reaction of PH_3 with CH_2O at 293 K, $[CH_2O] = 2.71$ mol/l, and $[En] = 1.09 \times 10^{-2}$ mol/l

$[NiCl_2] \times 10^2$, mol/l	$P_{PH_3} \times 10^{-5}$, Pa	x, %	$w \times 10^3$, mol l^{-1} min^{-1}		$k_{app} \times 10^3$, l mol^{-1} min^{-1}
			initial	maximum	
–	0.89	20	5	–	–
0.032	0.87	79	18	55	4.2
0.064	0.87	89	24	73	6.0
0.128	0.89	95	37	92	11
0.256	0.89	96	44	110	13.6

Table 5. Effect of the En concentration on the reaction rate at 293 K, $[CH_2O] = 2.71$ mol/l, and $[NiCl_2] = 0.256 \times 10^{-2}$ mol/l, and $P_{PH_3} = 0.89 \times 10^5$ Pa

$[En] \times 10^2$, mol/l	x, %	$w \times 10^3$, mol l^{-1} min^{-1}		$k_{app} \times 10^3$, l mol^{-1} min^{-1}
		initial	maximum	
–	75	4	15	1.1
0.272	81	18	37	3.1
0.545	82	44	73	4.1
1.09	96	44	110	13.6
2.18	94	37	92	10.6

The data listed in Table 8 show that the amount of PH_3 absorbed between 293 and 328 K is close to 100%, being only 77% at 338 K. The apparent rate constants increase between 293 and 318 K and then decrease. The decrease in the reaction rate is most likely due to the strong temperature dependence of the configuration of the nickel complexes: the complex with a larger coordination number prevails at a lower temperature, while the complex with a smaller coordination number predominates at a higher temperature [24]. It is most likely that, at elevated temperatures, En is displaced from the inner coordination sphere of the catalytic complex, and the rate of reaction (I) decreases.
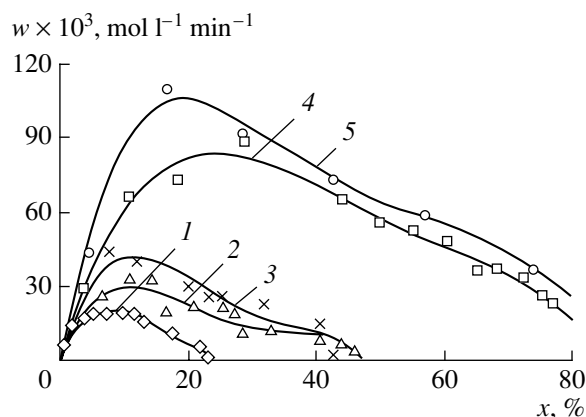
Fig. 4. Hydroxymethylation rate versus conversion at $P_{PH_3} = $ (*1*) 0.33×10^5, (*2*) 0.50×10^5, (*3*) 0.67×10^5, (*4*) 0.87×10^5, and (*5*) 0.89×10^5 Pa. Reaction conditions: 293 K; $[NiCl_2] = 0.256 \times 10^{-2}$ mol/l, $[En] = 1.09 \times 10^{-2}$ mol/l, $[CH_2O] = 2.71$ mol/l.
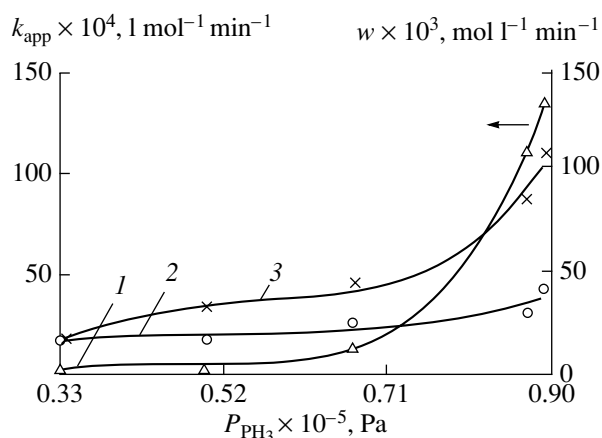
Fig. 5. (*1*) Rate constant k_{app}, (*2*) initial hydroxymethylation rate constant, and (*3*) maximum hydroxymethylation rate constant versus phosphine pressure.

