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

E. Balbolov [*], S.D. Dimitrov [1]

University Prof. As. Zlatarov, Department of Organic Synthesis, 1 Prof. Yakimov St., 8010 Bourgas, Bulgaria

Abstract

The acetoxylation of (E,E,Z)-1,5,9-cyclododecatriene to acetates and ketones in the presence of $Pd(OAc)_2$, $Cu(OAc)_2$ and air was studied. The experiments were carried out at 4.0 MPa pressure and a temperature range of 333, 343 and 353 K. A simplified general reaction network is presented that explains both the results of this work and earlier results from literature. Among several kinetic equations derived from this network, a model which assumes a significant inhibition effect of the acetates gave the best agreement with the experimental data. © 1997 Elsevier Science B.V.

Keywords: Acetoxylation; $Pd(OAc)_2$; (E,E,Z)-1,5,9-cyclododecatriene; Kinetic model

1. Introduction

The alkene acetoxylation products are known as important intermediates in organic chemistry. The ability of various nucleophiles to readily substitute the acetoxy group in the unsaturated acetates in the presence of a palladium catalyst makes these reactions of practical interest. There are several advantages to use the acetoxylation: first of all the high selectiveness and the moderate reaction condition. Because the direct cycloalkene oxidation does not result in passable yields of cycloalcohols or cycloketones, the selective transformation of cycloalkenes into such

more useful compounds considerably expands their sources. Some applications of these products have been reported [1,2], suggesting that cycloalkenes acetoxylation can afford an attractive opportunity for organic synthesis in the coming years.

The commonly appropriated mechanistic scheme for alkene oxidation carried out with a palladium based catalyst involves formation of alkene–palladium complexes [3–7]. In the case of alkenes and cycloalkenes acetoxylation the mechanistic studies suggest the formation of 1,2-acetoxypalladium or π-allyl complexes [8,9]. The interpretations of the results vary from strong identification of a single mechanism to the delicate balance between different 1,2-acetoxypalladium and π-allyl complexes, formed on the basis of the same substrate. Addi-
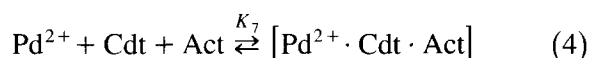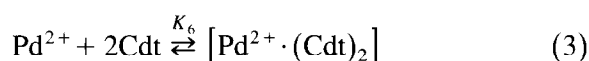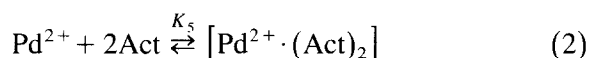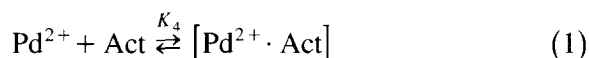
* Corresponding author. Tel.: +359-56-660017; fax: +359-56-686141; e-mail: @btu.bg.
[1] Department of Chemical Engineering

tional complication can be provoked by the inhibition properties of the reactants and reaction products.

The present work is a continuation of the study of the palladium — catalyzed cyclododecatriene (Cdt) acetoxylation in the presence of palladium acetate and copper(II) acetate monohydrate. The obtained results are satisfactorily fitted by the previously established kinetic model for the cyclododecene and cyclododecatriene acetoxylation carried with palladium acetate — manganese oxide system [10].

2. Reaction mechanism and general model formulation

From a theoretical point of view, the studied reaction mechanism may appear too complicated, due to the ability of the palladium based catalyst to take part in complexation with unsaturated substrates. The strong co-ordination ability and the additional double bounds result in the formation of a very complex reaction mixture. The products from cyclododecatriene acetoxylation fall into two general categories: unsaturated monoacetates (seven in number) were

Fig. 2. Simplified reaction network.

obtained in the highest selectivity, and unsaturated monoketones (five in number). The monoalcohols and diacetates were also presented but only as minor reaction products. In accordance with the products distribution, the reaction network can be expressed by the parallel formation of π-allyl and σ, π complexes and their decomposition to the above mentioned products: see Fig. 1.

In order to simplify the reaction network, the number of the reactive species was calculated by lumping all monoacetates (Act), as well as all ketones (Ket), into single components. On the other hand, because the amounts of the monoalcohols and diacetates were obtained in the range of the experimental error, their formation was considered to be negligible. These assumptions reduced the complicated reaction network to the following simplified scheme: see Fig. 2, where Pd^{2+} is a representation of the

Fig. 1. Reaction network for the cyclododecatriene acetoxylations.

catalytic species, K_1, k_2 and k_3 are composite equilibrium and rate constants, respectively. So, the complicated reaction network is reduced to two parallel decomposition reactions of the formed complexes.

