Reactions of Tertiary Alcohols with Palladium(II) Tetraaqua Complex. Formation of Palladium π-Allyl Complexes

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Abstract—Transformations of 2-methyl-2-propanol, 2-methyl-2-butanol, 2-methyl-2-pentanol, 1-methyl-1cyclohexanol, and 1-ethyl-1-cyclohexanol in the presence of tetraaquapalladium(II) ions in perchloric acid madium were studied. It was found that the reactions give rise to palladium(II) π -allyl complexes. The reaction rate increases and the yield of the corresponding π -allyl complex decreases with increasing hydrocarbon chain length. Addition of iron(III) ions to the systems essentially increases the yield of palladium π -allyl complexes. The olefin formed from the corresponding tertiary alcohol participates in the formation of the palladium π -allyl complex. Oxidation of 2-methyl-2-butanol with tetraaquapalladium(II) ions gives the isomeric palladium π -allyl complexes [Pd(η^3 -(CH₃)₂CCHCH₂)bpy]ClO₄ and [Pd(η^3 -(CH₂C(CH₃))CHCH₃))bpy]ClO₄, which were isolated using 2,2'-bipyridyl and characterized by ¹H and ¹³C NMR spectroscopy.

Earlier we studied transformations of 2-methyl-2propanol in its reaction with the complex $[Pd(H_2O)_4]$. $(ClO_4)_2$ (I) in perchloric acid in the range 45–75°C [1]. The major reaction product was a palladium methallyl complex. On the basis of kinetic regularities of the process we assumed that the reaction proceeds through intermediate formation of 2-methylpropene. Other saturated tertiary alcohols could also be assumed to transform to the corresponding isomeric palladium π -allyl complexes. To check this assumption, we studied in this work transformations of 2-methyl-2-butanol, 2-methyl-2-pentanol, 1-methyl-1cyclohexanol, and 1-ethyl-1-cyclohexanol in their reactions with complex I in perchloric acid medium.

The reactions were carried out at the following initial concentrations of the reagents, M: complex I 5.7×10^{-3} , perchloric acid 0.53–0.63, and alcohol 0.1 (except for 1-ethyl-1-cyclohexanol whose concentration did not exceed 0.05 M because of its restricted solubility in water).

The formation of palladium(II) π -allyl complex can be detected by the appearance of a characteristic absorption band at ~320 nm in the UV spectrum (extinction coefficient log ε 3) [2]. We observed these bands in all the UV spectra measured in the course of the reactions of the tertiary alcohols under study with complex **I**, which gave grouds to conclude that the reactions actually give palladium π -allyl complexes.

Palladium π -allyl complexes are usually formed by reactions of olefins with palladium(II) compounds. Tertiary alcohols are known to be readily dehydrated in acidic media to form olefins. To confirm the fact that palladium π -allyl complexes originate from olefins formed by dehydration of tertiary alcohols in the reaction solution, we studied the reactions by NMR spectroscopy and iodometry.

Analysis of the ¹H NMR spectra showed that secondary (internal) olefins are formed selectively from the corresponding tertiary alcohols in the presence of complex I: 2-methyl-2-butene from 2-methyl-2-butanol, 2-methyl-2-pentene from 2-methyl-2-pentanol, 1-methyl-1-cyclohexene from 1-methyl-1-cyclohexanol, and 1-ethyl-1-cyclohexene from 1-ethyl-1cyclohexanol.

Changes in the concentration of olefin in the course of reaction between tertiary alcohol and complex **I** were estimated by iodometry. It is necessary to note that the rates of olefin formation we impossible to determine because of the lack of data on equilibrium constants of dehydration of alcohols under our experimental conditions. Therefore, the kinetic curves given in Figs. 1 and 2 relate to olefin accumulation both in the presence of complex **I** and without it.