Table 6. Effect of the phosphine pressure on the rate of the reaction between phosphine and CH_2O at 293 K, $[CH_2O] = 2.71$ mol/l, $[NiCl_2] = 0.256 \times 10^{-2}$ mol/l, and $[En] = 1.09 \times 10^{-2}$ mol/l

$P_{PH_3} \times 10^{-5}$, Pa	x, %	$w \times 10^3$, mol l^{-1} min^{-1}		$k_{app} \times 10^3$, l mol^{-1} min^{-1}
		initial	maximum	
0.33	24	18	18	0.4
0.50	41	18	33	0.5
0.67	44	26	44	1.4
0.87	93	29	88	11.2
0.89	96	44	110	13.6

Table 7. Effect of the THMP concentration on the reaction rate at 293 K, $[CH_2O] = 2.71$ mol/l, $[NiCl_2] = 0.256 \times 10^{-2}$ mol/l, $[En] = 1.09 \times 10^{-3}$ mol/l, and $P_{PH_3} = (0.89-0.92) \times 10^5$ Pa

$[THMP] \times 10^2$, mol/l	x, %	$w \times 10^3$, mol l^{-1} min^{-1}		$k_{app} \times 10^3$, l mol^{-1} min^{-1}
		initial	maximum	
–	96	44	110	13.6
0.18	99	73	103	15.6
0.90	99	81	84	15.8

Table 8. The effect of temperature on the rate of the reaction of PH_3 with CH_2O at $[CH_2O] = 2.71$ mol/l, $[NiCl_2] = 0.256 \times 10^{-2}$ mol/l, and $[En] = 1.09 \times 10^{-2}$ mol/l

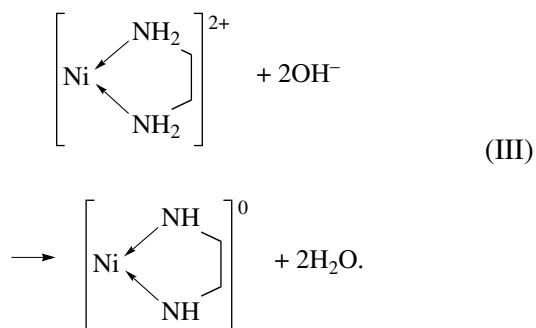| Temperature, K	$[PH_3] \times 10^2$, mol/l	x, %	$w \times 10^3$, mol l^{-1} min^{-1}		$k_{app} \times 10^2$, l mol^{-1} min^{-1}
			initial	maximum	
293	3.55	96.0	44	110	1.4
308	3.47	98.7	52	94	6.8
318	3.35	99.1	57	117	13.5
328	3.24	98.7	58	97	10.0
338	3.14	77.2	53	91	1.3

It is difficult to explain the high catalytic activity of the nickel complexes in the presence of primary amines in terms of the known models. Therefore, to explain the synergistic effect of the simultaneous presence of $NiCl_2$ and En, we carried out a chemical simulation of the process using published and our spectral data for the reactions in the $PH_3–CH_2O–RNH_2–NiCl_2–HOH$ system. Under the conditions examined, amines do not react with phosphines. They react only at a high pressure and 523–623 K [25]). Alkaline catalysts are assumed to activate PH_3 by deprotonation, and strong bases and anhydrous solvents are used for this purpose. Phosphine is a weaker acid than water and, hence, cannot form the PH_2^- anion in an aqueous medium [1, 9, 26–28]. Probably, PH_3 cannot be activated through the formation of a complex with nickel chloride, because we found that phosphine reduces $NiCl_2$ to metal in several cases. Nickel chloride forms stable complexes with amines. The stability constants of the Ni^{2+} complexes

with En in the presence of CH_2O ($b = 1.66 \times 10^5$, $\varepsilon = 2 \, l \, mol^{-1} \, cm^{-1}$), which were found by using a method suggested by Bjerrum [29], are close to the values presented in his monograph. Therefore, CH_2O reacts with the Ni^{2+} ethylenediamine complex:

$$\left[Ni \underset{NH_2}{\overset{NH_2}{\diagup\kern-1em\diagdown}} \right]^{2+} + 2CH_2O$$

