

Oxidation of (*E,E,Z*)-1,5,9-cyclododecatriene catalysed by palladium(II) acetate in the presence of copper(II) acetate and air: A kinetic study

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Abstract

The oxidation of (*E,E,Z*)-1,5,9-cyclododecatriene catalysed by Pd(OAc)₂/Cu(OAc)₂ was studied in methyl alcohol solutions at 2.5 MPa air pressure and temperature range of 358 to 383 K. The selectivity of ketones and ethers at conversion of cyclododecatriene up to 32.7% ranged within 87.5–96.0%. The reaction network and kinetic equations proposed suggested a significant inhibition effect of the ketones and ethers and gave the best agreement with the experimental data. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Pd(OAc)₂; (*E,E,Z*)-1,5,9-Cyclododecatriene; Kinetic model

1. Introduction

Cyclododecanone is a useful starting material for producing 12-lauro lactam [1], 1,10-decanedicarboxylic acid [2], macrocyclic compounds [3], etc. The cyclododecanone production consists of the thermal oxidation of cyclododecane in the presence of boric acid [4]. A disadvantage of this process is the use of additional equipment for the recovery of boric acid. Some alternative processes have been proposed [5], among which the direct catalytic oxidation of cyclododecene or cyclododecatriene seems to be attractive. In these processes, the resultant unsaturated ketones can be turned into cyclododecanone by hydrogenation in the presence of supported metal catalysts.

However, the oxidation of cycloalkenes and cyclopolyenes by aqueous solutions of palladium(II) salts does not result in decent yields of cycloketones. The primary difficulty with the direct oxidation of cycloalkenes and cyclopolyenes is their slight solubility in aqueous hydrochloric acid solution. This problem can be overcome by carrying out the ketonization in alcoholic solvents. The oxidation of cycloalkenes by alcoholic palladium(II) salts has been investigated by a number of authors [6–10]. The oxidation of (*E,E,Z*)-1,5,9-cyclododecatriene with respect to the preparation of allyl ethers has only been reported by Zacharkin et al. [11]. The reaction was performed in alcoholic solutions, using PdCl₂/CuCl₂ as a catalyst at 368–373 K and 2.5–5.0 MPa pressure of air. The hydrogenation of allyl ethers gave cyclododecylethyl ether or cyclododecylbutyl ether

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in good yields. The oxidation of the cyclopolymene by palladium(II) chloride to ketones was not discussed.

The commonly adopted mechanistic scheme for cycloalkene and cyclopolymene oxidation carried out in the presence of palladium-based catalyst in alcohols or acetic acid involves formation of 1,2-oxypalladium or (η^3 -allyl)palladium complexes [10,12–14]. The interpretation of the results vary from strong identification of a single mechanism to the delicate balance between different 1,2-oxypalladium and η^3 -allyl complexes, formed on the basis of the same substrate. Additional complication can be provoked by the inhibition effects of the reaction products.

The aim of this paper is to investigate the product composition and the kinetics of oxidation of (*E,E,Z*)-1,5,9-cyclododecatriene (Cdt) catalysed by palladium(II) acetate/copper(II) acetate and air.

2. Reaction mechanism and general model formulation

Relevant information about the mechanism of the cyclododecatriene oxidation can be obtained

from the dependence of the products distribution on the reaction conditions. The oxidation, double bond isomerization and oxidative coupling are competitive reactions, and they all proceed in alcoholic solvents. The decomposition of cyclododecatriene across the carbon–carbon bond and the following head dimerization are facilitated by higher temperatures and acidity of the reaction medium. The strong coordination ability and the additional double bonds result in the formation of a very complex mixture. The products from cyclododecatriene oxidation fall into two general categories: allyl monoethers (four in number) and unsaturated monoketones (two in number). The unsaturated alcohols and dimethyl ketals are also present but as minor reaction products only. The major by-products are condensation derivatives, formed by a self-oxidative coupling of 1,5,9-cyclododecatriene. In accordance with the desirable end products distribution, the reaction network can be expressed by the parallel formation of π -allyl and π,σ -complexes and their decomposition to the above mentioned products (see Fig. 1).