As seen from Fig. 1, curve 1, and Fig. 2, curve 2, in the absence of palladium olefin is accumulated at a constant rate from the very beginning of the reaction. At the same time, in the presence of complex I olefin either was not detected within a certain period (with 2-methyl-2-propanol; see Fig. 1, curve 3) or its content was insignificant (with 1-methyl-1-cyclohexanol; see Fig. 2, curve 3). The appearance of this period is attributable to a high rate of olefin consump-



Fig. 1. Plots of the concentration of complex **I** (C_{Pd}) and olefin (C_{Ol}) vs. time for the reaction with 2-methyl-2-propanol. C_{alc} 0.1 M, C_{HCIO_4} 0.5 M, and C_{Pd} 0.0057 M, 55°C. (1) Consumption of complex **I**, (2) accumulation of 2-methylpropene in the absence of complex **I**, and (3) accumulation of 2-methylpropene in the presence of complex **I**.

tion in reaction with palladium(II), and its duration depended on the rate of consumption of tetraaquapalladium(II) ions. As the concentration of complex I decreased (Fig. 1, curve 1, and Fig. 2, curve 2), the rate of alkene accumulation began to increase and reached a constant limiting value when complex I had been consumed completely. This limiting rate is equal the rate of olefin formation from alcohol in acidic medium in the absence of palladium(II).

As it was found earlier [1], the rate of formation of palladium π -allyl complex depends on alcohol concentration and does not depend on palladium(II) concentration. Thus, we suggested that the limiting stage of the reaction under study is dehydration of the parent tertiary alcohol, which is followed by fast reaction of alkene with complex **I**. The presence of an "inductive period," during which the rate of olefin consumption is much greater than the rate of its formation, confirms this mechanism. The obtained data provide indirect evidence showing that the oxidation of tertiary alcohols with tetraaquapalladium(II) ions occurs via olefin formation.

We studied the effect of alcohol structure on the rate of complex I consumption and found that the reaction rate increases in the order 2-methyl-2-propanol < 2-methyl-2-butanol < 2-methyl-2-pentanol < 1-methyl-1-cyclohexanol < 1-ethyl-1-cyclohexanol. It is important to note that the reactivity order of tertiary alcohols is opposite to the reactivity order of homo-



Fig. 2. Plot of the concentrations of complex **I** (C_{Pd}) and olefin (C_{Ol}) vs. time for the reaction with 1-methyl-1-cyclohexanol. C_{alc} 0.1 M, C_{HCIO_4} 0.63 M, and C_{Pd} 5.5×10⁻³ M, 40°C. (1) Consumption of complex **I**, (2) accumulation of 1-methyl-1-cyclohexene in the absence of complex **I**, (3) accumulation of 1-methyl-1-cyclohexene in the presence of complex **I**, and (4) accumulation of 1-methyl-1-cyclohexene in the presence of complex **I** and Fe(III).

logous alkenes toward palladium(II) chloride or acetate: The reaction rate increases with increasing hydrocarbon chain length in olefin, in particular, for olefins with internal double bonds [3–5].

It is known that reactions of linear and branched olefins with palladium(II) salts yield carbonyl compounds or palladium π -allyl complexes [6]. Therewith, several isomers are formed, the highest yield corresponding to a terminal π -allyl complex [reaction (1)]:



We earlier isolated and described a palladium methallyl complex obtained by oxidation of 2-methyl-2-propanol. Similarly, from the postreaction solution of complex I and 2-methyl-2-butanol we isolated, with the help of 2,2'-bipyridyl, a palladium compound which was characterized by ¹H and ¹³C NMR spectroscopy (Fig. 3).

Based on these and published data [7-10], we came to a conclusion that the resulting compound is a mix-





Fig. 3. (a) 1 H and (b) 13 C NMR spectra of compounds IIa and IIb.

