

The mechanism of the catalytic behaviour of platinum triphenylphosphine complexes in the ethylene hydrocarbonylation

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Abstract

High resolution ^1H , ^{13}C and ^{31}P NMR was used for step-by-step investigation of ethylene hydrocarbonylation into diethyl ketone (DEK) in the ' P_2PtX_2 (or P_4Pt)– $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' ($\text{P} = \text{PPh}_3$, $\text{X} = \text{CF}_3\text{COO}^-$; $[\text{H}_2\text{O}] \leq 30$ vol.%) catalytic systems. The so-called 'hydride mechanism' of the reaction was unambiguously determined. Six key Pt(II) intermediates, namely, $[\text{HPtP}_3]^+$, **1**, *trans*- $[\text{HPt}(\text{X})\text{P}_2]$, **2**, *trans*- $[\text{HPt}(\text{CO})\text{P}_2]^+$, **5**, *trans*- $[\text{HPt}(\text{C}_2\text{H}_4)\text{P}_2]^+$, **6**, *trans*- $[\text{C}_2\text{H}_5\text{Pt}(\text{C}_2\text{H}_4)\text{P}_2]^+$, **7**, and *trans*- $[\text{C}_2\text{H}_5\text{Pt}(\text{CO})\text{P}_2]^+$, **9**, were identified and characterized, and in addition their reactivity was studied. The relative thermodynamic stability of the Pt(II) hydride complexes turned out to determine the catalytic behaviour of the platinum systems investigated and was found to increase in $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ solutions in the order: $2 < 6 < 1 < 5$. In accordance with this, the ' $\text{P}_4\text{Pt}-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' system, in which rapid and quantitative conversion of initially formed complex **1** into the extremely inert to C_2H_4 complex **5** occurred under the reaction conditions, exhibited no detectable activity in DEK formation. The initial activity of the ' $\text{P}_2\text{PtX}_2-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' system in DEK formation was suggested to result from the generation of complex **9**, in addition to **5**, at the initial unsteady-state period of the reaction as a result of the kinetic competition of two rapid reaction sequences: $2 \rightarrow 6 \rightarrow 7 \rightarrow 9$ against $2 \rightarrow 5$. Isomerization of **9** into the corresponding platinum propionyl complex appeared to be the rate-determining stage of DEK formation. The kinetic regularities of the model catalytic reactions of ethylene hydrogenation and hydrogen isotopic heteroexchange with the ' $\text{P}_2\text{PtX}_2-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' and ' $\text{P}_4\text{Pt}-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' systems were also studied. The former system was found to exhibit a much higher initial activity due to formation of a more active platinum hydride complex **2**, while in the latter system a less active complex **1** was formed initially. The activities of both systems, however, leveled off during the reactions due to $2 \rightleftharpoons 1$ equilibration.

Keywords: Ethylene; Hydrocarbonylation; Mechanism; Platinum; Triphenylphosphine

1. Introduction

We have recently studied [1–4] the catalytic properties of the systems ' $\text{M}(\text{PPh}_3)_n\text{X}_m-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' (M is a transition metal of Group VIII; $\text{X}^- = \text{CF}_3\text{COO}^-$, CH_3COO^- , H^-) in the olefin hydrocarbonylation reaction and

found the palladium triphenylphosphine complexes, $\text{Pd}(\text{PPh}_3)_4$ and $(\text{PPh}_3)_2\text{Pd}(\text{OAc})_2$, to catalyze efficiently the synthesis of diethyl ketone (DEK) from ethylene, CO and H_2 in concentrated aqueous solutions of CF_3COOH under very mild conditions (70°C , 1 atm) according to Eq. (1) [2]:



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Based on the comprehensive kinetic and NMR spectroscopic studies, the mechanism of reaction (1) catalyzed by palladium triphenylphosphine complexes was elucidated. It involves (i) the formation of the Pd(II) hydride complex, $[\text{HPdP}_3]^+$ ($\text{P}=\text{PPh}_3$), as the initial rather slow stage, (ii) rapid stages of insertion of ethylene and CO molecules into the Pd–H and Pd– C_2H_5 bonds, respectively, with the formation of the propionyl intermediate, $[\text{P}_2\text{Pd}(\text{COC}_2\text{H}_5)]^+$, (iii) the second rather slow step of insertion of ethylene molecule into the Pd– COC_2H_5 bond and (iv) rapid decomposition of the resulting propionyl–ethyl complex, $[\text{P}_2\text{Pd}(\text{C}_2\text{H}_4\text{COC}_2\text{H}_5)]^+$ to yield DEK [3].

Pt(II) triphenylphosphine complexes also showed a detectable, but quite small catalytic activity in ethylene hydrocarbonylation according to Eq. (1) [4]. Since Pt is an electron homologue of Pd and tends to form Pt(0) and Pt(II) phosphine complexes similar in their composition and structure to the Pd(0) and Pd(II) analogs, one could expect that the mechanism of DEK synthesis in the presence of catalysts based on both metals should be the same. A low reaction rate for Pt catalysts could result from a higher strength of M–L bonds ($\text{L}=\text{H}^-$, CO, C_2H_4 , PPh_3) in Pt complexes as compared to Pd ones, which could lead to lower rate constants of individual stages of reaction (1).

It is, however, worth noting the following difference in behaviour of the catalytic systems based on Pd and Pt. For Pd systems, a nature of catalyst precursor (P_2PdX_2 or P_4Pd), provided that the same total P/Pd molar ratio is maintained during the reaction, did not affect the catalytic activity. By contrast, among the Pt systems, ' $\text{P}_2\text{PtX}_2\text{--CF}_3\text{COOH}/\text{H}_2\text{O}$ ' and ' $\text{PtP}_4\text{--CF}_3\text{COOH}/\text{H}_2\text{O}$ ' ($\text{P}=\text{PPh}_3$, $\text{X}^-=\text{CF}_3\text{COO}^-$), only the former was found to produce DEK with low yield (0.1 mol/g-at. Pt within 4 h) by reaction (1) at 70°C and 1 atm [4], the latter system being entirely inactive under these conditions. Moreover, the ' $\text{P}_2\text{PtX}_2\text{--CF}_3\text{COOH}/\text{H}_2\text{O}$ ' and ' $\text{PtP}_4\text{--CF}_3\text{COOH}/\text{H}_2\text{O}$ ' systems differed also in their catalytic activity in the reactions of hydrogen iso-

topic heteroexchange and ethylene hydrogenation which model the initial stages of reaction (1) [5].

Thus, it was of interest to study the mechanism of DEK formation in the catalytic systems ' P_2PtX_2 (or PtP_4)– $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ', to compare it with that for Pd complexes and to elucidate the reason for the difference in catalytic behaviour of the two Pt systems. For this purpose, we undertook a detailed NMR spectroscopic step-by-step investigation of the interaction of the reactants (H_2 , C_2H_4 , CO) with both Pt systems to determine and characterize the key reaction intermediates and to study their reactivity. We examined also the kinetic regularities of the model catalytic reactions of ethylene hydrogenation and hydrogen isotopic heteroexchange to extend our knowledge on the peculiarities of the catalytic behaviour of the platinum systems studied.

2. Experimental

$(\text{PPh}_3)_4\text{Pt}^0$ was prepared in a glass, thermostated (50–60°C), shaken reactor into which an ethanol/water (80 ml/20 ml) mixture, PPh_3 (3.67 g, 14 mmol) and LiOH (0.38 g, 16 mmol) were placed. A solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (1.05 g, 2.0 mmol) in water (5 ml) was added to the mixture through a rubber membrane using a syringe. Immediately a bright yellow precipitate of $(\text{PPh}_3)_4\text{Pt}$ began to appear. The mixture was shaken for several minutes and then $(\text{PPh}_3)_4\text{Pt}$ was filtered off, washed with hot aqueous ethanol, cold ethanol, pentane and dried in vacuum. All operations were carried out under argon in deaerated solvents. Yield: 98%. M.p. 118°C. Found: Pt, 16.5; C, 69.0; H, 5.0%. Calcd. for $\text{PtP}_4\text{C}_{72}\text{H}_{60}$: Pt, 16.7; C, 68.5; H, 4.8%.

cis- $(\text{PPh}_3)_2\text{Pt}(\text{CF}_3\text{COO})_2$ was prepared by adding CF_3COOH dropwise to a suspension of $(\text{PPh}_3)_2\text{PtCO}_3$ (2.0 g, 2.6 mmol) in boiling benzene (10 ml) until a clear solution was obtained. When pentane (20 ml) was added to the solution a white sediment of $(\text{PPh}_3)_2\text{Pt}(\text{CF}_3\text{COO})_2$ was precipitated. The complex was filtered off, washed with pentane and dried in vacuum. Yield: 95%.

