Kinetic Aspects of the Effect of CO Pressure and Methanol **Concentration on Cyclohexene Hydrocarbomethoxylation** in the Presence of the $Pd(PPh_3)_2Cl_2-PPh_3-p$ -Toluenesulfonic Acid **Catalytic System**

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Abstract—The dependence of the rate of the cyclohexene hydrocarbomethoxylation reaction catalyzed by the Pd(PPh₃)₂Cl₂-PPh₃-p-toluenesulfonic acid system on the CO pressure and methanol concentration at temperatures varied in the range of 358–388 K has been investigated. The data are interpreted in terms of the previously proposed mechanism involving as intermediates ion pairs containing cationic hydride, alkyl, and acyl palladium complexes. By the least squares technique, apparent constants relating to the effect of CO pressure and methanol concentration have been estimated for the rate equation derived earlier. The apparent activation energies have been determined for these constants, and the following stability series of palladium complexes has been proposed on their basis:

 $Pd(PPh_3)_2(CO)_2 > Pd(PPh_3)_4 > Pd(PPh_3)_2(CH_3OH)_2 > HS{}^{\oplus}ol[Pd(PPh_3)_2(Cl)(Sol)]^{\ominus}.$

Keywords: hydrocarbalkoxylation, cyclohexene, methylcyclohexanecarboxylate, palladium compounds, hydride complexes, rate equation, intermediates

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In [1-4], it was shown that studying the effect of temperature on the rate of the hydrocarbalkoxylation reaction opens the possibility of determining the activation parameters of apparent constants of rate equations and these data in conjunction with the results of direct kinetic experiments on the chemical behavior of certain suggested intermediates make it possible to compile a database of rate constants for the elementary steps of carbonylation reactions and their enthalpies and activation energies. The earlier studies of the effect of temperature on the dependence of the rate of the cyclohexene hydrocarbalkoxylation reaction with cyclohexanol upon the concentration of the reactants and catalyst components (Pd(PPh₃)₂Cl₂ and triphenylphosphine) enabled us to determine the apparent activation energy for some of the kinetic parameters and to estimate on their basis the enthalpies of the formation of the Pd complexes $Pd(PPh_3)_2(C_6H_{11}OH)_2$, $Pd(PPh_3)_2(CO)_2$, and $Pd(PPh_3)_4$ from $Pd(PPh_3)_2(C_6H_5CH_3)_2$ [4]. In continuation of these studies, we investigated the influence of temperature on the dependence of the rate of the cyclohexene hydrocarbomethoxylation reaction upon the concentrations of $Pd(PPh_3)_2Cl_2$ and free triphenylphosphine, determined the apparent activation energies of the relevant parameters of the rate equation, and estimated the enthalpies of the formation of the $[Pd(PPh_3)_4]$ and $HS^{\oplus}_{Ol}[Pd(PPh_3)_2(Cl)(Sol)]^{\ominus}$ complexes from $Pd(PPh_3)_2Cl_2$ [5]. In this paper, we present the results on the effect of temperature on the apparent rate constants for cyclohexene hydrocarbomethoxylation

$$+ CO + CH_3OH \xrightarrow{t, P, cat} \\ C''_OCH_3OH \xrightarrow{t,$$

in the presence of the $Pd(PPh_3)_2Cl_2-PPh_3-p$ -toluenesulfonic acid (TsOH) catalyst system that reflect the contribution of carbon monoxide and methanol to the rate of this reaction.

EXPERIMENTAL

The cyclohexene hydrocarbomethoxylation reaction was studied in the batch reactor described in [6]. All experiments were carried out in toluene. The reaction mass was analyzed by GLC using o-xylene as an internal standard; the analytical procedure is detailed in [5]. The details of the kinetic experiments are given in [7]. The accuracy of determining the reactant and product concentrations was $\pm 3\%$. Confidence intervals for the kinetic parameters determined are given in the text.

