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Dedicated to Academician of the Russian Academy of Sciences
Ilya Iosifovich Moiseev in connection with his jubilee

Isotope Effect in Catalytic Hydroallylation of Norbornadiene by Allyl Formate

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Abstract—Norbornadiene allylation by allyl formate in the presence of palladium catalytic systems has a number of features associated with different directions of β-hydride transfer in key intermediates, which can be carried out with the participation of allyl, norbornenyl, or formyl fragments. The value of the kinetic isotope effect and the nature of the limiting step in the reaction of hydroallylation of norbornadiene are determined using deuterated reagents.

Keywords: norbornadiene, allyl formate, palladium acetate, allylation, hydroallylation, homogeneous metal complex catalysis, hydride transfer, kinetic isotope effect

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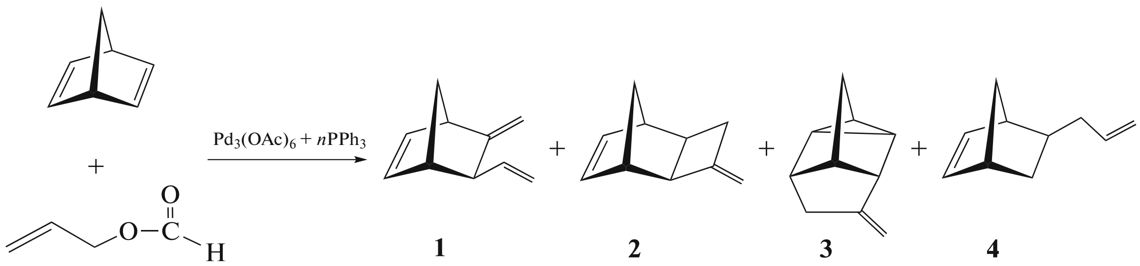
INTRODUCTION

Works of I.I. Moiseev and co-workers have become classical long ago and stimulated to a large extent the formation of a new research area, catalysis by metal complexes. Information on the mechanism of catalytic reactions makes it possible to directly influence the most important characteristics of the process: catalyst activity, product composition, and selectivity, and thus expand the range of basic monomers and intermediates and improve technical and economic indicators of the process. The principles, methods and approaches of metal-complex catalysis have proved extremely attractive for solving the problems of selectivity at various levels. This fully applies to outstanding achievements in the field of chemistry and the structure of η^3-allyl transition metal complexes [1–3]. Palladium η^3-allyl complexes are precursors, catalysts, or key intermediates in many reactions involving diene hydrocarbons, including bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) [4–6]. In catalytic chemistry of norbornadiene, reactions with allyl carboxylates, in particular, allyl formate (AF), catalyzed by complex compounds of nickel and palladium with organophosphorus ligands play a special role [7–14]. Thus, the interaction of norbornadiene and allyl formate in the presence of palladium acetate–triphenylphosphine in acetonitrile results in products **1**–**4** (Scheme 1).

The principal differences in the formation of compounds **1**–**3** and **4** are associated with the directions of hydride transfer. In the first case (for **1**–**3**), the allyl group undergoes addition to norbornadiene as a C_3H_4 fragment and loses a hydrogen atom (oxidative allylation). In another direction, leading to the formation of 5-allylnorbornene-2 (**4**), norbornadiene is hydroallylated (reductive allylation, the norbornadiene molecule formally adds the C_3H_6 fragment). The palladium–phosphine system catalyzes both processes. This is important in studying the variability of hydride transfer, a key step that determines the problem of selectivity.



Scheme 1. Catalytic allylation of norbornadiene by allyl formate.

Earlier, we studied hydride transfer using deuterated reagents—allyl acetate (C_3D_5OAc) and allyl formate with different types of deuterium positions: $C_3H_5OC(O)D$, $C_3D_5OC(O)H$, and $C_3D_5OC(O)D$ [15, 16]. We determined the positions of all deuterium labels in products **1**–**4** and the directions of hydride transfer in their formation. It was shown that the reactions are common in nature and are associated with the cleavage of the C–H bond in the β position relative to the metal atom. β-Hydride transfer can occur with the participation of allyl, norbornenyl, or formyl fragments. Nevertheless, the answer to the question about the nature of the limiting step and the values of the kinetic isotope effect (KIE) remains open. In a number of works, it was suggested that the hydride transfer steps limit the course of the entire catalytic cycle, but experimental evidence has not been obtained [16, 17]. In connection with this, the goal of this work was to study the nature of the limiting step in norbornadiene hydroallylation by the method of labeled atoms.