M.p. 230–235°C. Found: C, 50.4; H, 3.3%. Calcd. for $\text{PtP}_2\text{C}_{40}\text{F}_6\text{H}_{30}\text{O}_4$: C, 50.8; H, 3.1%. IR: $\nu_{\text{CO}} = 1684 \text{ cm}^{-1}$.

$[\text{HPt}(\text{PPh}_3)_3]^+$, *trans*- $\text{HPt}(\text{CF}_3\text{COO})(\text{PPh}_3)_2$, *cis*- $(\text{PPh}_3)_2\text{Pt}(\text{OAc})_2$, $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$, $(\text{PPh}_3)_2\text{PtCO}_3$ were prepared according to [6–8].

Reagent grade CF_3COOH and PPh_3 (twice recrystallized from ethanol) were used.

The ethylene hydrogenation and hydrogen isotopic exchange reactions were carried out in a static volumetric installation at 20–70°C and 1 atm using a glass, thermostated, shaken reactor into which a Pt complex and $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ were placed. The samples of gas phase during the course of the reactions were analyzed by GC (2 m column packed with activated charcoal, 150°C) as described in [3,4]. The reaction of hydrogen isotopic exchange ($^*\text{H}_2/\text{H}^+$ -or $\text{H}_2/^*\text{H}^+$ -exchange) was carried out using tritiated dihydrogen or solvent tritiated by a small amount of HTO, and was followed by means of gas phase radiochromatography. The specific radioactivities of dihydrogen (as well as of ethylene and ethane after their GC separation) were measured by means of a proportional flow counter placed after a thermal conductivity detector. The rates of hydrogen isotopic exchange were calculated as described [9].

To study the reactivity of Pt complexes towards gaseous H_2 , C_2H_4 and CO by means of NMR spectroscopy, solutions of the complexes (0.04–0.08 mol/l) in $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ($[\text{H}_2\text{O}] \leq 30 \text{ vol.}\%$) were prepared. All treatments of the solutions with H_2 , C_2H_4 and CO were carried out by bubbling the gases through the solutions directly in NMR ampoules prior to recording the spectra.

The ^1H , ^{13}C and ^{31}P NMR spectra were recorded on Bruker CXP-300 and MSL-400 spectrometers. ^{13}C and ^{31}P NMR spectra were recorded with proton decoupling or with selective decoupling of the phenyl protons. ^1H chemical shifts were measured against acetone as internal reference (2.08 ppm with respect to TMS). ^{13}C chemical shifts were measured with respect to the carbonyl group of CF_3COOH (166.0 ppm referred to TMS). ^{31}P

chemical shifts were measured with respect to external 85% H_3PO_4 . For all NMR spectra, down-field shifts were taken as positive.

3. Results and discussion

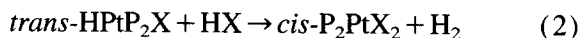
3.1. Key intermediates of ethylene hydrocarbonylation reaction studied by NMR spectroscopy

3.1.1. Formation of Pt(II) hydride complexes in CF_3COOH solutions

Dissolution of P_4Pt in concentrated aqueous solutions of CF_3COOH ($[\text{H}_2\text{O}] \leq 30 \text{ vol.}\%$) results [10] in quantitative formation of the known cationic hydride complex $[\text{HPtP}_3]^+$, **1**, which has a square-planar structure (see NMR spectra parameters in Table 1). **1** is stable to protolysis of the Pt–H bond with an acid and is retained in $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ solutions over a long period (more than a month).

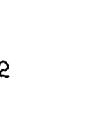
Interaction of H_2 with *cis*- P_2PtX_2 in CF_3COOH solutions at 60–70°C gives rise to a hydride complex of a different nature, namely, the covalent hydride *trans*- HPtP_2X , **2**, which also has a square-planar structure (see NMR spectral parameters in Table 1). Complex **2** in chloroform solution is stable over a long period. In CF_3COOH solutions, however, **2** decomposes at room temperature within an hour via two parallel pathways (see also Fig. 1):

(i) A comparatively rapid protolysis of the Pt–H bond with an acid, yielding H_2 and initial complex of Pt(II):



(ii) A slower transformation to the cationic hydride **1**, accompanied by the formation of the hydride complex **3** of unidentified composition (NMR: ^1H , $\delta = -26.18 \text{ ppm}$, doublet, $^2J(\text{H–P}) = 13.6 \text{ Hz}$, $^1J(\text{H–Pt}) = 1113 \text{ Hz}$; ^{31}P , $\delta = 33.3 \text{ ppm}$, $^1J(\text{P–Pt}) = 3070 \text{ Hz}$). One can suppose that the described transformation of **2** proceeds as a disproportionation process:

Table 1
NMR spectral parameters of Pt(II) triphenylphosphine complexes^a

Complex	Observed ligands	Chemical shifts, δ , ppm			Coupling constants, Hz
		¹ H	³¹ P{ ¹ H} ^b	¹³ C{ ¹ H} ^{b,c}	
[HPtP ₃] ⁺ ,	H ⁻	-5.86 (<i>dt</i>)			¹ J(H-Pt) = 771 ¹ J(P ¹ -Pt) = 2217
 1	P ¹		24.3(<i>t</i>) (<i>dt</i>) ^d	¹ J(P ² -Pt) = 2816 ² J(H-P ¹) = 160	
	P ²		23.3(<i>d</i>) (<i>dd</i>) ^{d,e}	² J(H-P ²) = 13 ² J(P ¹ -P ²) = 18	
<i>trans</i> -HPt(X)P ₂	H ⁻	-22.89(<i>t</i>)			¹ J(H-Pt) = 1190 ¹ J(P-Pt) = 3007 ² J(H-P) = 14
2	P		31.8(<i>s</i>) (<i>d</i>) ^d		² J(H-P) = 14
<i>cis</i> -[P ₂ Pt(CO)X] ⁺ ,	P ¹		16.9(<i>d</i>) ^f		¹ J(P ¹ -Pt) = 3110 ¹ J(P ² -Pt) = 3310
	P ²		1.5(<i>d</i>) ^g		¹ J(C-Pt) = 1270 ² J(P ¹ -P ²) = 50
	CO			172.3(<i>d</i>)	² J(P ¹ -C _{CO}) = 133
<i>trans</i> -[P ₂ Pt(CO)X] ⁺	P		23.6(<i>s</i>)		¹ J(P-Pt) = 1958 ¹ J(C-Pt) = 1850
	CO			157.8(<i>t</i>)	² J(P-C _{CO}) = 10
<i>trans</i> -[HPt(CO)P ₂] ⁺	H ⁻	-4.37(<i>t</i>)			¹ J(H-Pt) = 907 ¹ J(P-Pt) = 2529
	P		24.1(<i>s</i>) (<i>d</i>) ^d		¹ J(C-Pt) = 998 ² J(H-P) = 10
	CO			186.2(<i>t</i>) (<i>dt</i>) ⁴	² J(C _{CO} -P) = 6 ² J(C _{CO} -P) = 63
<i>trans</i> -[HPt(C ₂ H ₄)P ₂] ⁺ ^h	H ⁻	-5.18(<i>t</i>)			¹ J(H-Pt) = 1030 ¹ J(P-Pt) = 2677
	P		24.4(<i>s</i>)		¹ J(C-Pt) = 43 ² J(H-P) = 7
6	C ₂ H ₄	3.69(<i>s</i>) ⁱ		92.2(<i>s</i>) (<i>t</i>) ^d	¹ J(H-C) _{C₂H₄} = 166
<i>trans</i> -[(C ₂ H ₅)Pt(C ₂ H ₄)P ₂] ⁺	P		28.5(<i>s</i>)		¹ J(P-Pt) = 3038 ¹ J(C-H) _{C₂H₄} = 171
	C ₂ H ₄			94.0(<i>s</i>) (<i>t</i>) ^d	¹ J(C _{CH₂} -Pt) = 608
					² J(H _{CH₂} -Pt) ≈ 49 ³ J(H _{CH₃} -Pt) ≈ 40 ³ J(H-H) _{C₂H₅} ≈ 7
7	CH ₂ -gr.	1.45(<i>m</i>) ^j		25.7(<i>s</i>)	
	CH ₃ -gr.	-0.39(<i>t</i>)		18.2(<i>s</i>)	
<i>cis</i> -[P ₂ Pt(C ₂ H ₄)X] ⁺ ,	P ¹		18.8(<i>d</i>) ^k		¹ J(P ¹ -Pt) = 2562 ¹ J(P ² -Pt) = 2598
	P ²		7.5(<i>d</i>) ^g		¹ J(C-Pt) = 45 ² J(P ¹ -P ²) = 16
	C ₂ H ₄	5.15(<i>s</i>) ⁱ		108.9(<i>d</i>)	² J(P ¹ -C) = 9 ² J(P ² -C) ≈ 0 ¹ J(C-H) _{C₂H₄} = 170
8					