RESULTS AND DISCUSSION

To reveal the effect of temperature on the dependence of the cyclohexene hydrocarbomethoxylation rate upon the CO pressure, five sets of experiments in the temperature range of 368-388 K were performed with varying the CO pressure in each set from 0 to 6.1 MPa. Figure 1 presents the data obtained in these experiments as plots of the initial reaction rate versus p_{CO} for different temperatures. These curves are nonmonotonic in character for all of the temperatures.

Similar experiments were conducted on the effect of methanol concentration on the rate of hydrocarbomethoxylation at different temperatures (Fig. 2). The curves for the dependence of reaction rate r_0 upon [CH₃OH] are also nonmonotonic, having a maximum at 0.15 to 0.20 mol/L CH₃OH.

Based on the data of previous experiments on the effect of the reactants and the components of the catalytic system $(Pd(PPh_3)_2Cl_2-PPh_3-TsOH)$ on this reaction at a fixed temperature, we found that the reaction is first order in cyclohexene and TsOH, chloride anions inhibit the reaction, the reaction is insensitive to tosylate anions, and the methanol concentration and CO pressure dependences of the reaction rate are nonmonotonic [7]. These data were interpreted in terms of a mechanism that involves as catalytic cycle intermediates ion pairs of cationic hydride, alkyl, and acyl palladium complexes with tosylate anions (Scheme 1):

$$PdCl_2(PPh_3)_2 + CH_3OH \xrightarrow{k_0} Pd(PPh_3)_2 + CH_2O + 2HCl$$
(1)

$$\begin{array}{c} \operatorname{Pd}(\operatorname{PPh}_{3})_{2} + 2\operatorname{Sol} \quad \underbrace{\overset{k_{1}}{\overleftarrow{k_{-1}}}}_{(X_{0})} \quad \operatorname{Pd}(\operatorname{PPh}_{3})_{2} \left(\operatorname{Sol}\right)_{2} \quad (2) \end{array}$$

$$\begin{array}{c} \operatorname{Pd}(\operatorname{PPh}_{3})_{2} (\operatorname{Sol})_{2} + \operatorname{TsOH} \quad \underbrace{\frac{k_{2}}{k_{-2}}}_{(X_{2})} [\operatorname{HPd}^{\oplus}(\operatorname{Sol})(\operatorname{PPh}_{3})_{2}] \operatorname{TsO}^{\ominus} + \operatorname{Sol} \quad (3) \\ (X_{1}) \quad (X_{2}) \end{array}$$

$$\begin{bmatrix} HP\overset{\oplus}{d}(Sol)(PPh_{3})_{2}]T\overset{\odot}{sO} + \bigvee \overset{k_{3}}{\xrightarrow{k_{-3}}} [HP\overset{\oplus}{d}(PPh_{3})_{2}]Ts\overset{\ominus}{O} + Sol \\ (X_{2}) & (X_{3}) & (X_{3}) & (X_{4}) & (X_{5}) \\ (X_{2}) & (X_{5}) & (X_{3}) & (X_{4}) & (X_{5}) \\ (X_{2}) & (X_{3}) & (X_{4}) & (X_{4}) & (X_{5}) \\ (X_{3}) & (X_{4}) & (X_{5}) & (X_{4}) & (X_{5}) \\ (X_{4}) & (X_{5}) & (X_{5}) & (X_{5}) \\ (X_{5}) & (X_{5}) & (X_{5}) & (X_{5}) & (X_{5}) \\ (X_{5}) & (X_{5}) & (X_{5}) & (X_{5}) & (X_{5}) & (X_{5}) & (X_{5}) \\ (X_{5}) & (X_{5})$$

where Sol stands for solvent (toluene) molecules. Scheme 1.

