Oxidation of dicyclopentadiene catalyzed by palladium(II) acetate and *p*-benzoquinone in the presence of inorganic acid

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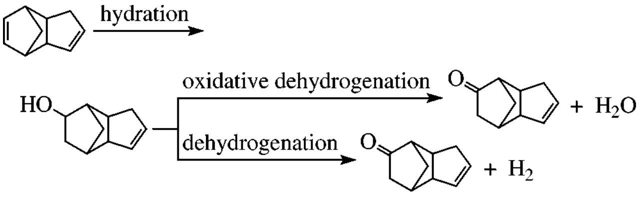
The oxidation of dicyclopentadiene catalyzed by palladium(II) acetate and benzoquinone in the presence of perchloric acid was studied. Tricyclodecenone in high selectivity (85–98%) at a conversion of dicyclopentadiene up to 76% was obtained. The kinetic model assumed the significant inhibition complexation between dicyclopentadiene and tricyclodecenone with the catalytic species.

Keywords: dicyclopentadiene, Wacker oxidation, $Pd(AcO)_2$, benzoquinone, kinetics

1. Introduction

The derivatives of the dicyclopentadiene (DCPD) and, in particular the oxygen containing ones, have a terpenic (diterpenic) structure. Therefore it is not surprising, that all of them have somewhat fragrance properties [1–10]. The great demands, in this sense, use unsaturated and saturated alcohols, ketones and esters. Thus, the 6-(or 7)-tricyclo[5.2.1.$0^{5,9}$]decen-2-one (tricyclodecenone, TCD) was obtained by hydration of dicyclopentadiene and subsequent oxidative dehydrogenation or catalytic dehydrogenation.



Scheme 1.

The water adds to the double bond of the norbornene fragment of the dicyclopentadiene molecule in the presence of acidic catalysts such as sulphuric acid or ionic exchangers [2,7,8]. Disadvantages of these methods are the multi-step synthesis and the low yields of target products.

The one-step palladium(II) oxidation of olefins to appropriate ketones (Wacker oxidation) is a well-known organic synthetic process. However, the oxidation of higher terminal olefins, and the internal and cyclic ones is extremely slow under the usual conditions [11]. This reaction is carried out on numerous cyclic alkenes and gives ketones in fair yields [12,13]. As an exception, a review [14] maintains that cyclopentene gives cyclopentanone in 97% yield.

No information has been published concerning the Wacker oxidation of the dicyclopentadiene. Oxidation of norbornene, which leads to the formation of the respective keto-derivative, has not been described in literature too. Only the palladium aqua-complexes, which are a part of the polymerization process, have been reported [15]. The oxidation of vinyl norbornene in the presence of Wacker-type catalysts leads to the formation of a new carbon cycle or various chlorine derivatives [16]. Cyclopentene is oxidized over a $PdCl_2$–dimethylacetamide complex to give cyclopentanone at 30% conversion and 65% selectivity [17]. The oxidation of cyclopentene [17–22] and cyclohexene [17,23] with alcoholic palladium(II) salts has also been investigated. The $PdCl_2$ complexes also catalyze the oxygenation of cyclopentene by *tert*-butyl hydroperoxide in alcoholic solvent [18,24].

Recently, an improved method for palladium(II)-catalyzed Wacker oxidation of cyclic and internal olefins is described [25,26]. Addition of strong inorganic acids to the palladium(II)/benzoquinone oxidation in a chloride free solution leads to significant rate enhancements. The oxidation of a number of olefins has been examined and internal and cyclic olefins are rapidly and quantitatively converted to their corresponding ketones. However, the oxidation of dicyclopentadiene to above mentioned tricyclodecenone has not been studied.

In this paper we report the results of our studies on the oxidation of dicyclopentadiene catalyzed by palladium(II) acetate and benzoquinone in the presence of perchloric acid and the kinetics of the reaction.