In order to simplify the reaction network, the reaction species number was conducted by lumping all monoethers (Eth), monoketones

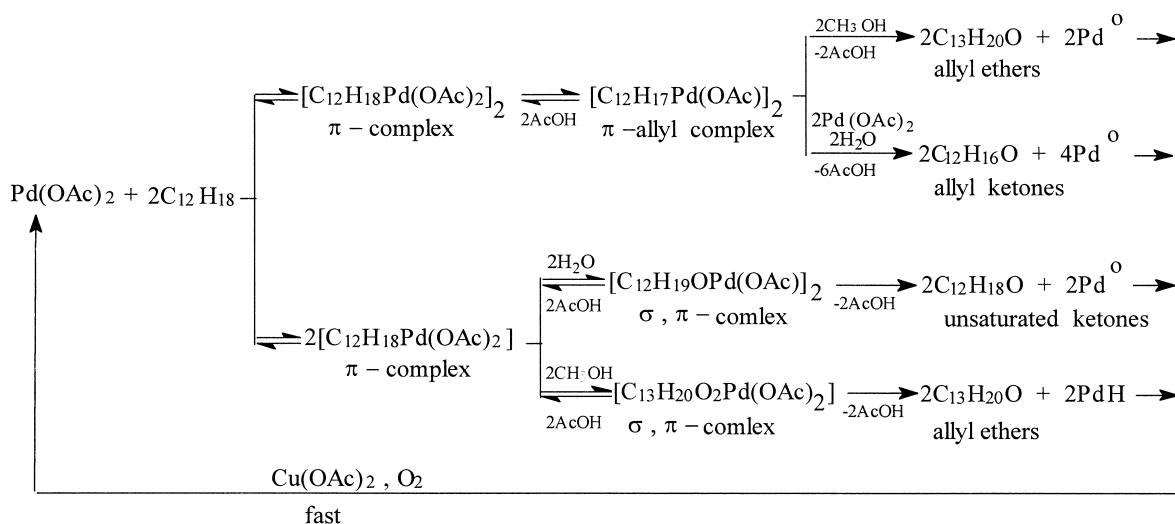
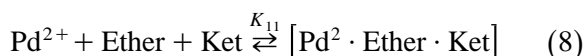
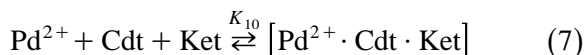
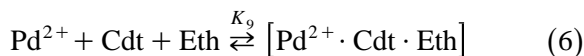
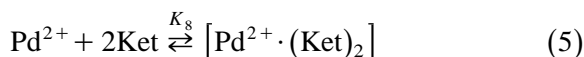
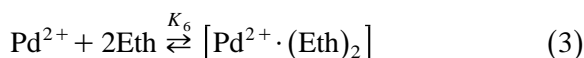
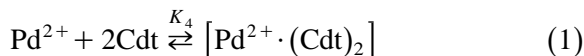


Fig. 1. Reaction network for the cyclododecatriene oxidation to the desirable end products.

(Ket), as well as all alcohols, dimethyl ketals and condensation derivatives (Oth) into single components, respectively. These assumptions reduced the complicated reaction network to the following simplified scheme (see Fig. 2) where Pd^{2+} is a representation of the catalytic species, K_1 and k_2 , k_3 and k_4 are composite equilibrium and rate constants, respectively. Therefore, the complicated reaction network is reduced to three parallel decomposition reactions of the formed complexes.

Our previous investigation [15] of 1,5,9-cyclododecatriene oxidation has indicated the formation of different inactive intermediates between the reactants, products and catalytic species. The isolated stable complexes included di-(μ -chloro)bis(1,5,9-cyclododecatriene)dipalladium, di-(μ -chloro)bis(2-hydroxycyclo-dodeca-5,9-diene)dipalladium and di-(μ -chloro)bis(2-methoxycyclododeca-5,9-diene)dipalladium. Furthermore, the ketones are also known as potential oxidation inhibitors [12]. In this respect, to explain the potential inhibiting effect of the reaction products, the simplified reaction scheme may be extended with the following equilibrium steps:



The application of the quasi-steady-state approximation [16] to the reduced reaction scheme

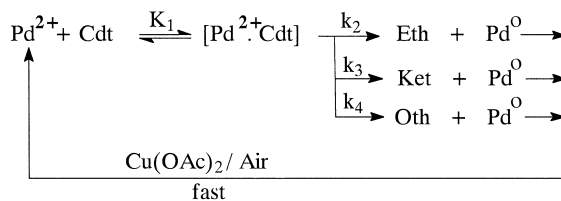


Fig. 2. Simplified reaction network.