Our previous investigation of alkene acetoxylation [10] has indicated the formation of different inactive intermediates between the reactants, products and catalytic species. The isolated stable complexes included di-(μ-acetato)-bis-(1,5,9-cyclododecatriene)-dipalladium and di-(μ-acetato)-bis-(2-acetoxycyclododeca-5,9-diene)-dipalladium. In this respect, to explain the potential inhibiting effect of the 1,5,9-cyclododecatriene and 2-acetoxycyclododeca-5,9-diene, the simplified reaction scheme may be extended with the following equilibrium steps:

$$Pd^{2+} + Act \overset{K_4}{\rightleftarrows} \left[Pd^{2+} \cdot Act\right] \qquad (1)$$

$$Pd^{2+} + 2Act \overset{K_5}{\rightleftarrows} \left[Pd^{2+} \cdot (Act)_2\right] \qquad (2)$$

$$Pd^{2+} + 2Cdt \overset{K_6}{\rightleftarrows} \left[Pd^{2+} \cdot (Cdt)_2\right] \qquad (3)$$

$$Pd^{2+} + Cdt + Act \overset{K_7}{\rightleftarrows} \left[Pd^{2+} \cdot Cdt \cdot Act\right] \qquad (4)$$

The application of the quasi-steady-state approximation [11] to the reduced reaction scheme (Fig. 2) coupled with Eqs. (1)–(4) simplified the corresponding rate expressions to the following system of kinetic differential equations:

$$\frac{dC_{Cdt}}{dt} = -(k_2 + k_3)C_{Pd}C_{Cdt}/F, \qquad (5)$$

$$\frac{dC_{Act}}{dt} = k_2 C_{Pd}C_{Cdt}/F, \qquad (6)$$

$$\frac{dC_{Ket}}{dt} = k_3 C_{Pd}C_{Cdt}/F, \qquad (7)$$

$$F = 1 + K_1'C_{Cdt} + K_4'C_{Act} + K_5'C_{Act}^2 + K_6'C_{Cdt}^2 + K_7'C_{Cdt}C_{Act}, \qquad (8)$$

where, K_j' are different products of the equilibrium constants K_i 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. (8)) could not reach the significant values within the studied experimental conditions. Neglecting the formation of such inactive intermediates, many different models may be derived from the general kinetic Eqs. (5)–(8).

It should be mentioned that the derived simplified reaction scheme, presented in Fig. 2 and Eqs. (1)–(4), and corresponding kinetics Eqs. (5)–(8) somewhat coincide with those proposed in a previous investigation [10]. This concurrence is only superficial and is corollary of the appropriate simplification of the studied mechanisms. The composite kinetic parameters belonging to the two acetoxylations carried out with dissimilar oxidant systems and isomers reflect different sets of chemical actions and there is no reason for their theoretical comparison.

3. Experimental section

All solvents and reagents were purchased from commercial source (Merck KGaA). (E,E,Z)-1,5,9-cyclododecatriene (99%), $n_D^{20} = 1.508$, $d = 0.892$; Copper(II)acetate monohydrate, Assay (min 99%), Palladium(II)acetate (47% Pd).

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

Cyclododecatriene acetoxylation was performed in a 100 ml magnetically stirred (10 Hz) glass reactor connected to a system with a volumetric gas balloon. All runs were conducted at 4.0 MPa pressure in temperature range of 333–353 K and for about 1.7 h of reaction time. The samples were drawn off at 10, 20, 40, 110, 220, 420 and 600 min.