Complex	Observed ligands	Chemical shifts, δ , ppm			Coupling constants, Hz
		^1H	$^{31}\text{P}\{^1\text{H}\}^b$	$^{13}\text{C}\{^1\text{H}\}^{b,c}$	
9 <i>trans</i> -[(C ₂ H ₅)Pt(CO)P ₂] ⁺	P		21.3(<i>s</i>) (<i>t</i>) ^d		$^1J(\text{P-Pt}) = 2842$ $^1J(\text{C}_{\text{CO}}\text{-Pt}) = 886$
	CO			181.7(<i>m</i>)	$^1J(\text{C}_{\text{CH}_2}\text{-Pt}) = 496$ $^2J(\text{C}_{\text{CH}_3}\text{-Pt}) = 29$
	CH ₂ -gr.	1.15(<i>m</i>) ⁱ		20.7 ^l	$^2J(\text{C}_{\text{CH}_2}\text{-P}) \approx 5$ $^2J(\text{C}_{\text{CO}}\text{-P}) \approx 10$
	CH ₃ -gr.	-0.16(<i>t</i>)		16.7(<i>s</i>)	$^2J(\text{H}_{\text{CH}_2}\text{-Pt}) \approx 61$ $^3J(\text{P-H}_{\text{CH}_2}) \approx 10$ $^3J(\text{H}_{\text{CH}_3}\text{-Pt}) = 37$ $^2J(\text{C}_{\text{CO}}\text{-C}_{\text{CH}_2}) = 24$ $^3J(\text{H-H}) \approx 8^b$

^a Measured in CF₃COOH ([H₂O] ≤ 0,7%) at 25°C. Designations (taking no account of ¹⁹⁵Pt satellites): *s*, singlet; *d*, doublet; *t*, triplet; *dd*, doublet of doublets; *dt*, doublet of triplets; *m*, multiplet.

^b Recorded with proton decoupling (unless otherwise specified).

^c ¹³C NMR spectra were recorded for samples of complexes prepared using ¹³CO (75.3% labelled) and ¹³CH₂=CH₂ (86.4% labelled).

^d Recorded with selective decoupling of the phenyl protons.

^e Integral intensity ratio of P² to P¹ resonances equals 2.

^f Superposition of doublet (≈ 25%) and doublet of doublets (≈ 75%) for the sample of *cis*-**4** prepared using ¹³CO (75.3% labelled).

^g Integral intensities of P¹ and P² resonances are related as 1:1.

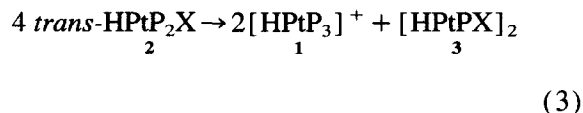
^h Measured at -10°C.

ⁱ Superposition of singlet (≈ 60%) and doublet (≈ 40%) for the sample of complex prepared using ¹³CH₂=CH₂ (86.4% labelled).

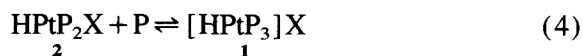
^j Integral intensities of proton resonances from the CH₂ and CH₃ groups are related as 2:3.

^k Superposition of doublet (≈ 60%) and doublet of doublets (≈ 40%) for the sample of complex prepared using ¹³CH₂=CH₂ (86.4% labelled).

^l Superposition of triplet (≈ 25%) and doublet of triplets (≈ 75%).



and **3** is a binuclear Pt complex formed upon the redistribution of the phosphine ligands and probably containing the Pt–H–Pt or Pt–X–Pt linkages. **3** easily picks up an excess of phosphine to form the mononuclear hydride **1**. Under H₂ atmosphere in the presence of excess PPh₃, **2** transforms eventually to **1**:



The rate of reaction (4) increases in CF₃COOH/H₂O solutions ([H₂O]H ≤ 30 vol.%) as compared to that in concentrated CF₃COOH. The structure of **3** was not studied in detail, since **3** was not detected in the catalytic systems under the conditions of reaction (1).

In addition to the two routes to Pt hydride complexes, mentioned above, the third pathway of

their formation can in principle occur, namely, the reduction of the initial Pt(II) complex with CO followed by protonation of the formed Pt(0) complex. Such a pathway was found to be realized for the Pd phosphine system in the absence of H₂ [1–3]. In the case of the Pt system interaction of *cis*-P₂PtX₂ with carbon monoxide in CF₃COOH/H₂O solutions ([H₂O] ≤ 30 vol.%) proceeds easily even at room temperature and is accompanied by the consumption of 1 mol CO/g-at. Pt within several minutes. ³¹P and ¹³C NMR spectra of the solutions evidence, however, that Pt(II) reduction followed by formation of any Pt(II) hydride complex does not occur. Instead, only the replacement of a weakly coordinated CF₃COO⁻ ligand by carbon monoxide takes place with the quantitative formation of the Pt(II) carbonyl phosphine complex *cis*-[P₂Pt(CO)X]⁺, *cis*-**4**. The latter then isomerizes easily at 25°C to the corresponding *trans*-isomer, *trans*-**4** (see NMR spectra parameters of both *cis*- and *trans*-**4** complexes in Table 1): within 1.5 h only about 20% of *cis*-**4** is

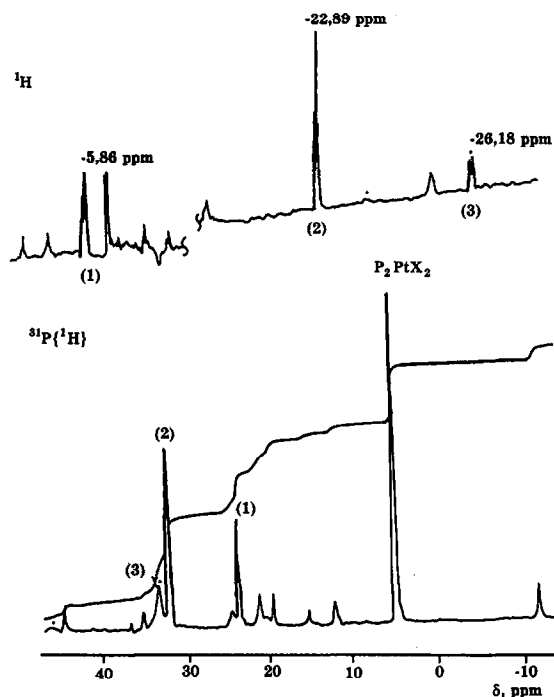


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra of *trans*-HPtXP₂, 2, 30 min after its dissolution in concentrated CF₃COOH at 25°C; 1 – [HPtP₃], 3 – unidentified platinum hydride complex (the second ^{195}Pt satellite in ^1H NMR spectrum is not shown).

still retained in solution. This indicates *cis*-4 to be a kinetically controlled product of Pt(II) reaction with CO, while *trans*-4 is a thermodynamically controlled one. Excess PPh₃ does not affect the formation of the Pt(II) carbonyl complexes.