The nonmonotonic character of the reaction rate dependence on the triphenylphosphine [5] and meth-

anol concentrations and the CO pressure can be interpreted in terms of the ligand exchange equilibriums:

$$\begin{array}{c} \operatorname{Pd}(\operatorname{PPh}_{3})_{2}(\operatorname{Sol})_{2} + 2\operatorname{PPh}_{3} & \xrightarrow{k_{8}} & \operatorname{Pd}(\operatorname{PPh}_{3})_{4} + 2\operatorname{Sol}, \\ (X_{1}) & (X_{7}) \end{array}$$
(9)

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Fig. 1. Effect of CO pressure on the initial rate of the cyclohexene hydrocarbomethoxylation reaction at temperatures of (1) 368, (2) 373, (3) 378, (4) 383, and (5) 388 K. Concentrations, mol/L: $[C_6H_{10}] = 0.1$, $[CH_3OH] = 0.45$, $[Pd(PPh_3)_2Cl_2] = 2.0 \times 10^{-3}, [PPh_3] = 8.0 \times 10^{-3},$ $[TsOH] = 2.4 \times 10^{-2}.$

 $Pd(PPh_3)_2(Sol)_2 + CH_3OH$



Fig. 2. Effect of methanol concentration on the initial rate of the cyclohexene hydrocarbomethoxylation reaction at $P_{\rm CO} = 2.1 \times 10^6$ Pa and temperatures of (1) 358, (2) 363, (3) 368, (4) 373, and (5) 378 K; concentrations, mol/L: $[C_6H_{10}] = 0.1, [Pd(PPh_3)_2Cl_2] = 2.0 \times 10^{-3}, [PPh_3] =$ 8.0×10^{-3} , [TsOH] = 2.4×10^{-2} .

$$\begin{array}{c} \operatorname{Pd}(\operatorname{PPh}_{3})_{2}(\operatorname{Sol})_{2} + \operatorname{CO} \xrightarrow{k_{9}} & \operatorname{Pd}(\operatorname{CO})(\operatorname{PPh}_{3})(\operatorname{Sol})_{2} + \operatorname{PPh}_{3}, \\ (X_{1}) & (X_{8}) \end{array}$$
(10)

$$= Pd(CH_3OH)(PPh_3)(Sol)_2 + PPh_3,$$
(11)
(X₀)

$$\begin{array}{c} Pd(PPh_{3})_{2}(Sol)_{2} + 2CH_{3}OH & \xrightarrow{k_{11}} & Pd(PPh_{3})_{2}(CH_{3}OH)_{2} + 2Sol, \\ (X_{1}) & (X_{10}) \end{array}$$
(12)

$$\frac{\text{Pd}(\text{PPh}_{3})_{2}(\text{Sol})_{2} + 2\text{CO}}{(X_{1})} = \frac{k_{12}}{k_{-12}} = \frac{\text{Pd}(\text{PPh}_{3})_{2}(\text{CO})_{2} + 2\text{Sol.}}{(X_{11})}$$
(13)

However, we believe that the observed decline in the specific catalytic activity of the precursor with an increase in its concentration is due to the formation of the inactive complex X from V by the

$$\frac{\text{HCl} + \text{Pd}(\text{PPh}_3)_2 \text{Sol}_2}{(X_1)} \xrightarrow{k_{13}} \frac{\text{HSol}}{k_{-13}} = \frac{\text{HSol}}{(X_{12})} \frac{\text{Pd}(\text{PPh}_3)_2(\text{Cl}) \text{Sol}}{(X_{12})} \xrightarrow{\ominus} (14)$$

The inactivity of X_{12} is caused by the anionic character of its Pd-containing moiety. On the other hand, the factor responsible for the formation of X_{12} type complexes is a higher ability of the chloride ion to coordinate to the central palladium atom compared with the acetate or tosylate anion [8-10].