2. Experimental

2.1. Chemicals

Dicyclopentadiene (Aldrich, 95%), palladium(II) acetate (Fluka, purum), perchloric acid (VEB Laborchemie Apolda,

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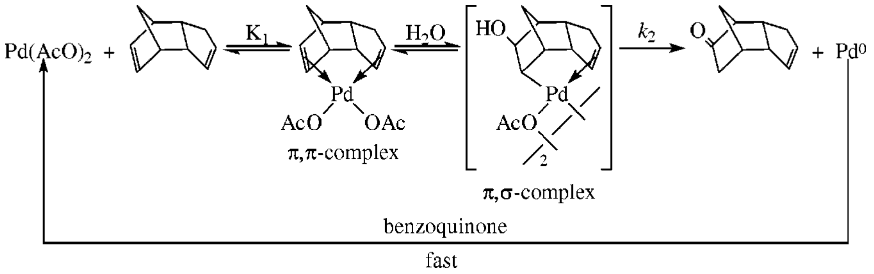
Table 1
Infuence of perchloric acid concentration on the oxidation of dicyclopentadiene at 100 °C.

Time (h)	Concentration of dicyclopentadiene and tricyclodecenone ($\times 10^2$ mol l^{-1})					
	0.24 mol l^{-1} $HClO_4$		0.36 mol l^{-1} $HClO_4$		0.48 mol l^{-1} $HClO_4$	
	DCPD	TCD	DCPD	TCD	DCPD	TCD
0	13.8	0	13.8	0	13.8	0
0.5	10.8	2.2	9.7	3.2	8.4	5.2
1.0	8.7	4.0	7.5	5.3	5.7	8.0
1.5	8.2	4.8	6.8	6.2	4.1	9.4
2.0	7.1	5.8	5.4	7.5	3.5	10.3
2.5	6.8	6.2	4.7	8.0	3.3	10.4
3.0	6.2	6.5	4.2	8.5	3.1	10.5



Scheme 2.

70%) and acetonitril (Riedel-de Haën, min. 99.7%) were purchased and used without further purification. Benzoquinone (VEB Laborchemie Apolda) was sublimated and recrystallized from hexane.

2.2. Apparatus and procedure

The experiments were carried out in a thermostated (±0.1 °C) batch reactor (50 ml) fitted with a reflux condenser and magnetic stirrer. Palladium(II) acetate (0.1 mmol), benzoquinone (4.5 mmol), and the perchloric acid (6–12 mmol) were dissolved in acetonitril (22 ml) and water (3 ml). The reactor was purged with argon for 30 min and stirred intensively until the palladium acetate had dissolved. The dicyclopentadiene (5 mmol) was then added to the reactor by a syringe.

The kinetics runs were monitored by periodically removing an aliquot of 1 ml (by syringe) from the reaction mixture. The products were separated from the catalyst by extraction into 1 ml toluene or tetraline, washed with 5 ml 30% aqueous sodium hydroxide and analysed.

2.3. Analyses

Products were identified by a gas chromatographic method using a Sigma 2000 (Perkin–Elmer, Norwalk, CT, USA) with authentical samples of the product having the keto-group within the norbornene ring and the compound having the keto-group within the non-norbornene five-memberred ring. The quantitative analysis was performed using heneicosan as an internal standard on a capillary column (50 m) coated with CPMS-1701 stationary phase at injection temperature 200 °C, column temperature 150 °C and nitrogen gas flow of 1.2 ml min^{-1}.

3. Results and discussion

The reaction conditions were selected on the basis of preliminary results and some literature data [25]. It is necessary to keep the degree of conversion at an optimum level, which depends on the overall economic efficiency of the process. It is for this reason why the experimental series were carried out using perchloric acid in amount of 120–230 mol% concerning the amount of dicyclopentadiene. At higher acid concentrations an inhibition effect was observed.