Each sample was analyzed by Sigma 2000 gas chromatograph (Perkin Elmer, Norwalk, CT, USA), equipped with a flame-ionization detector. The thick film (0.9 μm) Carbowax 20 m 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.
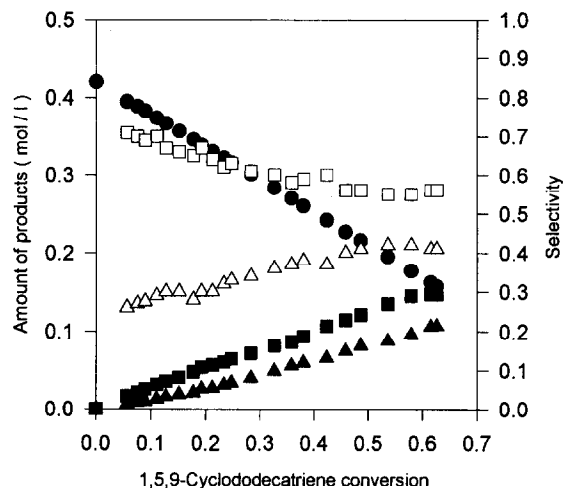

Fig. 3. Dependence of product distribution and selectivity on the degree of conversion. Amount: cyclododecatriene (●), acetates (■), ketones (▲). Selectivity: acetates (□), ketones (△).

4. Results and discussion

The dependencies of the reaction mixture composition and selectivity on the degree of conversion are shown in Fig. 3. The curves are typical for parallel reactions. The acetoxylation reaction is retarded above 50–60% conversion of the cyclododecatriene. This is presumably associated with a decrease in the cyclododecatriene concentration, and also with the effect of the products formed. The higher the temperature, the higher degree of conversion at which the process is retarded. This determines the optimum conversion in the liquid phase process.

The overall selectivity of the monoacetates and monoketones at cycloalkene conversion up to 63% ranges within 93–97%. A small amount of alcohols and diacetates was obtained under these conditions (not shown in Fig. 3). In all experiments the selectivity of monoacetates was found to be higher as compared to monoketones and ranges within 56–71%. 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.

In order to reduce the computing time, the fit between experimental data and different models derived from the general kinetic Eqs. (5)–(8)

was carried out by short-cut differential method [12]. So, many 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 fourth-order Runge–Kutta method combined with the method of Marquardt [13]. The best fit, evaluated on the basis of the values of the sum of squares of residuals (SSR), the average relative errors ($\Delta \varepsilon$) and the values and significance of the parameters, was performed by the following rate equations:

$$\frac{dC_{Cdt}}{dt} = -\frac{(k_2 + k_3)C_{Pd}C_{Cdt}}{1 + K_5'C_{Act}^2} \qquad (9)$$

$$\frac{dC_{Act}}{dt} = \frac{k_2 C_{Pd}C_{Cdt}}{1 + K_5'C_{Act}^2} \qquad (10)$$

$$\frac{dC_{Ket}}{dt} = \frac{k_3 C_{Pd}C_{Cdt}}{1 + K_5'C_{Act}^2} \qquad (11)$$

This model assumes the significant inhibition complexation between monoacetates and catalytic species. In Table 1 are summarized the results of the fitting obtained with model Eqs. (9)–(11).
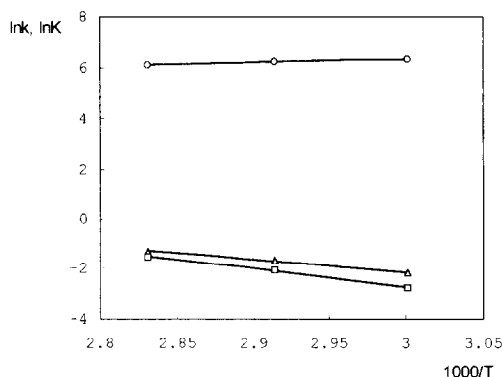
Fig. 4. Arrhenius plot of kinetic parameters. $\triangle$ – $\ln k_2$, $\square$ – $\ln k_3$, $\bigcirc$ – $\ln K_5'$, ————— – Eqs. (12)–(14).

Fig. 5. Parity plot comparing measured and calculated concentrations.

The parameters from Table 1 can be expressed as a function of temperature by the usual Arrhenius form, Fig. 4:

$$k_2 = A_2 \exp(-E_2/RT), \qquad (12)$$

$$k_3 = A_3 \exp(-E_3/RT), \qquad (13)$$

$$K_5' = \exp(\Delta S_5/R)\exp(-\Delta H_5/RT), \qquad (14)$$

were the gas constant R is 8.3143 J mol^{-1} K^{-1}, $E_2 = 41,920$ J mol^{-1} and $E_3 = 60,830$ J mol^{-1} are the apparent activation energies; $A_2 = 4.424 \times 10^5$ l mol^{-1} min^{-1} and $A_3 = 2.242 \times 10^8$ l mol^{-1} min^{-1} are the Arrhenius constants; and $\Delta S_5 = 20.79$ J mol^{-1} K^{-1} and $\Delta H_5 = -10,670$ J mol^{-1} are the entropy and enthalpy changes for the complexation of monoacetates with catalyst species. The negative value of ΔH_5 indicates that the complex formation between acetylacetates and catalyst species is an exothermic reaction. The predicted value of E_3 is higher than E_2 and this points out that the reactions to ketones is more sensitive to the reaction temperature.