At room temperature [P₂Pt(CO)X]⁺ (mixture of *cis*- and *trans*-isomers) in CF₃COOH/H₂O solutions is inert towards dihydrogen. However, when heated (60–70°C) it easily reacts with H₂ to form the known [11] square-planar hydrido-carbonyl complex of Pt(II), *trans*-[HPt(CO)P₂]⁺, 5, (see NMR spectra parameters in Table 1). 5 is easily obtained also from the treatment of CF₃COOH solutions of both hydride complexes 1 and 2 with carbon monoxide at room temperature. According to [6,11], in aprotic solvents 1 does not react with CO to give 5. Indeed, we found 1 to interact with CO in benzene solution with a quantitative formation of 5 only after addition of a considerable amount of CF₃COOH (more than 25 mol/g-at. Pt) into the solution. This points to the necessity to assist the substitu-

tion of a PPh₃ ligand by the CO ligand, released by this interaction, with the protonation of PPh₃ [Eq. (5)].



The equilibrium (5) is essentially shifted to the right in CF₃COOH/H₂O ([H₂O] ≤ 30 vol.%) solutions, which is indicated by a positive ^{31}P chemical shift value ($\delta = 7\text{--}8$ ppm) of the phosphine noncoordinated to Pt(II) as compared to a negative chemical shift ($\delta \approx -5$ ppm) of the free phosphine in benzene solution.

The hydrido-carbonyl complex 5 is stable to protolysis of the Pt–H bond and is retained in CF₃COOH/H₂O solutions over a long period.

Hydrido-ethylene and ethyl-ethylene complexes of Pt(II)

Unlike complexes 1 and 5, which do not react with ethylene to any extent detectable by NMR, the hydride 2 interacts easily with C₂H₄ in CF₃COOH/H₂O solutions ([H₂O] ≤ 30 vol.%) to form the known [11] hydrido-ethylene complex of Pt(II), *trans*-[HPt(C₂H₄)P₂]⁺, 6 (see NMR spectral data in Table 1). Dissolution of 2 at –10°C in CF₃COOH, preliminary saturated with ethylene, resulted in a quantitative conversion of 2 to 6. Within the temperature range of (–10°C)–0°C, 6 transformed rather slowly to the Pt(II) ethyl-ethylene complex, *trans*-[(C₂H₅)Pt(C₂H₄)P₂]⁺, 7 (see Table 1 and Fig. 2). Unlike complex 6, a coordinated ethylene molecule in complex 7 exchanges rapidly (on the NMR time scale) with ethylene dissolved. This shows up in the ^1H NMR spectra as a broadened C₂H₄ line shifted to high field as compared with a line of ethylene dissolved in pure CF₃COOH (Fig. 3). Even at 0°C, complexes 6 and 7 are protolyzed slowly with CF₃COOH to evolve H₂ and C₂H₆, respectively, and to form *cis*-P₂PtX₂. As the temperature increases up to 25°C, the rates of the transformation of 6 to 7 and subsequent decomposition of 7 dramatically increase (Fig. 4). The resulting complex *cis*-P₂PtX₂ was found by NMR to exist in CF₃COOH solutions in the presence of

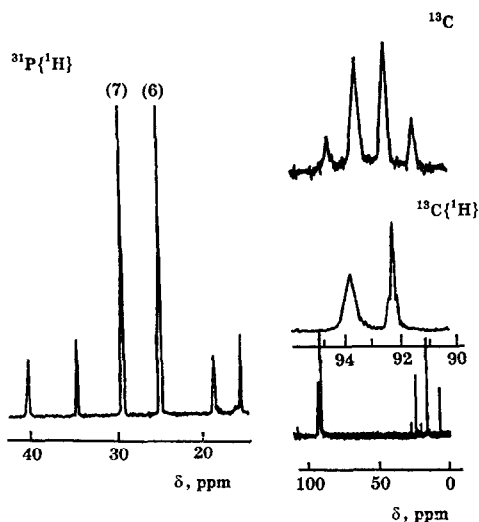


Fig. 2. $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^{13}C NMR spectra of the mixture of $[\text{HPt}(\text{C}_2\text{H}_4)\text{P}_2]^+$, **6**, and $\text{trans}-[(\text{C}_2\text{H}_5)\text{Pt}(\text{C}_2\text{H}_4)\text{P}_2]^+$, **7**, prepared in situ by interaction of $^{13}\text{CH}_2=\text{CH}_2$ (86.4% labelled) with complex **2** in CF_3COOH solution at -10°C .

dissolved C_2H_4 in equilibrium with the rather unstable Pt(II) ethylene complex, $\text{cis}-[\text{P}_2\text{Pt}(\text{C}_2\text{H}_4)\text{X}]^+$, **8** (see NMR data in Table 1). Complex **8** easily converts to P_2PtX_2 when removing C_2H_4 from solution.

Ethyl-carbonyl complex of Pt(II)

Carbon monoxide easily displaces ethylene from the Pt(II) coordination sphere of the hydrido-ethylene **6** and ethyl-ethylene **7** complexes; this is accompanied by a rapid (within a few minutes) and quantitative formation of the hydrido-carbonyl complex **5** and complex **9**, respectively. NMR data (see Table 1) show **9** to be the ethyl-carbonyl derivative of Pt(II), $\text{trans}-[(\text{C}_2\text{H}_5)\text{Pt}(\text{CO})\text{P}_2]^+$ [10]. Complex **9** was the last spectroscopically observed intermediate on the way to DEK via Eq. (1). We did not manage to detect by NMR the formation of a propionyl complex as a product of intramolecular insertion of CO into the Pt– C_2H_5 bond of **9**, that was a consequence of inertness of **9**. Indeed, complex **9** is rather stable in $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ solutions and remains in the solutions at room temperature for several weeks, only slowly decomposing with the formation of ethane and trace amounts of propionic acid. After heating (70°C) the solution of

9 under ethylene atmosphere for several hours, ^1H NMR spectra detected the formation of traces of

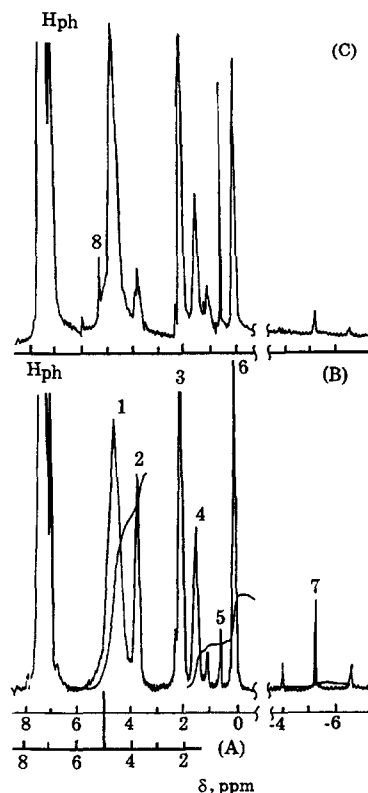


Fig. 3. ^1H NMR spectra of the mixture of $\text{trans}-[\text{HPt}(\text{C}_2\text{H}_4)\text{P}_2]^+$, **6**, and $\text{trans}-[(\text{C}_2\text{H}_5)\text{Pt}(\text{C}_2\text{H}_4)\text{P}_2]^+$, **7**, in CF_3COOH solution at 25°C as a function of time (time interval between the spectra (B) and (C) is about 30 min). 1—the fast exchange line of ethylene dissolved and C_2H_4 ligand of **7**; 2—line of the C_2H_4 ligand of **6**; 3—line of acetone (internal standard); 4 and 6 are the lines of CH_2 and CH_3 groups of the ethyl ligand of **7**, respectively; 5—line of C_2H_6 ; 7—resonance of the H ligand of **6**; 8—line of the C_2H_4 ligand of **8**. (A) represents the ^1H NMR spectrum of C_2H_4 dissolved in pure CF_3COOH .