The influence of perchloric acid concentration on the oxidation of dicyclopentadiene at 100 °C is shown in table 1.

The experimental curves of the tricyclodecenone formation *versus* reaction time at a variety of perchloric acid concentration are tending to a constant value, that is typically for the parallel reactions.

Attempts to oxidize the dicyclopentadiene in the above mentioned conditions led us to obtain the tricyclodecenone in high selectivity (85–98%) at a conversion of dicyclopentadiene up to 76%. The amount of by-products is negligible.

It has been shown that dicyclopentadiene forms chelate π,π-palladium(II) complexes, which react with nucleophiles to dimeric π,σ-bonded palladium(II) complexes [27–29]. The formation of tricyclodecenone can be explained by scheme 2, where K_1 and k_2 are the equilibrium and rate constants, respectively.

Our previous investigation [30] on the 1,5,9-cyclododecatriene oxidation has indicated the formation of different inactive intermediates between the transition metal and the substrate, solvent and products. Furthermore, the ketones are known as potential oxidation inhibitors [31]. In this respect, to explain the potential inhibiting effect of the re-

Table 2
Calculated values of the kinetic parameters at various acid concentration.[a]

$[HClO_4]$ $(mol\,l^{-1})$	k_{eff} $(l\,mol^{-1}\,min^{-1})$	k_2 $(l\,mol^{-1}\,min^{-1})$	K_1 $(l\,mol^{-1})$	K_3 $(l\,mol^{-1})$	SSR $\times 10^5$	$F_{exp.}$
0.24	1.930	1.880	245.0	2639.0	1.680	0.056
0.36	3.360	3.280	329.0	1920.0	2.910	0.097
0.48	6.200	6.100	341.7	1176.0	8.150	0.272

[a] $F_{tabl.}(0.05, 3, 2) = 19.2$.

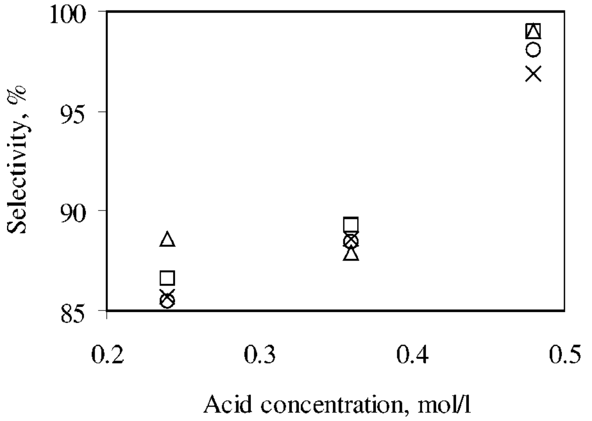


Figure 1. Dependence of the selectivity on the acid concentration. Reaction time 1.5 (×), 2 (□), 2.5 (△) and 3 h (○).

action products the reaction scheme may be extended to the following equilibrium steps:

$$2Pd^{2+} + 2TCD \overset{K_3}{\rightleftharpoons} \left[Pd^{2+}\cdot TCD\right]_2 \tag{1}$$

$$Pd^{2+} + DCPD \overset{K_4}{\rightleftharpoons} \left[Pd^{2+}\cdot DCPD\right] \tag{2}$$

$$Pd^{2+} + TCD \overset{K_5}{\rightleftharpoons} \left[Pd^{2+}\cdot TCD\right] \tag{3}$$

$$Pd^{2+} + DCPD + TCD \overset{K_6}{\rightleftharpoons} \left[Pd^{2+}\cdot DCPD\cdot TCD\right] \tag{4}$$

where Pd^{2+} is the catalytic species.