In [9, 11] it was shown that the rate-determining step of the catalytic cycle is the nucleophilic attack of

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action of HCl produced from
$$Pd(PPh_3)_2Cl_2$$
 in reac-
tion (1) [5]:

the alcohol molecule at the acyl carbon atom in the
$$X_6$$
 complex. The arguments in favor of this point of view are presented in [9–13]. In this context, all the preceding reversible steps can be considered quasi-equilibrium. Then the reaction rate can be expressed by the equation:

$$r = k_7[X_6][CH_3OH].$$
 (15)

In the case of formation of the complex X_{12} , the amount of bound and free HCl can be comparable. Then the expression of K_{13} takes the following form:

$$K_{13} = \frac{[X_{12}]}{[X_1]([HCl]_0 - [X_{12}])},$$

where $[HCl]_0$ is the amount of hydrogen chloride released during the decomposition of $Pd(PPh_3)_2Cl_2$ via reaction (1).

Consequently,

$$[\mathbf{X}_{12}] = \frac{K_{13}[\mathbf{X}_1][\mathbf{HCl}]_0}{1 + K_{13}[\mathbf{X}_1]}.$$
 (16)

An analysis of Eq. (16) shows that the second term in its denominator can be neglected. Apparently, reaction (14) should be characterized by slight exothermicity and a decrease in entropy; thus, the value of K_{13} must be less than 1. At the same time, $[X_1]$ cannot be greater than the initial catalyst concentration, which was 1×10^{-3} to 1.5×10^{-2} mol/L. Owing to these conditions, the inequality $1 \ge K_{13}[X_1]$ holds and Eq. (16) takes the compact form $[X_{12}] = K_{13}[X_1][\text{HCI}]_0$. With allowance for the relation $[\text{HCI}]_0 = 2C_{\text{M}}$, the equation in this form appears as $[X_{12}] = 2K_{13}[X_1]C_{\text{M}}$.

The kinetic analysis of the data reported in [5] showed that the contribution of complexes X_8 and X_9 to the overall balance of catalytic forms is negligible. The application of the quasi-steady-state approximation to the given mechanism with allowance for this fact and the above speculations about the concentration of the intermediate X_{12} result in the following rate equation:

$$r = \frac{kC_{\rm M}[{\rm CO}][{\rm ol}][{\rm TsOH}][{\rm CH}_{3}{\rm OH}]}{1 + a[{\rm CH}_{3}{\rm OH}]^{2} + b[{\rm CO}]^{2} + e[{\rm PPh}_{3}]^{2} + fC_{\rm M}},$$
 (17)

where $C_{\rm M}$ is the total concentration of all forms of the catalyst, $C_{\rm M} = X_0 + X_1 + X_2 + X_3 + \dots + X_{12}$, which is equal to the initial concentration of Pd(PPh_3)₂Cl₂; [ol] is the concentration of cyclohexene; $a = \frac{K_1K_{11}}{1+K_1}$, $b = \frac{K_1K_{12}}{1+K_1}$, $e = \frac{K_1K_8}{1+K_1}$, $f = \frac{2K_1K_{13}}{1+K_1}$, $K = \frac{K_1K_2K_3K_4K_5K_6}{1+K_1}$, and $k = k_7K$.

The linearization of reaction rate equation (17) in the single-factor experiment for $Pd(PPh_3)_2Cl_2$ and PPh_3 in [5] led to the following expressions for the parameters of the linearized forms:

$$\frac{f}{k_{\text{app.1}}} = 10^{-6.70} \exp\left(\frac{70 \pm 3 \,\text{kJ/mol}}{RT}\right), \quad \frac{\text{L} \cdot \text{min.}}{\text{mol}}$$

and

$$\frac{e}{k_{\text{app.2}}} = 10^{-14.84} \exp\left(\frac{143 \pm 7 \text{ kJ/mol}}{RT}\right),$$
$$\frac{\text{L}^3 \cdot \text{min.}}{\text{mol}^3},$$

where
$$k_{app.1} = \frac{k}{H_{CO}} P_{CO} [ol] [TsOH] [CH_3OH], k_{app.2} = \frac{k}{H_{CO}} C_M P_{CO} [ol] [TsOH] [CH_3OH], and H_{CO} is$$

Henry's constant for CO solubility in toluene.