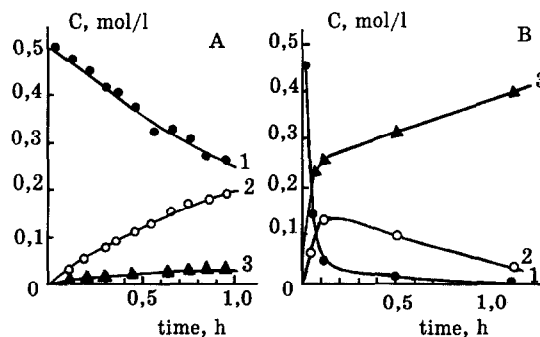
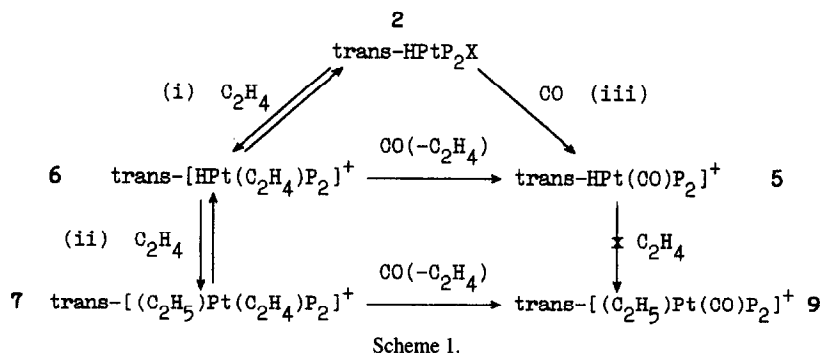


Fig. 4. Kinetic curves of transformations of $\text{trans}-[\text{HPt}(\text{C}_2\text{H}_4)\text{P}_2]^+$, **6** (curve 1) to the complexes **7** (curve 2) and $\text{cis}-\text{P}_2\text{PtX}_2$ (curve 3) at 0°C (A) and 25°C (B) as illustrated by ^{31}P NMR.



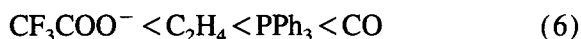
DEK. This suggests occurrence of a very slow isomerization of **9** into a propionyl complex, the latter being able to react with ethylene to give DEK and to undergo hydrolysis yielding propionic acid. Thus, the stage of M–C bond carbonylation, which was the most rapid for DEK synthesis in the Pd-based system [3], appears to be the rate-determining step of reaction (1) in the case of the Pt(II)–phosphine system studied.

Note, that the carbonylation rates of the complexes $trans\text{-[MBr(Ph)(PPh}_3\text{)}_2]$ for M = Pt and Pd measured under 1 atm CO in CH_2Cl_2 solution were related as 1:184, respectively [12]. The low reaction rate for Pt was ascribed (i) to a slower (as compared to Pd) ligand substitution in the initial complex with formation of carbonyl-phenyl derivative and (ii) to a slower isomerization of the latter to the corresponding acyl complex [13]. The second point appears to occur in our platinum system, where the ethyl-carbonyl complex **9** has a $trans$ -disposition of CO and C_2H_5 ligands, which is unfavourable for insertion and exhibits the low rate of $trans$ – cis isomerization.

It was of interest to study the comparative reactivity of hydrides **1** and **2** towards C_2H_4 and CO under the conditions when these substrates were present in the system simultaneously as the 1:1 mixture. The only product of the transformation of complex **1** under ($\text{C}_2\text{H}_4 + \text{CO}$) in $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ solutions ($[\text{H}_2\text{O}] \leq 30 \text{ vol.}\%$) at room temperature was the hydrido-carbonyl complex **5** (^{31}P NMR data). This agrees well with the above spectral data on high tolerance of complexes **1** and **5** towards ethylene. On the contrary, interaction of complex **2** with the mixture of C_2H_4 and CO under

similar conditions led to two complexes, **5** and **9**, in comparable amounts (^{31}P NMR data) and appeared to proceed according to Scheme 1.

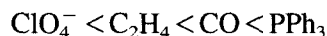
The observed phenomena can be rationalized on the basis of the different thermodynamic stabilities of the platinum hydride complexes, $trans\text{-[HPt(L)P}_2]$ with various ligands, $\text{L} = \text{CF}_3\text{COO}^-$, C_2H_4 , CO, PPh_3 . Based on all the above NMR data, we conclude that the stability in $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ solutions increases in the order: $2 < 6 < 1 < 5$, i.e. in the following series for ligand L:



In accordance with this series, C_2H_4 easily substitutes a weakly coordinated CF_3COO^- ligand in **2** to give **6**, but does not react to any significant extent with **1** and **5**. On the other hand, in $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ solutions, CO rather rapidly replaces both CF_3COO^- (in **2**) and PPh_3 (in **1**) ligands as well as C_2H_4 coordinated to Pt(II) in **6** and **7** to yield stoichiometric amounts of the corresponding carbonyl complexes **5** or **9**.

In this connection, the formation of **9** and **5** in comparable amounts during the reaction of **2** with ($\text{C}_2\text{H}_4 + \text{CO}$) appears to be surprising. The result can be explained by the successful kinetic competition of the stages (i) and (ii) with thermodynamically more favourable stage (iii) (Scheme 1), the equilibrium for which, thus, is not reached. Success of such a competition seems to be promoted by the approximately one order of magnitude higher solubility of C_2H_4 compared to CO in our reaction medium.

Note that previously [11] a stability series different from (6) was found for the complexes *trans*-[HPt(L)P₂] (P = PPh₃) with various ligands L in benzene solutions, namely,



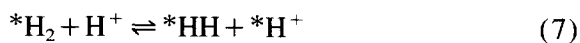
Such an interchange of the positions of CO and PPh₃ ligands in the stability order when passing from benzene to CF₃COOH/H₂O solutions is obviously due to the equilibrium (5) that promotes the process of PPh₃ ligand substitution (*vide supra*).

Thus, summarizing the results of the above spectroscopic part of our investigation, we can conclude that the difference in the catalytic behaviour of the systems 'P₄Pt–CF₃COOH/H₂O' and 'P₂PtX₂–CF₃COOH/H₂O' in the ethylene hydrocarbonylation reaction results from the formation of platinum hydride complexes of different nature: 1 and 2, respectively.

3.2. Comparative study of catalytic behaviour of the 'P₄Pt–CF₃COOH/H₂O' and 'P₂PtX₂–CF₃COOH/H₂O' systems in the model reactions of hydrogen isotopic heteroexchange and ethylene hydrogenation

To obtain additional information on the peculiarities of the catalytic behaviour of the platinum systems studied and on the properties of the reaction intermediates, we investigated the kinetic regularities of the hydrogen isotopic heteroexchange and ethylene hydrogenation reactions proceeding in CF₃COOH/H₂O solutions under mild conditions (20–70°C, 1 atm).

The hydrogen isotopic heteroexchange between dihydrogen molecules and solvent (CF₃COOH + H₂O) protons:



was studied with tritium T as ^{*}H (see Experimental).