The quasi-steady-state approximation [32] to the reaction scheme (scheme 2) coupled with equilibria (1)–(4) provides the corresponding rate expressions to the following system of kinetic differential equations:

$$\frac{dC_{DCPD}}{dt} = -\frac{k_{eff}C_{Pd^{2+}}C_{DCPD}}{F}, \tag{5}$$

$$\frac{dC_{TCD}}{dt} = -\frac{k_2 C_{Pd^{2+}}C_{DCPD}}{F}, \tag{6}$$

$$\begin{aligned} F = 1 &+ K_1C_{DCPD}^2 + K_3C_{TCD}^2 + K_4C_{DCPD} \\ &+ K_5C_{TCD} + K_6C_{DCPD}C_{TCD}, \end{aligned} \tag{7}$$

where F is the so-called complex formation function.

Some of the potential complexes can be quite unstable and the corresponding monomials in the denominator (equation (7)) could not reach significant values within the studied experimental conditions. Neglecting the formation of such intermediates, many different models may be derived from the general kinetic equations (5)–(7). In order to reduce the computing time, the fit between experimental data obtained in the oxidation of dicyclopentadiene and the models was evaluated out by a short-cut differential method [33]. To this purpose, a number of rate models were eliminated early on the basis of negative parameters or unexpected trends in the calculated concentrations. The refinement of the parameters of the remained rival models was carried out by the fourth-order Runge–Kutta method combined with the method of Marquardt [34]. The best fit, on the basis of the values of the sum of residuals squares (SSR), the average relative errors ($\Delta\varepsilon$) and the values and significance of the parameters, was performed by the following rate equations:

Table 3
Infuence of temperature on the oxidation of dicyclopentadiene at 0.24 $mol\,l^{-1}$ perchloric acid concentration.

Time	Concentration of tricyclodecenone $(\times 10^2\ mol\,l^{-1})$		
(h)	80 °C	100 °C	120 °C
0	0	0	0
0.5	1.2	2.2	2.8
1.0	2.3	4.0	4.3
1.5	3.2	4.8	5.0
2.0	4.0	5.8	6.0
2.5	4.8	6.2	6.5
3.0	5.1	6.5	–

$$\frac{dC_{DCPD}}{dt} = -\frac{k_{eff}C_{Pd^{2+}}C_{DCPD}}{1 + K_1C_{DCPD}^2 + K_3C_{TCD}^2}, \tag{8}$$

$$\frac{dC_{TCD}}{dt} = -\frac{k_2 C_{Pd^{2+}}C_{DCPD}}{1 + K_1C_{DCPD}^2 + K_3C_{TCD}^2}. \tag{9}$$

This model assumes the significant inhibition complexation between dicyclopentadiene and tricyclodecenone with the catalytic species.

The comparison of the measured concentrations of dicyclopentadiene and tricyclodecenone with the calculated ones by equations (8) and (9) is illustrated in figure 1. The model prediction agreed very well with the experimental results.

The results of the fitting and calculated parameter values obtained with model equations (8) and (9) are summarised in table 2.

The effect of temperature on the rate of oxidation of dicyclopentadiene was examined in the temperature range 80–120 °C in order to obtain activation parameters. Table 3 shows the tricyclodecenone formation versus reaction time at a variety of temperatures at 0.24 $mol\,l^{-1}$ perchloric acid concentration.

In table 4 are listed the calculated parameter values obtained with model equations (8) and (9), the values of the sum square of residuals and average relative errors.

Table 4
Calculated values of the kinetic parameters.[a]

T (°C)	k_{eff} ($\mathrm{l\,mol^{-1}\,min^{-1}}$)	k_2 ($\mathrm{l\,mol^{-1}\,min^{-1}}$)	K_1 ($\mathrm{l\,mol^{-1}}$)	K_3 ($\mathrm{l\,mol^{-1}}$)	SSR $\times 10^5$	$F_{\mathrm{exp.}}$
80	1.107	1.075	288.9	2599.5	2.243	0.075
100	1.930	1.880	245.0	2639.0	1.680	0.056
120	2.957	2.900	309.1	4079.6	1.416	0.072

[a] $F_{\mathrm{tabl.}}(0.05, 3, 2) = 19.2$.