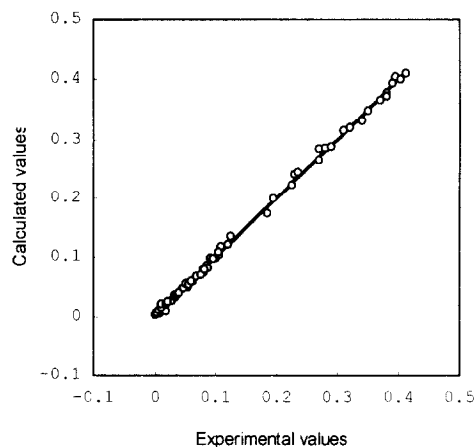Fig. 5 is a parity plot summarizing the comparison of the predicted by Eqs. (9)–(14) with the measured concentrations of cyclododecatriene, acetates and ketones. The model predictions agreed very well with the experimental results over all conversion levels and temperatures. It should be mentioned, that because of the small values of the ketones concentrations the average relative error obtained at 343 K is considerably higher than the errors at the two other temperatures. At the same conditions the mean errors for the cyclododecatriene and acetates concentrations were 2.3 and 11%, respectively.

5. Conclusions

The palladium-catalyzed acetoxylation of (E,E,Z)-1,5,9-cyclododecatriene in the presence of copper(II) acetate monohydrate as oxidant and air as cooxidant was studied in a laboratory batch reactor. A simplified theoretical mechanism network was derived on the basis of the products distribution and prior in-

Table 1
Estimated parameter values for kinetic model Eqs. (9)–(11)

T (K)	k_2 (l mol^{-1} min^{-1})	k_3 (l mol^{-1} min^{-1})	K_5' (l^2 mol^{-2})	SSR $\times 10^4$	$\Delta \varepsilon$ (%)
333	0.116 ± 0.018	0.0631 ± 0.041	574 ± 164	2.2	8.0
343	0.191 ± 0.058	0.130 ± 0.041	513 ± 262	7.5	26
353	0.273 ± 0.053	0.219 ± 0.043	462 ± 148	6.4	7.8

formation for the potential inhibition effects of the reactants and products. The best fit of the experimental data was obtained when the acetates were assumed to be inhibitor agents for the studied reaction. This result is in consistent with previously selected rate equations for cyclododecatriene acetoxylation carried out with manganese dioxide as oxidant and benzoquinone as cooxidant [10].

References

[1] K. Bauer, D. Garbe, H. Surburg, in: W. Gerhartz (Ed.), vol. A11, Ullman's Encyclopedia of Industrial Chemistry, VCH, Weinheim, 1988, p. 141.

[2] G.W. Parshall, W.A. Nugent, Chemtech. 6 (1988) 376.

[3] I.I. Moiseev, M.N. Vargaftik, Y.K. Syrkin, Dokl. Akad. Nauk. SSSR 133 (1960) 377.

[4] J. Smith, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier, A. Sabel, Angew. Chem. Int. Ed. Engl. 1 (1962) 80.

[5] P.M. Henry, J. Am. Chem. Soc. 86 (1964) 3246.

[6] A. Aguilo, Adv. Organomet. Chem. 5 (1967) 321.

[7] J. Tsuji, Adv. Org. Chem. 6 (1969) 106.

[8] W. Kitching, Z. Rappoport, S. Winstein, W.G. Young, J. Am. Chem. Soc. 88 (1966) 2054.

[9] S. Hansson, A. Heumann, T. Rein, B. Akermark, J. Org. Chem. 55 (1990) 975.

[10] E. Balbolov, S.D. Dimitrov, React. Kinet. Catal. Lett. (1997), in press.

[11] R. Schmid, V.N. Sapunov, Non-Formal Kinetics, Verlag Chemie, Basel, 1982.

[12] D.I. Kamenski, S.D. Dimitrov, Comput. Chem. Eng. 17 (1993) 643.

[13] D.W. Marquardt, J. Soc. Ind. Appl. Math. 11 (1963) 431.