(Fig. 2) coupled with Eqs. (1)–(8) simplified the corresponding rate expressions to the following system of kinetic differential equations:

$$\begin{aligned} \frac{dC_{\text{Cdt}}}{dt} &= - \frac{(k_2 + k_3 + k_4)C_{\text{Pd}}C_{\text{Cdt}}}{F} \\ &= - \frac{k_{\text{eff}}C_{\text{Pd}}C_{\text{Cdt}}}{F} \end{aligned} \quad (9)$$

$$\frac{dC_{\text{Eth}}}{dt} = \frac{k_2C_{\text{Pd}}C_{\text{Cdt}}}{F} \quad (10)$$

$$\frac{dC_{\text{Ket}}}{dt} = \frac{k_3C_{\text{Pd}}C_{\text{Cdt}}}{F} \quad (11)$$

$$\frac{dC_{\text{Oth}}}{dt} = \frac{k_4C_{\text{Pd}}C_{\text{Cdt}}}{F} \quad (12)$$

$$\begin{aligned} F &= 1 + K_1C_{\text{Cdt}} + K'_4C_{\text{Cdt}}^2 + K'_5C_{\text{Eth}} + K'_6C_{\text{Eth}}^2 \\ &\quad + K'_7C_{\text{Ket}} + K'_8C_{\text{Ket}}^2 + K'_9C_{\text{Cdt}}C_{\text{Eth}} \\ &\quad + K'_{10}C_{\text{Cdt}}C_{\text{Ket}} + K'_{11}C_{\text{Eth}}C_{\text{Ket}} \end{aligned} \quad (13)$$

where, K'_j are different products of the equilibrium constants K_1 and F is the so-called complex formation function.

Some of the potential complexes can be quite unstable and the corresponding monomials in the denominator (Eq. (13)) could not reach the significant values within the experimental conditions studied. After neglecting the formation of such inactive intermediates, many different models may be derived from the general kinetic equations (Eqs. (9)–(13)).

3. Experimental section

All solvents and reagents were purchased from commercial source (Merck). (*E,E,Z*)-1,5,9-cyclododecatriene (99%), n_{D}^{20} 1.508, d

0.892; copper(II) acetate monohydrate (min. 99%), palladium(II) acetate (47% Pd); methanol (min. 99.5%, water < 0.1%).

The reaction was performed in methyl alcohol solution, using palladium acetate as a catalyst, copper(II) acetate as an oxidant and air as a cooxidant under various conditions such as cyclododecatriene and catalyst concentrations, temperature and reaction time.

Cyclododecatriene oxidation was performed in a 100-ml thermostatted magnetically stirred batch reactor, connected to a system with a volumetric gas balloon. All runs were conducted at 2.5 MPa pressure in a temperature range of 358–383 K. From a series of oxidation to a known degree of conversion, determined by analyses of the reaction mixtures, time dependencies were obtained for the concentrations of the reaction products.

Each sample was analysed using a Sigma 2000 gas chromatograph (Perkin–Elmer, Norwalk, CT, USA), equipped with a flame ionisation detector. The thick film (0.9 μm) Carbowax 20M fused silica capillary column necessary for the analysis was obtained from Perkin–Elmer. The GC conditions were: column length 50 m, column tube 0.23 mm, carrier gas nitrogen, temperature 180°C. The error of determination was 3% rel. Additionally, the identification of the reaction products was accomplished on a Hewlett Packard 5890II, 5970B GCMS spectrometer by comparing the corresponding retention times with those of authentic samples and by inspecting the mass spectra.

4. Results and discussion

The dependencies of the reaction mixture composition and selectivity on the degree of conversion by the oxidation of cyclododecatriene at 358–383 K are shown in Fig. 3. The curves are typical for parallel reactions. At 21.8–32.7% conversion of cyclododecatriene the selectivity with respect to the ether–ketone mixture ranges from 87.5 to 94.0%. The unsaturated

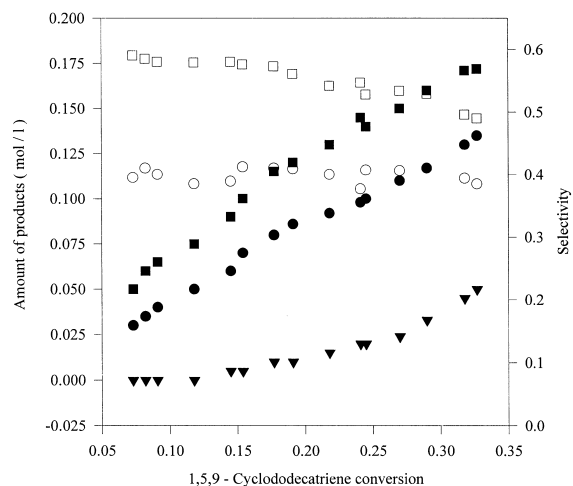


Fig. 3. Dependence of product distribution and selectivity on the degree of conversion. Amount of ethers (●), ketones (■), by-products (▼). Selectivity of ethers (○), ketones (□). Reaction temperature, 358–383 K; air pressure, 2.5 MPa; Pd(OAc)₂, 2.2 mmol; Cu(OAc)₂·H₂O, 1.4 mmol; cyclododecatriene, 10 ml; alcohol, 50 ml.

monoketones were formed, rather than the expected allyl ethers and their yield was close to 52%. Since the production of acetates involves the formation of water, the accumulation of the latter in the reaction medium results in an increase in the yield of ketones. A small amount of alcohols, dimethyl ketals and condensation derivatives formed by a self-oxidative coupling of 1,5,9-cyclododecatriene was also obtained under these conditions.