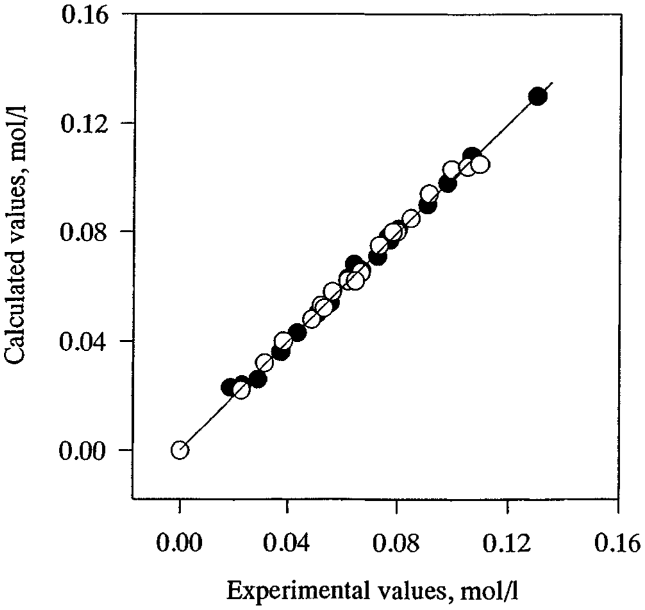


Figure 2. Comparison of the measured and calculated concentrations of dicyclopentadiene (●) and tricyclodecenone (○).

The Arrhenius plots can be summarized by the equations

$$k_{\mathrm{eff}} = A_{\mathrm{eff}} \exp\left(-\frac{E_{\mathrm{eff}}}{RT}\right), \qquad (10)$$

$$k_2 = A_2 \exp\left(-\frac{E_2}{RT}\right), \qquad (11)$$

$$K_1 = \exp\left(\frac{\Delta S_1}{R}\right) \exp\left(-\frac{\Delta H_1}{RT}\right), \qquad (12)$$

$$K_3 = \exp\left(\frac{\Delta S_3}{R}\right) \exp\left(-\frac{\Delta H_3}{RT}\right), \qquad (13)$$

where the gas constant R is 8.3143 $\mathrm{J\,mol^{-1}\,K^{-1}}$, $E_{\mathrm{eff}} = 28370\ \mathrm{J\,mol^{-1}}$ and $E_2 = 28652\ \mathrm{J\,mol^{-1}}$ are the apparent activation energies, $A_{\mathrm{eff}} = A_2 = 18034\ \mathrm{l\,mol^{-1}\,min^{-1}}$ are Arrhenius constants, and $\Delta S_1 = 52.4\ \mathrm{J\,mol^{-1}\,K^{-1}}$, $\Delta S_3 = 101.4\ \mathrm{J\,mol^{-1}\,K^{-1}}$, $\Delta H_1 = 1935\ \mathrm{J\,mol^{-1}}$ and $\Delta H_3 = 12932\ \mathrm{J\,mol^{-1}}$ are the entropy and enthalpy changes for the complexation of DCPD and TCD with catalyst species. The low values of the effective activated energies obtained in the study can be explained by a rapid exothermic pre-equilibrium preceding the palladium–DCPD complexes decomposition.

4. Conclusions

It was found that palladium(II)-acetate-catalyzed oxidation of dicyclopentadiene with benzoquinone in the presence of perchloric acid is a convenient one-step method for obtaining tricyclodecenone. The kinetic investigation of the process showed a significant inhibition effect of dicyclopentadiene and tricyclodecenone because of their complexation with the palladium center. The influence of perchloric acid concentration and temperature on the rate of reaction was studied. The best results were found at acid concentration up to 0.5 $\mathrm{mol\,l^{-1}}$ and temperature 100–120 °C.

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