(II)

$$\longrightarrow \left[Ni \underset{H_2C=N}{\overset{H_2C=N}{\diagup\kern-1em\diagdown}} \right]^{2+} + 2H_2O.$$
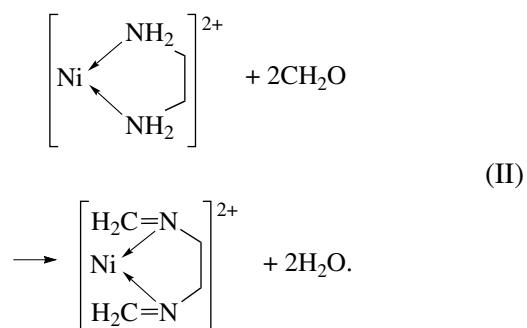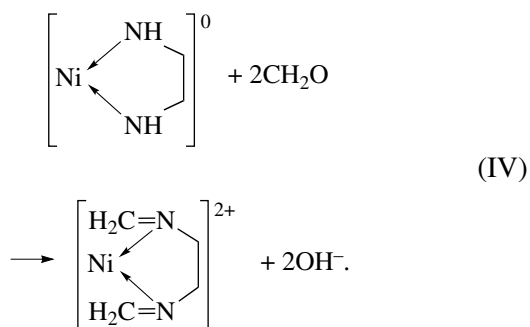
The inner-sphere condensation of the coordinated diamine with CH_2O results in Ni^{2+} ethylenediamine
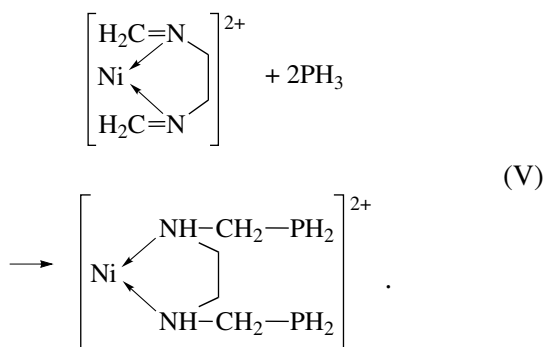
complexes. Similar products were found for the reactions of the Ni^{2+}, Cu^{2+}, Ru^{3+}, Os^{3+}, and Pt^{4+} diamine complexes with acetone, β-diketone, and keto acids [25, 30]. Numerous experimental data [25, 30] indicate that Schiff bases, which are unstable in the free state, are stabilized in these complexes. Condensation reactions (II), which proceed rather readily, are accelerated by bases [30], which stimulate the acidic dissociation of ethylenediamine:
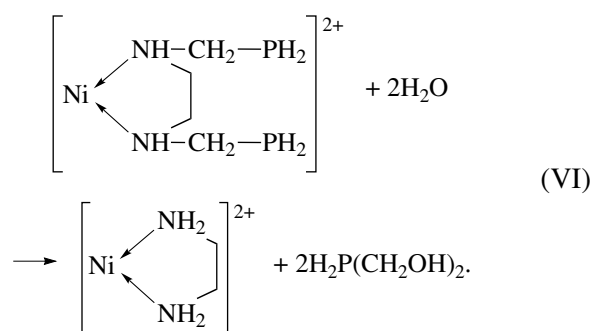
$$\left[Ni \left\langle \begin{array}{c} NH_2 \\ NH_2 \end{array} \right] ^{2+} + 2OH^- \quad (III)$$

$$\longrightarrow \left[Ni \left\langle \begin{array}{c} NH \\ NH \end{array} \right] ^{0} + 2H_2O.$$

The Ni^0 diamide reacts with formaldehyde to form ethylenediimine complexes of Ni^{2+}:

$$\left[Ni \left\langle \begin{array}{c} NH \\ NH \end{array} \right] ^{0} + 2CH_2O \quad (IV)$$

$$\longrightarrow \left[Ni \left\langle \begin{array}{c} H_2C=N \\ H_2C=N \end{array} \right] ^{2+} + 2OH^-.$$

We found that nickel was not virtually reduced by phosphine in the presence of amines and formaldehyde and, therefore, PH_3 reacts with the Ni^{2+} ethylenediimine complex via an inner-sphere mechanism:

$$\left[Ni \left\langle \begin{array}{c} H_2C=N \\ H_2C=N \end{array} \right] ^{2+} + 2PH_3 \quad (V)$$