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Table 1. Effect of alcohol structure on the yield of the corresponding palladium π -allyl complex; $C_{\rm alc}$ 0.1 M, $C_{\rm Pd(II)}$ 5.5 × 10⁻³ M, and $C_{\rm HClO_4}$ 0.53 M

Alcohol	<i>T</i> , ℃	Yield, % [per consumed Pd(II)]	In the presence of Fe(III)		
			$C_{\text{Fe(III)}} \times$, 10 ³ , M	yield, % [per consumed Pd(II)]	
2-Methyl- 2-propanol	55	58	at 3 to 25	99	
2-Methyl-	45	50	3	77	
2-butanol			5.5	87	
			30	93	
2-Methyl-	40	16	13	42	
2-pentanol			30	39	
			60	48	
			120	54	
1-Methyl-	40	—	10	1	
1-cyclo-			60	37	
hexanol			120	41	
1-Ethyl-	40	1.2	13	28	
1-cyclo			30	52	
hexanol ^a			60	58	
			120	79	

^a C_{alc} 0.05 M.

palladium π-allyl ture of two isomeric complexes $Pd(\eta^3-(CH_3)_2CCHCH_2)bpy]ClO_4$ (IIa) and $[Pd(\eta^3-(CH_2C(CH_3)CHCH_3))bpy]ClO_4$ (**IIb**). The selectivities with respect to complexes IIa and IIb were 83 and 17%, respectively. These data suggest that the dominating direction of the formation of palladium π -allyl complex in the reaction of 2-methyl-2-butanol with complex I is a pathway in involving retention of methyl groups at the quaternary carbon atom. This feature distinguishes the method of synthesis of π -allyl complexes, developed in this work from earlier described methods. We managed to isolate palladium π -allyl complexes from solutions of other tertiary alcohols. Presently we are studying them by physicochemical methods. It is likely that the distribution of possible isomers will be the same.

Table 1 lists the yields of palladium π -allyl complexes for various alcohols.

The formation of palladium(0) in the reactions of all the alcohols under study with complex I point to occurring redox reactions. Taking into account published data, we attempted to find carbonyl compounds in the reaction system using 2,4-dinitrophenylhydrazine. In the systems with 2-methyl-2-pentanol and

2-methyl-2-butanol no carbonyl compounds were found, whereas in the systems with 1-methyl-1-cyclohexanol and 1-ethyl-1-cyclohexanol the yields of carbonyl compounds were 7 and 14%, respectively, with respect to consumed palladium(II).

The yields of target products of olefin oxidation with palladium(II) are commonly improved by using various oxidants (co-oxidants) for regeneration of palladium(II) in the catalytic cycle. In this work we used as co-oxidants *p*-benzoquinone, copper(II) and iron(III) sulfates, and a solution of thallium(III) perchlorate.

It is known that *p*-benzoquinone is the best cooxidant for olefin oxidation with palladium(II) in halide-free [11]. However, in our case *p*-benzoquinone and Cu(II) appeared to be inert in the transformations of alcohols both to π -allyl complexes and to oxidation products. In the presence of Tl(III), complex I was not consumed for a long time, until Tl(III) had completely reduced to Tl(I). Later on Tl(I) exerted no effect on alcohol oxidation with complex I.

We obtained unexpected results in the oxidation of alcohols with complex I in the presence of iron(III) ions. The accumulation of 1-methyl-1-cyclohexene with time in the presence of complex I and Fe(III) is shown in Fig. 2, curve 4. As seen from the figure, in the presence of iron(III) ions the induction period was much longer, since iron(III) affected the rate of complex I consumption: The lower the rate of complex I consumption, the longer the period when olefin is not accumulated in the solution.

With aliphatic alcohols, the rate of complex **I** consumption varied insignificantly with initial concentration of iron(III). With cyclic alcohols, this rate noticeably decreased with increasing iron(III) concentration (Fig. 4). Therewith, the ionic strength *I* of 1.5 was kept constant by adding NaClO₄.

Irrespective of the nature of tertiary alcohol, the yield of palladium π -allyl complexes in the presence of iron(III) ions essentially increased (Table 1). In all the systems under study iron(II) formed, implying that iron(III) ions take part in redox reactions. Addition of iron(III) ions to the reaction solution resulted in a considerable reduction in the amount of palladium(0) (Table 2).