EXPERIMENTAL

Allyl formate, norbornadiene, and allyl alcohol with a purity of at least 99.5% and D_2-formic acid with a deuterium content of at least 99% were used.

Deuterated allyl formate was synthesized by esterification of formic acid DCOOD and allyl alcohol C_3H_5OH. After distillation, the fraction with b.p. of 82.5–83°C was collected. The product yield was 75%. The composition of deuterated allyl formate and its purity were monitored by NMR and chromatography–mass spectrometry. After additional purification, the content of the target product was at least 98%.

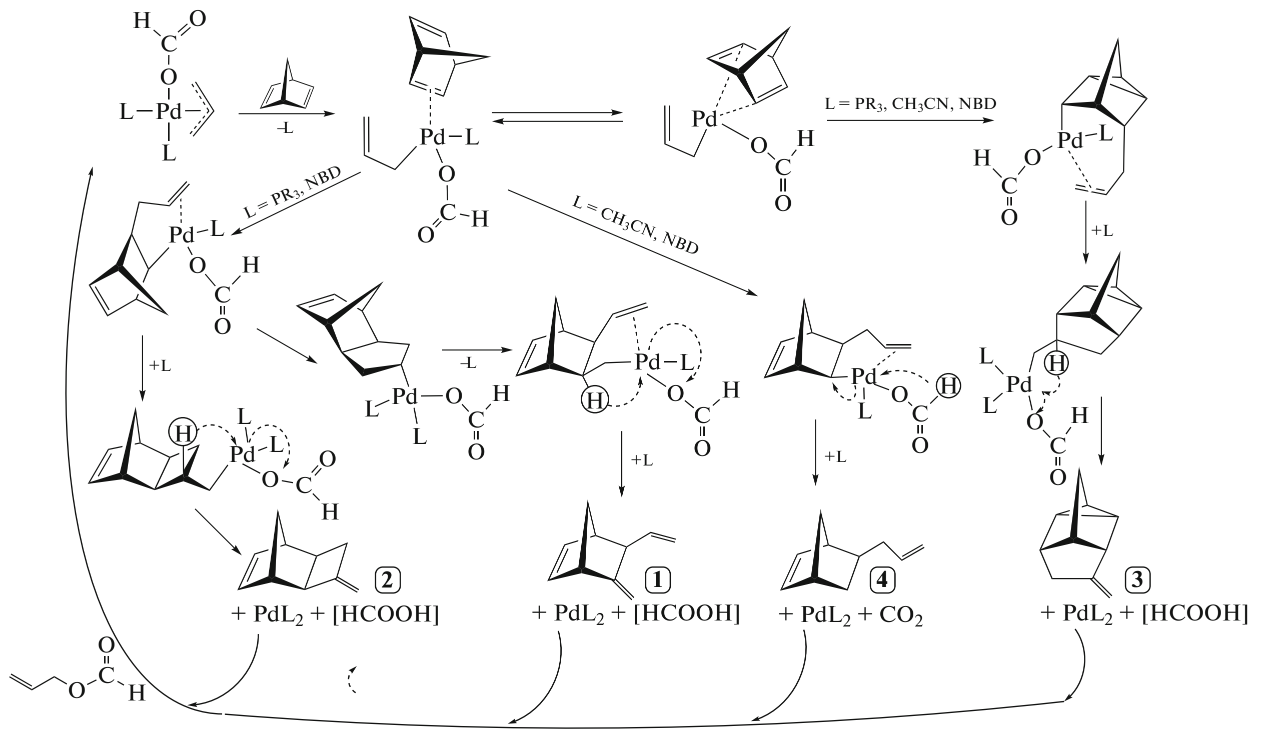
The source of palladium, $Pd_3(OAc)_6$, was prepared by the known technique [19]. Triphenylphosphine (Aldrich) was recrystallized under nitrogen from the methanol–chloroform mixture (volume ratio 4 : 1; 15 mL of mixture per 1 g of PPh_3). Before an experiment, acetonitrile was distilled over P_2O_5.

Reactions were carried out in an argon atmosphere at temperatures of 25 and 60°C in a thermostated vacuumed reactor equipped with a magnetic stirrer and a sampling device.