$$\longrightarrow \left[Ni \left\langle \begin{array}{c} NH-CH_2-PH_2 \\ NH-CH_2-PH_2 \end{array} \right] ^{2+}.$$
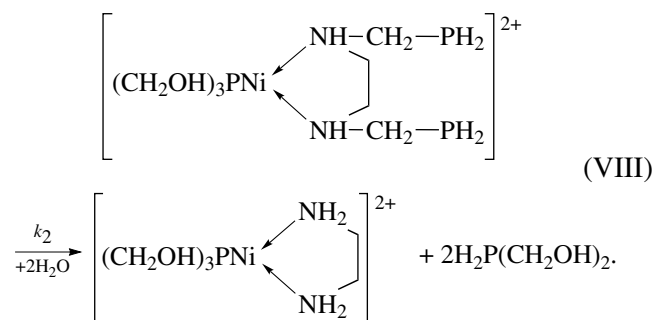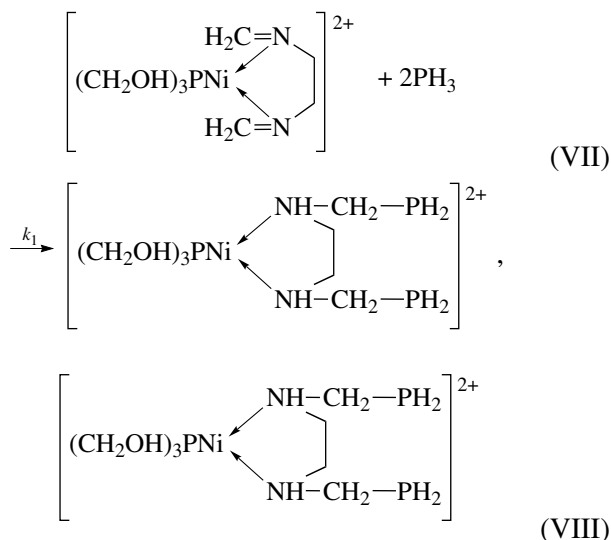
Since ethylenediaminophosphine, which is formed in reaction (V), is not detected in the reaction system, we can assume that it is hydrolyzed to evolve the starting Ni^{2+} ethylenediamine complex and the reaction product (hydroxymethylphosphine):

$$\left[Ni \left\langle \begin{array}{c} NH-CH_2-PH_2 \\ NH-CH_2-PH_2 \end{array} \right] ^{2+} + 2H_2O \quad (VI)$$

$$\longrightarrow \left[Ni \left\langle \begin{array}{c} NH_2 \\ NH_2 \end{array} \right] ^{2+} + 2H_2P(CH_2OH)_2.$$

In the reaction sequence (II)–(VI), the hydrogen atom of phosphine is first replaced by a hydroxymethyl group; the other atoms are replaced more rapidly, because $H_2P(CH_2OH)$ and $HP(CH_2OH)_2$ are more reactive than PH_3 [12]. As a result, THMP appears in the reaction system. Tetrahydroxymethylphosphine will not catalyze PH_3 hydroxymethylation if a complex between nickel chloride and a primary amine is not formed. However, in the presence of phosphine, the stability of the nickel chloride complexes with En increases ($b = 2.34 \times 10^5$, $\varepsilon = 10^4\,l\,mol^{-1}\,cm^{-1}$) and a fast reaction pathway appears.

An analysis of the mechanism by the steady-state concentration method [7, 18] led us to assume that tris(hydroxymethyl)phosphine can participate in the following reaction steps:

$$\left[(CH_2OH)_3PNi \left\langle \begin{array}{c} H_2C=N \\ H_2C=N \end{array} \right] ^{2+} + 2PH_3 \quad (VII)$$

$$\xrightarrow{k_1} \left[(CH_2OH)_3PNi \left\langle \begin{array}{c} NH-CH_2-PH_2 \\ NH-CH_2-PH_2 \end{array} \right] ^{2+},$$

$$\left[(CH_2OH)_3PNi \left\langle \begin{array}{c} NH-CH_2-PH_2 \\ NH-CH_2-PH_2 \end{array} \right] ^{2+} \quad (VIII)$$

$$\xrightarrow[+2H_2O]{k_2} \left[(CH_2OH)_3PNi \left\langle \begin{array}{c} NH_2 \\ NH_2 \end{array} \right] ^{2+} + 2H_2P(CH_2OH)_2.$$

The kinetic equation describing the rate of PH_3 hydroxymethylation in the presence of the nickel complexes with primary amines was found to be

$$w = k_1 k_2 [CH_2O][PH_3][Ni^{2+}]_\Sigma \quad (4)$$
$$\times [amine][THMP]/(k_2 + k_1[CH_2O][PH_3][amine]).$$

Table 9. Rate constants and the thermodynamic and activation parameters of phosphine hydroxymethylation with formaldehyde in the presence of $NiCl_2$ and En