These data point to a catalytic nature of the oxidation of tertiary alcohols with complex I in the presence of iron(III), where iron(III) ions appear to function as the co-oxidant regenerating the oxidized form of palladium. As seen from Table 2, the ratio of the total number of Pd(0) moles formed in the reaction without Fe(III) to the change in the number of Fe(III) moles within the same reaction time in the presence of Fe(III) ions was not 1/2, as expected for a usual catalysis with iron(III) ions as co-oxidant.

Our present data and the kinetic data obtained in [1] allow us to propose the following scheme (with aliphatic alcohols as example) of the reaction of a tertiary alcohol with complex **I**.

$$(CH_3)_2COH(CH_2)_nCH_3 \xleftarrow{[H^+]}{H_2O} (CH_3)_2C=CH(CH_2)_nCH_3$$
$$\xrightarrow{Pd(II)}{k_1} [\pi-Allyl],$$
$$[\pi-Allyl] \xrightarrow{Pd(II)}{k_2} \text{``Oxidation products''} + Pd(0).$$

The tertiary alcohol undergoes a slow acid-catalyzed dehydration reaction to give the corresponding olefin. The olefin rapidly reacts with complex **I** to form a π -allyl complex. This organometallic compound is oxidized with complex **I** to the corresponding products, and Pd(0) is formed. It is important to note that iron(III) ions do not oxidize the palladium π -allyl complex.

The rate of accumulation of the palladium π -allyl complex [π -Allyl] can be described by kinetic equation (2):

$$d[\pi-\text{allyl}]/d\tau = k_1[\text{Pd}(\text{H}_2\text{O})_4]^{2+}[\text{O}]$$

- $k_2[\pi-\text{allyl}][\text{Pd}(\text{H}_2\text{O})_4]^{2+}.$ (2)

Here [OI] is olefin concentration.

Equation (2) is an equation of a self-catalyzed reaction.

Mathematical analysis of the kinetic equation allows the following assumptions. When the rate constant k_1 considerably exceeds the rate constant k_2 , the yield of the palladium π -allyl complex will increase and palladium(0) will be formed in minor amounts. Such a situation seems to take place with aliphatic alcohols, particularly in the oxidation of 2-methyl-2-propanol and 2-methyl-2-butanol. When the rate constants are equal to each other or when k_2 is higher than k_1 , the amount of the palladium(0) formed will increase, and the yield of the π -allyl complex will decrease, as is observed with tertiary cyclic alcohols. Iron(III) additives prevent accumulation of palladium(0). As a result, the rate of formation and the yield of the π -allyl complex increase and, on the other hand, its decomposition rate decreases.

Solution of differential equations for 2-methyl-2propanol and 1-methyl-1-cyclohexanol with account

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Fig. 4. Plots of the concentration of complex **I** vs. time for the oxidation of 1-methyl-1-cyclohexanol at various Fe(III) concentrations. $C_{Pd(II)}$ 5.5×10⁻³ M, C_{alc} 0.1 M, and C_{HCIO_4} 0.63 M, 40°C, *I* 1.5. $C_{Fe(III)}$, M: (*I*) 0, (2) 0.01, (3) 0.025, (4) 0.06, and (5) 0.12.

for material balance both in the presence and in the absence of Fe(III) [Eqs. (3) and (4), respectively] for various k_1/k_2 ratios allowed us to compare the experimental and calculated kinetic curves.

$$C^{0}_{Pd(II)_{aq}} = [Pd(H_2O)]^{+2} + [\pi-Allyl],$$
 (3)

$$C_{Pd(II)_{aq}}^{0} = [Pd(H_2O)]^{+2} + [\pi-Allyl] + Pd(0)].$$
 (4)

Table 2. Effect of reaction conditions on the amount of the Pd(0) formed; $C_{Pd(II)}$ 5.5 × 10⁻³ M, C_{HCIO_4} 0.5 M, and C_{alc} 0.1 M

	<i>T</i> , ℃	Pd(0), %		v[D4(0)]/
Alcohol		without Fe(III)	with Fe(III) ^a	Δ [Fe(III)] ^b
2-Methyl-2- propanol	55	40	0 ^c	1/0.5
2-Methyl-2-butanol	45	51	5	1/1
2-Methyl-2- pentanol	40	56	25	1/1
1-Methyl-1-cyclo- hexanol	40	87	7	1/1.5
1-Ethyl-1-cyclo- hexanol ^d	40	96	7	1/1.5

^a At the Fe(III) concentration 0.12 M. ^b Ratio of the total number of Pd(0) moles (v) formed in the reaction without Fe(III) to the change in the number of Fe(III) moles within the same reaction time in the presence of Fe(III) ions. ^c At Fe(III) concentrations of 3×10^{-3} M and higher. ^d C_{alc} 0.05 M.