It was found that when passing from concentrated CF₃COOH to CF₃COOH/H₂O solutions ([H₂O] = 30 vol.%), which was accompanied by decrease of the acidity and increase of the polarity

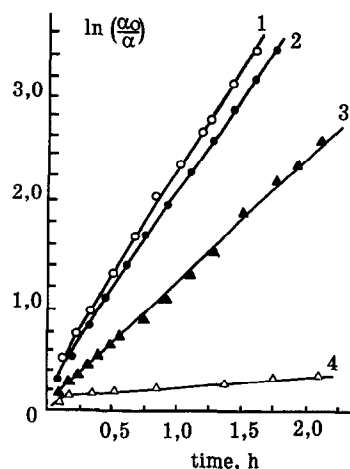


Fig. 5. Kinetic curves of ^{*}H₂/H⁺ exchange in the 'P₄Pt–CF₃COOH/H₂O' system as a function of [H₂O], vol. %: 1 –0.7; 2 –10; 3 –20; 4 –30. Experimental conditions: [P₄Pt] = 1 · 10⁻² mol/l; [P] = 1 · 10⁻² mol/l; total P/Pt = 5; 60°C; 1 atm; volume of gas phase is 16 ml, volume of liquid phase is 15 ml. α₀ and α are the specific radioactivities of dihydrogen at the initial and instant moments of time, respectively.

of the solvent, the rate of ^{*}H₂/H⁺-exchange in the 'P₄Pt–CF₃COOH/H₂O' system (where hydride 1 is formed) drastically decreased. The exchange rates, calculated from the slopes of the straight lines of the semi-logarithmic time dependence of dihydrogen specific radioactivity, were 7.5, 7.0, 4.7 and 0.4 mol H₂/g-at. Pt · h for the solutions with 0.7, 10, 20 and 30 vol.% of H₂O, respectively (Figs. 11 and 5).

The rate of ^{*}H₂/H⁺-exchange in the 'P₄Pt–CF₃COOH/H₂O' ([H₂O] ≈ 0.7 vol.%) system was found to decrease dramatically on addition of excess phosphine up to 4 mol PPh₃/mol P₄Pt and then to remain essentially unchanged at a higher excess of PPh₃ (Fig. 6). The exchange rates for the solutions with 0, 1, 4, 6, 10 and 16 mol of excess PPh₃ per mol of P₄Pt were 18.6, 7.5, 1.3, 1.1, 0.9, and 0.8 mol H₂/g-at. Pt · h, respectively.

The above data suggest the occurrence of the equilibrium stage of PPh₃ ligand dissociation from the hydride complex 1 within the mechanism of reaction (7) in the 'P₄Pt–CF₃COOH/H₂O' system. Furthermore, taking into account the general view of the kinetic curves of ^{*}H₂/H⁺-exchange (Fig. 6), one can suppose that the equilibrium is established at 60°C over a period of about an hour.

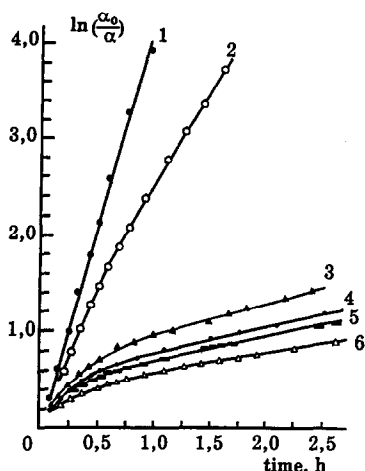


Fig. 6. Kinetic curves of $^*\text{H}_2/\text{H}^+$ exchange in the ' $\text{P}_4\text{Pt}-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' system ($[\text{H}_2\text{O}] \leq 0.7$ vol.%) as a function of added excess of PPh_3 , mol $\text{PPh}_3/\text{mol P}_4\text{Pt}$: 1–0; 2–1; 3–4; 4–6; 5–10; 6–16. The other experimental conditions were exactly the same as for Fig. 5.

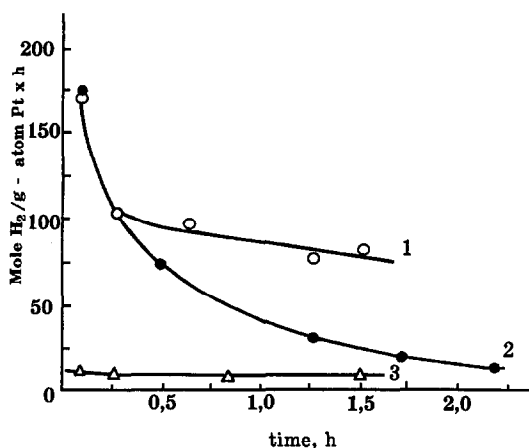


Fig. 7. Time dependence of the rate of $^*\text{H}_2/\text{H}^+$ exchange performed in CF_3COOH ($[\text{H}_2\text{O}] \leq 0.7$ vol.%) with the following catalyst precursors: 1– P_2PtX_2 (total $\text{P}/\text{Pt}=2$); 2– $\text{P}_2\text{PtX}_2 + 3\text{P}$ (total $\text{P}/\text{Pt}=5$); 3– $\text{P}_4\text{Pt} + \text{P}$ (total $\text{P}/\text{Pt}=5$). The other experimental conditions were exactly the same as for Fig. 5.

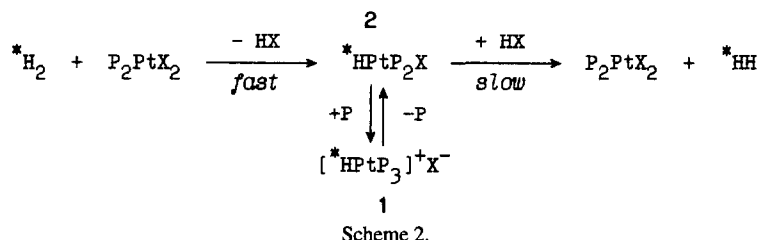
The rate of $^*\text{H}_2/\text{H}^+$ -exchange in the ' $\text{P}_4\text{Pt}-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' system (total $\text{P}/\text{Pt}=5$, $[\text{H}_2\text{O}] \approx 0.7$ vol.%) at 60°C does not depend on the partial pressure of dihydrogen. This indicates

reaction (7) to be limited by the stage of the Pt–hydrogen bond protolysis rather than by the stage of this bond formation in a reaction with dihydrogen molecule. The activation energy for $^*\text{H}_2/\text{H}^+$ -exchange measured within the temperature range of $20\text{--}70^\circ\text{C}$ was 76 kJ/mol.

Contrary to a rather low but steady-state rate of $^*\text{H}_2/\text{H}^+$ -exchange observed for the ' $\text{P}_4\text{Pt}-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' system, the initial rate of the exchange in the ' $\text{P}_2\text{PtX}_2-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' system (where the hydride complex 2 is initially formed) was more than one order of magnitude higher. However, it gradually decreased during the reaction and within two hours approached the value exhibited by the former system, provided the total P/Pt ratio in both systems was the same (Fig. 7). This result is in a good agreement with the above NMR spectroscopy data which evidence for the equilibrium [Eq. (4)] between the covalent 2 and cationic 1 hydride complexes to be reached within an hour.

According to Ugo et al. [14], a shift of equilibrium (4) towards the cationic platinum hydride complex is favoured by the presence of a counterion of low inner-sphere coordination ability (CF_3COO^- in our case) as well as by increasing the solvent polarity and excess of phosphine ligand in solution. Thus, the observed inhibiting effect of the two latter factors on the rate of $^*\text{H}_2/\text{H}^+$ -exchange (Fig. 5 and Fig. 6) seems to be due to their influence on equilibrium (4). One further important factor in this context is a solvent acidity which influences equilibrium (4) by the mediation of equilibrium (5).

From the above discussion, the catalytic cycle of hydrogen isotopic heteroexchange for both platinum systems investigated can be represented as depicted in Scheme 2.