The process was monitored by GC using a Kristall PM 2000 chromatograph (Khromatek, Russia) with a flame ionization detector and an Agilent J&W HP-50+ capillary column (Agilent Technologies, USA). The products were identified by chromatography–mass spectrometry using an Automass-120 instrument (Delsi-Nermag, France) with a CPS CP-Sil 5 CB capillary column in electron impact mode; the m/z scanning range was 15–300, the scan rate was 1 scan per 300 ms, and the ionization energy was 70 eV. In analyzing and interpreting the mass spectra, standard databases and data from [16, 20, 21] were used. ^1H and ^{13}C NMR spectra were recorded on a DPX 300 spectrometer (Bruker, Germany); the operating frequency was 300.13 MHz for ^1H and 75.033 MHz for ^{13}C nuclei.

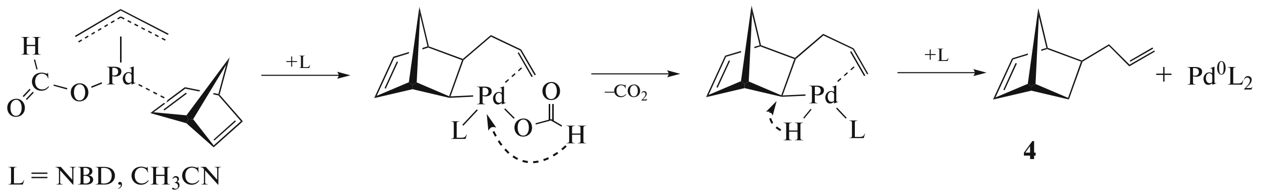
DISCUSSION

The mechanism for allylation and hydro-allylation of norbornadiene, taking into account the formation of the main products, was proposed in [16] (Scheme 2).



Scheme 2. Mechanism of the catalytic allylation of norbornadiene.

Routes leading to each of compounds **1**–**4** include the necessary step of β-hydride transfer. The nature of the hydrogen atoms involved in these steps is significantly different, and the parallel routes themselves are related through a common material balance and can be coupled. In such cases, it is advisable to simplify the reaction system by eliminating a number of directions from it. Norbornadiene hydroallylation using a ligand-free palladium system ($Pd_3(OAc)_6$ precursor in acetonitrile) makes it possible to obtain **4** with a selectivity higher than 95%. The stereochemistry of its formation is determined solely by the direction of the exo-attack of β-hydride transfer with respect to the norbornene ring (Scheme 3).



Scheme 3. Mechanism of 5-allylnorbornene-2 formation.

The hydrogen atom of formyl is involved in this stage. Therefore, to estimate the KIE, allyl formates with the usual and deuterated formyl groups were used ($C_3H_5OC(O)H$ and $C_3H_5OC(O)D$). The first series of experiments consisted in their joint participation in the reaction to create competitive conditions. KIE was estimated by comparing the concentrations of products **4** and its deuterated analog D_1-**4** formed in parallel in the presence of the $Pd_3(OAc)_6$ catalytic system and using equal amounts of allyl formate and D_1-allyl formate ($0.5C^0_{\mathrm{NBD}} = C^0_{\mathrm{AF}} = C^0_{\mathrm{AF\text{-}D1}} = 0.25$ mol L^{-1}).

Assuming that the reaction mechanism does not change when using different isotopes, the formation of products **4** and D_1-**4** should be described by the same kinetic equations. Then, the ratio of the concentrations of products will be constant in time and equal to the ratio of the observed rate constants:

$$\mathrm{KIE} = C_{4_\mathrm{H}}/C_{4_\mathrm{D}} = k_\mathrm{H}/k_\mathrm{D}, \qquad (1)$$

where KIE is the value of the kinetic isotope effect; k_H and k_D are the apparent rate constants; C_{4_H} and C_{4_D} are the concentrations of **4** and D_1-**4**.

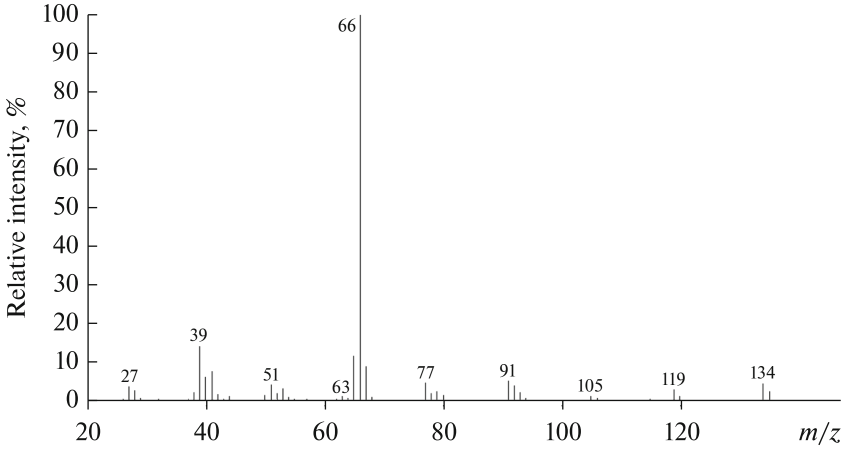


Fig. 1. Mass spectrum of the mixture of products **4** and D$_1$-**4**.