Fig. 5. Plots of the concentration of complex **I** vs. time (a) for the reaction with 2-methyl-2-propanol and (b) for the same reaction in the presence of Fe(III). (1) Calculation and (2) experiment.

In all the cases the calculated curves fairly fitted experimental (Figs. 5 and 6) at a k_1/k_2 ratio of 40 for 2-methyl-2-propanol and of 2.5 for 1-methyl-1-cyclohexanol.

EXPERIMENTAL

The NMR spectra were obtained on a Bruker PDX-300 instrument in $(CD_3)_2CO$.

All reactions were carried out in a temperaturecontrolled bubbling reactor equipped with a sampler.

Complex I was prepared by the procedure in [12]. Chemical grade 2-methyl-2-propanol and 2-methyl-2pentanol were used. 2-Methyl-2-butanol, 1-methyl-1cyclohexanol, and 1-ethyl-1-cyclohexanol were prepared by the procedure in [13]. The concentration of perchloric acid in the initial solution of complex I was determined by acid-base titration. The concentration of complex I was determined by spectrophotometry



Fig. 6. Plots of the concentration of complex **I** vs. time (a) for the reaction with 1-methyl-1-cyclohexanol and (b) for the same reaction in the presence of Fe(III).

(1) Calculation and (2) experiment.

using the absorption band of a palladium–tin complex (λ_{max} 635 nm) [14]. The concentration of palladium bound in π -allyl complex was determined by the difference in the palladium(II) concentrations in a sample with added aqua regia and without it. Before analysis palladium(0) was removed from solutions by centrifugation. The concentration of iron(III) in the course of reaction was determined by spectrophotometry using the color reaction with 10% 2-hydroxy-5-sulfobenzoic acid (λ_{max} 510 nm) [15]. The optical densities were measured on an FEK-56M photoelectrocolorimeter.

The progress of olefin formation was controlled as follows. Argon was continuously passed through the reaction solution and then directed through a glass outlet tube to an ice-cooled methanol trap. The traps were changed at intervals dictated by the kinetics. Quantitative analysis for alkenes was performed by iodometric titration [16], and their structures were determined by NMR spectroscopy after replacement of the methanol in the traps by deuterochloroform.

The concentrations of alcohols were determined by GLC on a Tsvet-100 chromatograph (flame-ionization detector, 1000×3 -mm metallic column, liquid phase Apiezon-L). The oven temperature was $100-140^{\circ}$ C (depending on alcohol structure), carrier gas nitrogen (34 ml/min), internal standard isopropanol.

Palladium π -allyl complexes were isolated by adding excess 2,2'-bipyridyl to the reaction solutions after reaction completion. The resulting white precipitate was filtered off and washed with water and ether.

Complex Ia. ¹H NMR spectrum, δ , ppm: 1.46 s (3H, *anti*-CH₃) 1.84 s (3H, *syn*-CH₃), 3.94 d (1H, *syn*-H³, ³J 13.3 Hz), 4.38 d (1H, *syn*-H³, ³J 8.2 Hz), 5.74 d.d (1H, H², ³J_{HH-anti} 13.3, ³J_{HH-syn} 8.2 Hz).

Complex IIb. ¹H NMR spectrum, δ , ppm: 1.68 d (3H, CH₃, ³J 7.2 Hz), 2.25 s (3H, CH₃), 3.46 s (1H, *anti*-H¹), 4.27 s (1H, *syn*-H¹), 4.16 q (1H, H³, ³J 7.2 Hz).

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