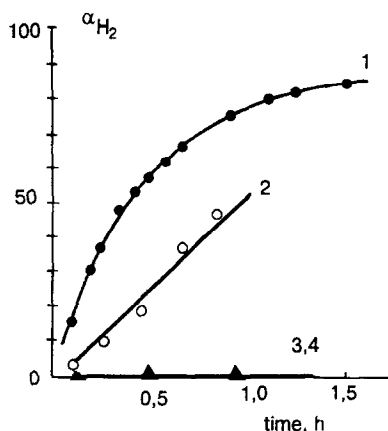


Fig. 8. Time dependence of dihydrogen specific radioactivity (α) in the course of $\text{H}_2/\text{*H}^+$ exchange performed in the ' $\text{P}_4\text{Pt}-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' system in the presence of C_2H_4 and/or CO. Gas mixtures: 1 – $\text{H}_2:\text{Ar} = 1:3$; 2 – $\text{H}_2:\text{C}_2\text{H}_4:\text{Ar} = 1:2:1$; 3 – $\text{H}_2:\text{CO} = 1:1$; 4 – $\text{H}_2:\text{C}_2\text{H}_4:\text{CO} = 1:2:1$. Experimental conditions: $[\text{PtP}_4] = 5 \cdot 10^{-3}$ mol/l; $[\text{P}] = 5 \cdot 10^{-3}$ mol/l; total P/Pt = 5; 60°C ; gas phase volume is 16 ml, liquid phase volume (conc. $\text{CF}_3\text{COOH} + 65 \mu\text{l}$ of HTO) is 15 ml.

This scheme is rather similar to the mechanism of reaction (7) found recently for the ' $\text{Pd}(\text{OAc})_2$ -phosphine-protic acid' catalytic systems [15]. However, whereas the equilibrium between the cationic and covalent hydride complexes of palladium, at least in concentrated CF_3COOH , is attained rapidly and shifted towards covalent hydride, equilibrium (4) for platinum systems even in concentrated CF_3COOH is shifted towards cationic hydride 1 and is reached at 60°C within 1–2 h.

Thus, the difference in the initial rates of the hydrogen isotopic exchange reaction catalyzed by the ' $\text{P}_4\text{Pt}-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' and ' $\text{P}_2\text{PtX}_2-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' systems results from significantly different concentrations of the platinum hydride complex 2 in these systems at the initial stage of the reaction; during the course of the reaction, however, the difference in rates disappears gradually due to $2 \rightleftharpoons 1$ equilibration.

When C_2H_4 was introduced into the $\text{H}_2/\text{*H}^+$ -exchange reaction catalyzed by both Pt systems studied, the exchange rate was found to decrease substantially (see, for example, Figs. 2 and 8, curves 1 and 2). Simultaneously the ethylene hydrogenation reaction proceeded at a high rate, and incorporation of tritium in both ethane formed

and ethylene was detected (Fig. 9). Moreover, the specific radioactivity of ethylene was about 25 times higher than that of dihydrogen, indicating the occurrence of intensive $\text{C}_2\text{H}_4/\text{*H}^+$ -exchange. Taking Scheme 2 into account, these observations can be attributed to the interaction of 2 with C_2H_4 accompanied by the rapid (as compared with the rate of protolysis of the Pt–H bond in 2) and quantitative but reversible formation of the hydrido-ethylene 6 and ethyl-ethylene 7 complexes of Pt(II).

To explain the intensive $\text{C}_2\text{H}_4/\text{*H}^+$ -exchange, it is necessary also to consider the possibility of the rapid exchange of hydrogen atom in some of the Pt hydride complexes with the solvent protons ($\text{Pt}-\text{H}/\text{*H}^+$ -exchange). The latter exchange can occur through the reversible acid type dissociation of Pt–H bond (as it was supposed for Pd–H bond of the hydride complex $[\text{HPdP}_3]^+$ [9]), or through the oxidative addition of *HX molecule to Pt(II) hydride complex followed by reductive elimination of HX molecule from Pt(IV) dihydride complex formed. Pt–H/ *H^+ -exchange appears most likely to proceed with the cationic hydrido-ethylene complex 6, the latter being in an equilibrium with the ethyl-ethylene complex 7 responsible for $\text{C}_2\text{H}_4/\text{*H}^+$ exchange and ethylene hydrogenation.

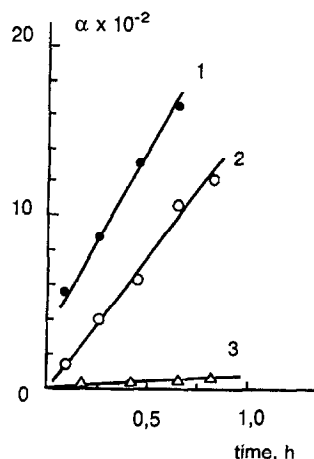


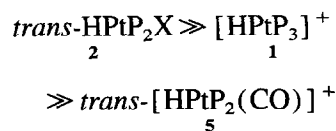
Fig. 9. Time dependence of specific radioactivities (α) of ethane (1), ethylene (2) and dihydrogen (3) in the course of $\text{H}_2/\text{*H}^+$ exchange performed in the ' $\text{P}_4\text{Pt}-\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ ' system in the presence of C_2H_4 (gas mixture $\text{H}_2:\text{C}_2\text{H}_4:\text{Ar} = 1:2:1$). The other experimental conditions were exactly the same as for Fig. 8.

It should be pointed out that the initial rate of ethylene hydrogenation to give ethane in the 'P₂PtX₂-CF₃COOH/H₂O' system (total P/Pt=4, [H₂O]=5 vol.%, 60°C, H₂:C₂H₄=1:1) was more than one order of magnitude higher than that for the 'P₄Pt-CF₃COOH/H₂O' system: 280 and 15 mol C₂H₆/g-at. Pt·h, respectively. The rate of hydrogenation in the former system gradually decreased, however, within a period of about an hour it approached the rate value found for the latter system. This kind of catalytic behaviour of the 'P₂PtX₂-CF₃COOH/H₂O' system in the ethylene hydrogenation reaction is essentially similar to that observed for the hydrogen isotopic heteroexchange reaction and, by analogy with the latter reaction, can be explained in terms of equilibrium (4). In the presence of the hydride complex **2**, which in a high initial concentration is active towards C₂H₄, the hydrogenation rate is also high. However, the concentration of **2** gradually drops during the reaction owing to **2** ⇌ **1** equilibration.

Introduction of CO into the H₂/^{*}H⁺-exchange reaction catalyzed by both Pt systems rapidly and completely inhibited the reaction (see, for example, Figs. 2 and 8, curve 3). When ethylene along with CO was introduced into the H₂/^{*}H⁺-exchange reaction, for both Pt systems the reactions of H₂/^{*}H⁺ exchange (Fig. 8, curve 4), C₂H₄/^{*}H⁺ exchange and ethylene hydrogenation were completely inhibited. These results together with the above NMR data on formation and properties of complexes **5** and **9** evidence for: (i) rather rapid and essentially irreversible formation of the hydrido-carbonyl complex **5** upon interaction of CO with both **1** and **2**; (ii) extremely high resistance of **5** to protolysis of the Pt-H bond and to insertion of ethylene into this bond; (iii) stereochemical rigidity of the ethyl ligand in the ethyl-carbonyl complex **9** (formed along with **5** from complex **2** in the presence of CO and C₂H₄, according to Scheme 1), which is in contrast to the dynamic behaviour of the ethyl ligand in the ethyl-ethylene complex **7** that manifests itself in C₂H₄/^{*}H⁺ exchange.

To summarize this part of our investigation, we can conclude that the comparative catalytic behav-

our of the 'P₄Pt-CF₃COOH/H₂O' and 'P₂PtX₂-CF₃COOH/H₂O' systems in the hydrogen isotopic exchange and ethylene hydrogenation reactions is rather similar to that in the ethylene hydrocarbonylation reaction. In every reaction the latter platinum system shows a much higher initial catalytic activity which, however, gradually drops to a level of the former platinum system. The essential difference is that, in the case of the hydrogen isotopic exchange and ethylene hydrogenation reactions, the catalytic activity of the 'P₂PtX₂-CF₃COOH/H₂O' system is inhibited by excess PPh₃ ligand within 1–2 h due to **2** ⇌ **1** equilibration (or, alternatively, by the disproportionation process (3)). On the contrary, in the case of the ethylene hydrocarbonylation reaction, the catalytic activity of the 'P₂PtX₂-CF₃COOH/H₂O' system seems to be inhibited eventually owing to quantitative conversion of Pt complexes into thermodynamically the most favourable and extremely inert hydride complex **5**. Thus, an important factor determining the variation with the time of the catalytic activity for the platinum systems in the ethylene hydrocarbonylation (and hydrogenation) reactions is the comparative reactivity of the hydride complexes **1**, **2** and **5** to ethylene. This reactivity strongly decreases in the following order:



This series seems to show the reducing ability of ethylene to be inserted into the Pt-H bond of complexes **1**, **2** and **5** via a dissociative mechanism involving the square-planar intermediates, such as the hydrido-ethylene complex **6**. This, in its turn, appears to be determined by the increase of the relative strength of the Pt-L bonds in the L sequence: X⁻ (CF₃COO⁻) < P (PPh₃) < CO (in accordance with the sequence (6)), as well as by general increase of the strength of the Pt-ligand bonds in the sequence of complexes **2** < **1** < **5**, taking into account a cationic character of **1** and **5** and the additional increase of a positive charge on

the platinum ion in **5** due to the presence of a strong π -acceptor ligand CO.