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 that the next experimental series were carried out using *p*-toluenesulphonic acid in amounts of 20–40 mol% with respect to the amount of cyclopolyene [17]. At higher acid concentrations an inhibition effect was observed. The dependencies of the reaction mixture composition on the degree of conversion at 358–378 K is shown in Fig. 4. At constant air pressure the dependence of the reaction mixture composition on the degree of conversion became complicated. Under the condition of a low

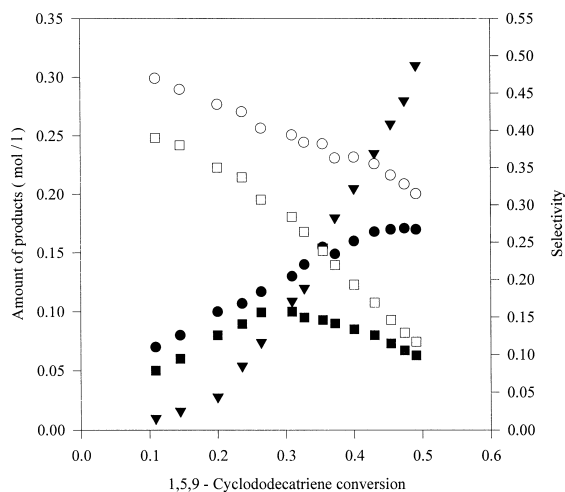


Fig. 4. Dependence of product distribution and selectivity on the degree of conversion. Amount of ethers (●), ketones (■), by-products (▼). Selectivity of ethers (○), ketones (□). Reaction temperature, 358–378 K; air pressure, 2.5 MPa; Pd(OAc)₂, 2.2 mmol; Cu(OAc)₂·H₂O, 1.4 mmol; cyclododecatriene, 10 ml; alcohol, 50 ml; *p*-toluenesulphonic acid, 20 mol%.

conversion, an increase of the latter resulted in a larger amount of unsaturated ketones. As a certain conversion limit was reached, a maximum was obtained, after which the amount of unsaturated ketones began to decrease. It was found that the amount of condensation derivatives is higher compared with monoketones above 30% conversion of the cyclododecatriene.

It was interesting to study the kinetics of oxidation of (*E,E,Z*)-1,5,9-cyclododecatriene catalysed by palladium(II) acetate/copper(II) acetate/air in the absence of *p*-toluenesulphonic acid at a temperature range of 358, 368 and 378 K. To reduce the computing time, the fit between experimental data obtained in the oxidation of cyclododecatriene and the different models derived from the general kinetic equations (Eqs. (9)–(13)) was evaluated by a short-

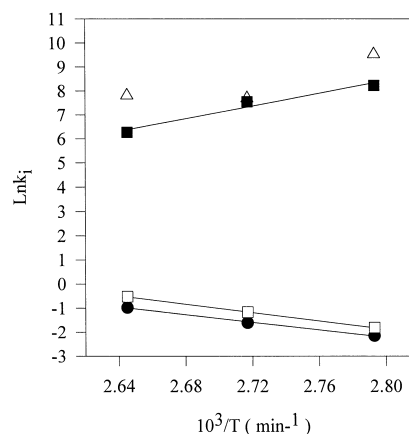


Fig. 5. Arrhenius plot of $\ln k_i$ upon $10^3/T$; k_2 (●), k_3 (□), K_6 (△), K_8 (■), Eqs. (14)–(16) (—).

cut differential method [18]. 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 [19]. The best fit, on the basis of the values of the sum of residual squares (SSR), the average relative errors ($\Delta \varepsilon$) and the values and significance of the parameters, was performed by the following rate equations:

$$\frac{dC_{\text{Cdt}}}{dt} = - \frac{(k_2 + k_3)C_{\text{Pd}}C_{\text{Cdt}}}{1 + K'_6 C_{\text{Eth}}^2 + K'_8 C_{\text{Ket}}^2} \quad (14)$$

$$\frac{dC_{\text{Eth}}}{dt} = \frac{k_2 C_{\text{Pd}} C_{\text{Cdt}}}{1 + K'_6 C_{\text{Eth}}^2 + K'_8 C_{\text{Ket}}^2} \quad (15)$$

$$\frac{dC_{\text{Ket}}}{dt} = \frac{k_3 C_{\text{Pd}} C_{\text{Cdt}}}{1 + K'_6 C_{\text{Eth}}^2 + K'_8 C_{\text{Ket}}^2} \quad (16)$$