Rate equation (17) allows for quantitative substantiation of the observed dependences of the reaction rate on the CO pressure and the methanol concentration. Thus, in a single-factor experiment on P_{CO} this equation reduces to

$$r = \frac{k_{\rm app.3} \frac{P_{\rm CO}}{H_{\rm CO}}}{A_3 + b \frac{P_{\rm CO}^2}{H_{\rm CO}^2}},$$
(18)

where $A_3 = 1 + a[CH_3OH]^2 + e[PPh_3]^2 + fC_M$, $k_{app.3} = kC_M[ol][TsOH][CH_3OH]$, and H_{CO} is Henry's constant for CO.

Further transformation of Eq. (18) leads to the following expression:

$$\frac{P_{\rm CO}}{r} = \frac{A_3 H_{\rm CO}}{k_{\rm app,3}} + \frac{b}{k_{\rm app,3} H_{\rm CO}} P_{\rm CO}^2.$$
 (19)

Representation of these relationships between r_0 and P_{CO} (Fig. 1) in the coordinates of Eq. (19) leads to linear relations (Fig. 3). Their least squares treatment led to the values for the parameters of the equation as shown in the table.

In turn, the temperature dependence of the term A_3H_{CO} is characterized by spread of data, indicating a

 $k_{app.3}$ large uncertainty of determination of this parameter

by extrapolation. At the same time, the data on

 $\frac{b}{k_{\text{app.}3}\text{H}_{\text{CO}}}$ are satisfactorily described by the Arrhenius equation:

$$= 10^{-14.8} \exp\left(\frac{\frac{b}{k_{app.3}H_{CO}}}{RT}\right), \quad \frac{L \cdot \min}{Pa \cdot mol}.$$

In a single-factor experiment on the effect of methanol concentration on the reaction rate, rate equation (17) reduces to:

$$r = \frac{k_{\text{app.4}} [\text{CH}_3\text{OH}]}{\text{A}_4 + a [\text{CH}_3\text{OH}]^2},$$
(20)

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where $A_4 = 1 + b \frac{P_{CO}^2}{H_{CO}^2} + e [PPh_3]^2 + fC_M$, and $k_{app.4} = kC_M \frac{P_{CO}}{H_{CO}} [ol] [TsOH].$

Further transformation of Eq. (20) leads to the following expression:

$$\frac{[CH_{3}OH]}{r} = \frac{A_{4}}{k_{app.4}} + \frac{a}{k_{app.4}} [CH_{3}OH]^{2}.$$
 (21)

The least squares processing of the data for Eq. (21) has shown that the parameter $\frac{A_4}{k_{3\phi,4}}$ is statistically insignificant. Then this equation appears as

$$\frac{[\mathrm{CH}_{3}\mathrm{OH}]}{r} = \frac{a}{k_{\mathrm{app},4}} [\mathrm{CH}_{3}\mathrm{OH}]^{2}.$$
 (22)

The plots of $\frac{[CH_3OH]}{r_0}$ versus $[CH_3OH]^2$ in Fig. 4

 r_0 show good agreement between the calculated (solid line) and experimental (symbols) data. The statistical insignificance of the parameter $\frac{A_4}{k_{app,4}}$ is supported by the fact that these curves pass through the origin. The $\frac{a}{k_{app,4}}$ data are satisfactorily described by the Arrhenius law:

$$\frac{a}{k_{\text{app.4}}} = 10^{-6.88} \exp\left(\frac{75 \pm 1 \,\text{kJ/mol}}{RT}\right),$$

$$\frac{\underline{L^2 \cdot \min.}}{\text{mol}^2}.$$
(23)

Note that we verified earlier the adequacy of this kinetic model for a temperature of 378 K [14].