Compounds **4** and D$_1$-**4** are almost inseparable chromatographically due to the proximity of the composition (the difference in molecular masses is one unit). To analyze their concentrations in the reaction solutions, we used the method of deconvolution of GC–MS spectra in AMIDIS software. The method allows processing the mass spectrum of the mixture (Fig. 1) using an algorithm designed to extract the desired signal or signals from the experimental data (Fig. 2).

The calculated values of m/z in characteristic ions of products **4** and D$_1$-**4** (134/135, 119/120, 91/92) coincide with an error of at most 10%, which make is possible to estimate the ratios of concentrations of products **4** and D$_1$-**4.** The obtained value of KIE is 2.2 ± 0.2.

In the second series of experiments, studies involving $C_3H_5OC(O)H$ and $C_3H_5OC(O)D$ were carried out separately in identical conditions that minimize the formation of byproducts: double allylation of norbornadiene and its hydration and hydroformylation. With this goal, allyl formate was taken in deficient amount (10%) compared to norbornadiene. With the same purpose, product concentrations were determined at low reagent conversions (not higher than 5%). The countdown began immediately after the end of the induction period. It follows from data obtained in the processing of dependences that KIE is 2.3 ± 0.2 (Fig. 3).

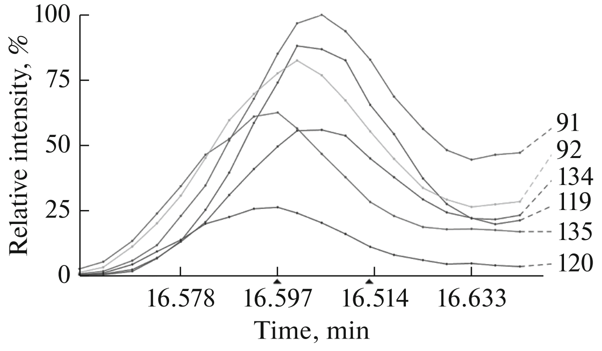


Fig. 2. Deconvolution of signals corresponding to characteristic ions in the mixture of products **4** and D$_1$-**4**.

CONCLUSIONS

Thus, the results obtained in the two series of experiments completely coincide. A rather high KIE value (greater than 1.4) confirms the hypothesis about the preference of breaking the formyl C–H bond at the limiting step of the process [18]. This means that β-hydride transfer is the limiting step in the catalytic cycle of norbornadiene hydroallylation in the presence of palladium compounds. However, such a conclusion

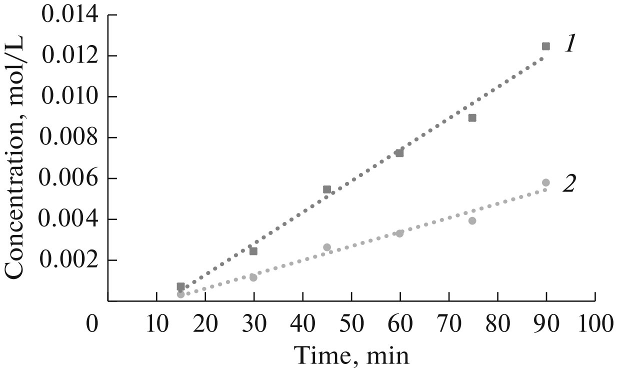


Fig. 3. Dependence of the ratio of the products of norbornadiene hydroallylation (*1*) **4** and (*2*) D$_1$-**4** on time on the $Pd_3(OAc)_6$ catalyst. Molar ratio: $C^0_{\mathrm{NBD}} : C^0_{\mathrm{Pd}} = 100 : 1$. $C^0_{\mathrm{NBD}} = 0.275$ mol L^{-1}, $C^0_{\mathrm{AF}} = C^0_{\mathrm{AF\text{-}D1}} = 0.250$ mol L^{-1}; acetonitrile solvent, $T = 25°\mathrm{C}$.

should not be extended to the formation of oxidative allylation products of norbornadiene **1–3**, for which the limiting step may be different. The combined use of isotope and kinetic methods will provide an answer to this question.

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