Constant	Temperature, K					$\Delta E^{\#}$, kJ/mol	$\Delta H^{\#}$, kJ/mol	$\Delta S^{\#}$, J K^{-1} mol^{-1}	$\Delta G^{\#}$, kJ/mol
	298	308	318	328	338				
$k_1 \times 10^{-3}$, l^4 mol^{-4} s^{-1}	3.6	7.8	12.8	12.1	12.1	39.5	36.4	−50.9	52.6
k_2, l mol^{-1} s^{-1}	0.87	1.16	1.6	1.12	0.86	18.4	16.1	−192.1	77.2

To calculate the k_1 and k_2 constants and compare the calculated and observed data, the rate equation (4) was converted to

$$[CH_2O][PH_3][Ni^{2+}]_{\Sigma}[\text{amine}][THMP]/w$$
$$= 1/k_1 + [CH_2O][PH_3][\text{amine}]/k_2. \quad (5)$$

The experimental data fall close to a straight line in the coordinates of Eq. (5) (Fig. 6). The value of $1/k_2$ was found from the slope of this line, and $1/k_1$ was found from the ordinate intercept. At 293 K, $k_1 \times 10^{-2} = 7.33$, 14.83, 23.83, and 35.66 l^4 mol^{-4} s^{-1} for NH_3, CH_3NH_2, $C_2H_5NH_2$, and En, respectively, and $k_2 = 0.23$, 0.39, 0.64, and 0.87 l mol^{-1} s^{-1}, respectively.

Using similar anamorphoses at five different temperatures in the temperature range 298–338 K, we found the reaction rate constants in the presence of $NiCl_2$ activated by ethylenediamine and the activation energies of steps (VII) and (VIII). These values, together with the thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$, are presented in Table 9.

Thus, the mechanism of the action of the nickel chloride complexes with ethylenediamine in PH_3 hydroxymethylation with formaldehyde differs radically from the mechanism of the action of other known catalysts. The catalytic cycle consists of two key steps, namely, the interaction of phosphine with the formaldehyde–ethylenediamine complex of nickel chloride (rate-determining step) involving THMP and the hydrolysis of the resulting complex at the C–N bond yielding hydroxymethylphosphine and regenerating the catalyst.

The present study of the regularities of phosphine hydroxymethylation with formaldehyde made it possible to determine conditions for the high-selectivity synthesis of tris(hydroxymethyl)phosphine, which is a valuable intermediate product of organic synthesis [17, 31].

$\{[CH_2O][PH_3][Ni^{2+}][\text{Amine}][THMP]/w\} \times 10^7$, M^4 min

$[CH_2O][PH_3][\text{Amine}] \times 10^5$, M^3

Fig. 6. Linear anamorphoses of the rate equation (5) for phosphine hydroxymethylation in the presence of (*1*) 1.06×10^{-2} mol/l $C_2H_5NH_2$, (*2*) 1.12×10^{-2} mol/l CH_3NH_2, (*3*) 1.44×10^{-2} mol/l NH_3, and (*4*) 1.09×10^{-2} mol/l $NH_2C_2H_4NH_2$. Reaction conditions: 293 K; $P_{PH_3} = $ (*1*, *2*) 0.91×10^5, (*3*) 0.87×10^5, and (*4*) 0.89×10^5 Pa; $[CH_2O] = 2.71$ mol/l, $[NiCl_2] = 0.256 \times 10^{-2}$ mol/l.

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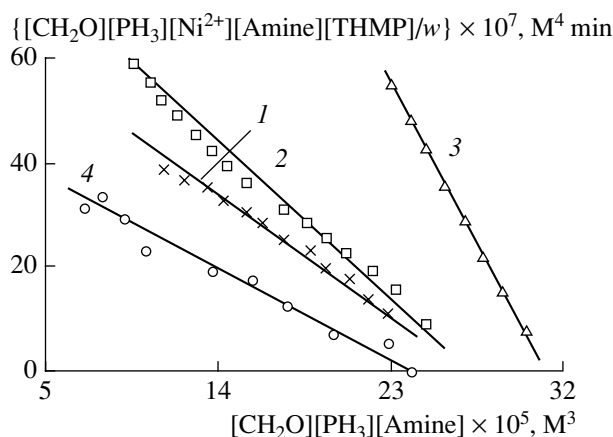13. Nakanisi, K., *Infrared Absorption Spectroscopy,* San Francisco: Holden-Day, 1962.

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