Since the amount of the unsaturated alcohols, dimethyl ketals and condensation derivatives

Table 1

Estimated parameter values for kinetic model Eqs. (14)–(16)

T (K)	k_2 ($\text{l mol}^{-1} \text{min}^{-1}$)	k_3 ($\text{l mol}^{-1} \text{min}^{-1}$)	K'_6 ($\text{l}^2 \text{mol}^{-2}$)	K'_8 ($\text{l}^2 \text{mol}^{-2}$)	$\text{SSR} \times 10^4$	$\Delta \varepsilon$ (%)
358	0.116 ± 0.002	0.163 ± 0.002	13778 ± 3657	3756 ± 420	5.1	1.9
368	0.240 ± 0.032	0.372 ± 0.059	5000 ± 851	1330 ± 197	6.6	2.3
378	0.376 ± 0.008	0.590 ± 0.006	2480 ± 692	528 ± 63	11.4	2.6

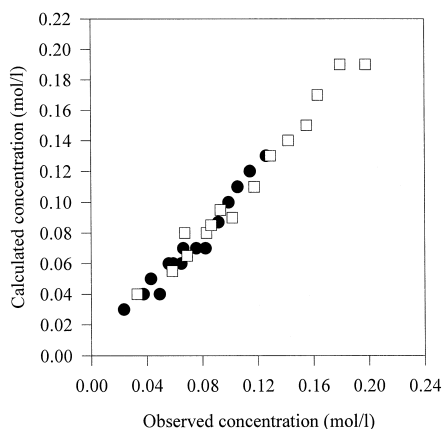


Fig. 6. Global comparison of model to data: ethers (●), ketones (□).

were obtained within the range of the experimental error, their formation was considered to be negligible. This model assumes the significant inhibition complexation between unsaturated monoethers and monoketones with the catalytic species. The results of the fitting obtained with model Eqs. (14)–(16) are summarised in Table 1. It is obvious from this table that the values of K'_6 are not well estimated. The width of the intervals is such that the Arrhenius plot is not clearly outlined. For all remaining cases, the estimated parameters are fitted into the Arrhenius relationship, Fig. 5:

$$k_2 = A_2 \exp(-E_2/RT) \quad (17)$$

$$k_3 = A_3 \exp(-E_3/RT) \quad (18)$$

$$K'_8 = \exp(\Delta S_8/R) \exp(-\Delta H_8/RT) \quad (19)$$

Here the gas constant R is $8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$, $E_2 = 65,768 \text{ J mol}^{-1}$ and $E_3 = 72,098 \text{ J mol}^{-1}$ are the apparent activation energies; $A_2 = 4.4 \times 10^8 \text{ l mol}^{-1} \text{ min}^{-1}$ and $A_3 = 5.3 \times 10^9 \text{ l mol}^{-1} \text{ min}^{-1}$ are the Arrhenius constants; and $\Delta S_8 = -236.9 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H_8 = -109,642 \text{ J mol}^{-1}$ are the entropy and enthalpy changes for the complexation of monoketones with catalyst species. The negative value of ΔH_8 indicates that the complex formation between ketones and catalyst species is an exothermic reaction. The predicted value of E_3 is higher than that of E_2 suggesting that the

reactions to ketones are more sensitive to the reaction temperature.

Fig. 6 is a parity plot summarising the comparison of the concentration predicted by Eqs. (13)–(18) with the concentrations of cyclododecatriene, unsaturated ethers and ketones, determined experimentally. The model predictions were found to have a good agreement with the experimental results over all of the conversion levels and temperatures. The mean errors for the cyclododecatriene, ethers and ketones concentrations were 0.8, 11.0 and 5.6%, respectively.

5. Conclusions

The palladium-catalysed oxidation of (*E,E,Z*)-1,5,9-cyclododecatriene in the presence of copper(II) acetate monohydrate as oxidant and air as cooxidant takes place with a good selectivity at relatively high substrate conversions. A simplified theoretical mechanism network has been derived on the basis of the product distribution and prior information for the potential inhibition effects of the reactants and products. The best fit of the experimental data was obtained as the allyl ethers and unsaturated ketones were assumed to be inhibiting agents for the reaction studied.

Acknowledgements

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