Analysis of the apparent activation energies allows the ratios between enthalpies of ligand-exchange reactions (9), (12), and (13) responsible for the removal of

Т, К	358	363	368	373	378	383	388
$\frac{A_3H_{\rm CO}}{k_{\rm app.3}}10^{-10}, \frac{\rm Pa\ L\ min}{\rm mol}$	_	-	0.14 ± 0.03	0.10 ± 0.04	0.08 ± 0.02	0.13 ± 0.01	0.12 ± 0.01
$\frac{b}{k_{\text{app.}3}H_{\text{CO}}}10^4, \frac{\text{L min}}{\text{Pa mol}}$	_	-	9.1 ± 0.1	4.9 ± 0.2	2.9 ± 0.1	1.32 ± 0.07	0.80 ± 0.05
$\frac{a}{k_{\rm app.4}} 10^{-3}, \ \frac{L^2 \min}{\mathrm{mol}^2}$	10.0 ± 0.1	7.68 ± 0.06	5.42 ± 0.08	3.66 ± 0.05	2.74 ± 0.04	_	_

Apparent constants of Eqs. (19) and (22)



Fig. 3. Fitting of the experimental data to Eq. (19). Concentrations, mol/L: $[C_6H_{10}] = 0.1$, $[CH_3OH] = 0.45$, $[Pd(PPh_3)_2Cl_2] = 2.0 \times 10^{-3}$, $[PPh_3] = 8.0 \times 10^{-3}$, $[TsOH] = 2.4 \times 10^{-2}$. Temperatures, K (*I*) 368, (*2*) 373, (*3*) 378, (*4*) 383, and (*5*) 388.

the active forms of the catalyst from the catalytic cycle to be estimated. So, from Eqs. (16), (17), and (19), it follows that

$$\Delta H_{b/k_{app.3}} = \Delta H_{12} - \Delta H_{H} - E_7 - \Delta H_2 - \Delta H_3 - \Delta H_4 - \Delta H_5 - \Delta H_6$$
(24)

and
$$\frac{\Delta H_{a/k_{app,4}}}{-\Delta H_4 - \Delta H_5 - \Delta H_6}.$$
 (25)

As
$$\Delta H_H = -6$$
 kJ/mol [15], then

$$\Delta H_{12} - \Delta H_{11} = \Delta H_{b/k_{app.3}} - \Delta H_{a/k_{app.4}} + 2\Delta H_{\rm H}$$

= -146 - (-75) + 2 \cdot (-6) = -83 kJ , (26)

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Fig. 4. Fitting of the experimental data to Eq. (22). $P_{CO} = 2.1 \times 10^6$ Pa; concentrations, mol/L: $[C_6H_{10}] = 0.1$, $[Pd(PPh_3)_2Cl_2] = 2.0 \times 10^{-3}$, $[PPh_3] = 8.0 \times 10^{-3}$, $[TsOH] = 2.4 \times 10^{-2}$, and [o-xylene] = 5.0×10^{-2} ; Temperatures, K: (1) 358, (2) 363, (3) 368, (4) 373, and (5) 378.

Similarly, using the previously calculated [5] values for the apparent activation energy of the parameters

 $\frac{f}{k_{\text{app.1}}} = 10^{-6.70} \exp\left(\frac{70 \pm 3 \text{ kJ/mol}}{RT}\right), \quad \frac{\text{L} \cdot \text{min}}{\text{mol}} \text{ and}$ $\frac{e}{k_{\text{app.2}}} = 10^{-14.84} \exp\left(\frac{143 \pm 7 \text{ kJ/mol}}{RT}\right), \quad \frac{\text{L}^3 \cdot \text{min}}{\text{mol}^3}, \text{ we get}$ $\Delta H_{f/k_{\text{app.1}}} = \Delta H_{13} + \Delta H_{\text{H}} - E_7 - \Delta H_2 - \Delta H_3$ $- \Delta H_4 - \Delta H_5 - \Delta H_6, \quad (27)$

$$\Delta H_{11} - \Delta H_{13} = \Delta H_{a/k_{app.4}} - \Delta H_{f/k_{app.1}}$$

$$= -75 - (-70) = -5 \,\text{kJ}.$$
(28)