It is noteworthy, that the reactivity of **5** (unlike that of **1**), towards ethylene insertion into the Pt–H bond drastically changed upon addition of the catalytic amounts of tin(II) acetate (Sn/Pt \leq 0,01) [10]. Thus, in the presence of Sn(OAc)₂ the CF₃COOH solution of **5** rapidly interacted with ethylene at 70°C to give the ethyl-carbonyl complex **9** with the essentially quantitative yield. The further transformations of **9** on the way to DEK were, however, unaffected by the presence of Sn(OAc)₂.

Tin(II) chloride has been widely used as a promoter of the platinum phosphine complex based catalysts for olefin hydrogenation and hydroformylation. The complex [HPt(CO)(PPh₃)(SnCl₃)] was supposed to be a catalytically active intermediate in hydroformylation of olefins [16,17]. The promoting effect of SnCl₃[−] ligand was ascribed to its ability to stabilize the five-coordinated state of Pt(II) ion [18,19], that can favour the olefin insertion into the Pt–H bond via the trigonal bipyramidal intermediates [20]. Taking this into account, we propose that the ethylene insertion into the Pt–H bond of the hydrido-carbonyl complex **5** proceeded in the CF₃COOH solution in the presence of the Sn(OAc)₂ additives via an associative mechanism involving the formation of the five-coordinated intermediate – [HPt(CO)(C₂H₄)P(Sn)]⁺, (Sn) being a tin-containing ligand, probably, Sn(CF₃COO)₂. The much higher reactivity of **5**, compared to **1**, to C₂H₄ insertion via an associative mechanism appeared to be due to the presence in **5** of a strong π -acceptor ligand CO, which facilitated the coordination of C₂H₄ to Pt(II) ion.

3.3. On the mechanism of the ethylene hydrocarbonylation reaction in the systems 'platinum triphenylphosphine complex–CF₃COOH/H₂O'

From all of the above discussions, one can draw an unambiguous conclusion that the so-called 'hydride mechanism' of the reaction of ethylene

hydrocarbonylation to DEK is realized in the 'platinum triphenylphosphine complex–CF₃COOH/H₂O' systems investigated. This mechanism involves the following key stages which promote or prevent DEK formation in the course of interaction of the 'P₂PtX₂–CF₃COOH/H₂O' and 'P₄Pt–CF₃COOH/H₂O' systems with the reactant gases C₂H₄, CO and H₂ as depicted in Scheme 3.

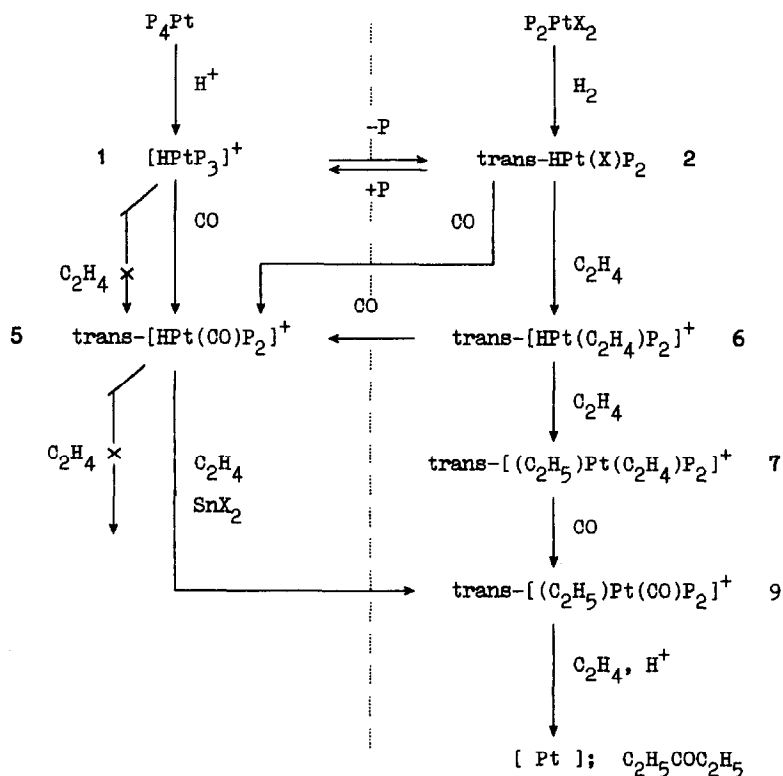
Thus, transformations of Pt complexes during interaction of the 'P₄Pt–CF₃COOH/H₂O' system with C₂H₄, CO and H₂ result in the rapid and quantitative formation of inert hydrido-carbonyl complex **5** (the left side of Scheme 3), that determine the inactivity of the system in the ethylene hydrocarbonylation reaction.

For the 'P₂PtX₂–CF₃COOH/H₂O' system, where the concentration of the key complex **2** seems to be rather high at the initial period of the reaction, the sequence of transformations of the hydride **2** (the right side of Scheme 3) results, within the first few minutes of the reaction, in the formation of a mixture of complexes **5** and **9**.

Further transformations of **9** on the way to DEK (Scheme 3) is the complex stage and, by analogy with the Pd system [3], may involve (i) isomerization of **9** to the corresponding propionyl complex through the intramolecular insertion of CO into the Pt–C₂H₅ bond, (ii) interaction of propionyl complex with C₂H₄ and (iii) decomposition of the Pt ketoalkyl intermediate formed, to give DEK. It is likely that any of the above transformations and at least isomerization of **9** to a propionyl complex proceeds much slower than spectroscopically observed stages of the complex **9** formation and seems to be the rate-determining step of the hydrocarbonylation reaction. As this takes place, the rate of DEK formation will be described by the equation.

$$W_{\text{DEK}} \approx k[\mathbf{9}] \quad (8)$$

where k is an effective rate constant of the stage of ethyl-carbonyl complex **9** transformation (Scheme 3), and $[\mathbf{9}]$ is an instant concentration of **9** in solution.



In the course of the reaction, as **9** converts to DEK and the initial complex P_2PtX_2 , within a period of several hours, the ' P_2PtX_2 -CF₃COOH/H₂O' system (in accordance with the Pt hydride complex stability order (6)) also seems to achieve a steady state which was found for the ' P_4Pt -CF₃COOH/H₂O' system. This state, as mentioned above, is characterized by a quantitative conversion of Pt complexes into extremely inert complex **5** leading to complete deactivation of the ' P_2PtX_2 -CF₃COOH/H₂O' system. Thus, one can conclude that a slight amount of DEK (0.1 mol/g-at. Pt) [4], produced by the ' P_2PtX_2 -CF₃COOH/H₂O' system under the ethylene hydrocarbonylation reaction conditions, arises from complex **9** formed at the initial period of the reaction.

On the other hand, taking into account the catalytic effect of Sn(OAc) additives on the reactivity of the hydrido-carbonyl complex **5** (Scheme 3) found previously [10], one can expect both platinum-tin systems, ' P_2PtX_2 (or P_4Pt)-

Sn(OAc)₂-CF₃COOH/H₂O', to possess the steady-state and uniform catalytic activity in the ethylene hydrocarbonylation reaction. The rate of DEK formation, determined by Eq. (8), seems to have a maximum value in this case due to [**9**] being approximately equal to total [Pt].

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