Correspondingly,

$$\Delta H_{e/k_{app,2}} = \Delta H_8 + \Delta H_H - E_7 - \Delta H_2 - \Delta H_3$$

- $\Delta H_4 - \Delta H_5 - \Delta H_6,$ (29)

$$\Delta H_{12} - \Delta H_8 = \Delta H_{b/k_{app,3}} - \Delta H_{e/k_{app,2}}$$
(30)

$$+2\Delta H_H = -146 - (-143) + 2 \cdot (-6) = -15 \text{ kJ}.$$

These data can be converted using as a standard

one of the compounds involved in the ligand exchange, for example, $Pd(PPh_3)_2(CH_3OH)_2$:

$$Pd(PPh_{3})_{2}(CH_{3}OH)_{2} + 2CO$$

$$\implies Pd(PPh_{3})_{2}(CO)_{2} + 2CH_{3}OH,$$
(31)

where $\Delta H_1 = \Delta H_{12} - \Delta H_{11} = -83$ kJ in accordance with Eq. (26);

$$Pd(PPh_3)_2(CH_3OH)_2 + 2PPh_3$$

$$\implies Pd(PPh_3)_4 + 2CH_3OH,$$
(32)

for which the enthalpy is defined as

$$\Delta H_2 = \Delta H_{e/k_{app,2}} - \Delta H_{a/k_{app,4}} = \Delta H_8 - \Delta H_{11}$$

= -143 - (-75) = -68 kJ. (33)

$$Pd(PPh_{3})_{2}(CH_{3}OH)_{2} + HCl + 2Sol$$

$$\implies HSol[Pd(PPh_{3})_{2}(Cl)Sol] + 2CH_{3}OH,$$
(34)

for which ΔH_3 is defined by the equation:

$$\Delta H_3 = \Delta H_{f/k_{app.1}} - \Delta H_{a/k_{app.4}} = \Delta H_{13} - \Delta H_{11}$$

= -70 - (-75) = 5 kJ. (35)

Relationships (26), (33), and (35) actually reflect the stability series of the complexes

$$\mathrm{Pd}(\mathrm{PPh}_{3})_{2}(\mathrm{CO})_{2} > \mathrm{Pd}(\mathrm{PPh}_{3})_{4} > \mathrm{Pd}(\mathrm{PPh}_{3})_{2}(\mathrm{CH}_{3}\mathrm{OH})_{2} > \mathrm{HS}^{\oplus}_{\mathrm{O}}\mathrm{I}[\mathrm{Pd}(\mathrm{PPh}_{3})_{2}(\mathrm{Cl})(\mathrm{Sol})]^{\ominus}$$

which differs from the one obtained on the basis of data on hydrocarbalkoxylation of cyclohexene with cyclohexanol [4]:

$$Pd(PPh_3)_4 > Pd(PPh_3)_2(CO)_2$$

> Pd(PPh_3)_2(C_6H_{11}OH)_2

regarding the inversion of the formation enthalpies of the complexes $Pd(PPh_3)_4$ and $Pd(PPh_3)_2(CO)_2$. In this context, it should be recognized that the enhancement of the donor–acceptor properties of the ligands in the order $C_6H_{11}OH < CH_3OH < Cl < PPh_3$ is not the only factor responsible for the stability of palladium complexes in solution. Apparently, the solvation factor should make additional contribution to the stabilization of these complexes. Then the stabilization of the $Pd(PPh_3)_2(CO)_2$ complex can be enhanced on passing from cyclohexanol to methanol owing to stronger specific solvation of the coordinated carbonyl groups by methanol [16]. Thus, the higher stability of the $Pd(PPh_3)_2(CO)_2$ complex in the presence of methanol must inevitably lead to a reduction in its enthalpy of formation in comparison with the $Pd(PPh_3)_4$ complex, which does not contain carbonyl ligands.

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