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

Kinetics and Mechanism of Thermal Decomposition of Bis(η^3-Allyl)Nickel Complexes

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Abstract—The kinetics of thermal decomposition of bis(η^3-allyl) nickel complexes in various media is studied. The specific features of the mechanism are determined, including the combination of the stages of *trans-cis* isomerization of $\mathrm{Niall_2}$ and the bimolecular decomposition of the *cis*-isomer with diallyl formation. The effect of autocatalytic decomposition of complexes with metallic nickel is been detected. The qualitative dependences of the process rate on the nature of the solvent and the structure of the allyl ligand are determined. The activation parameters of individual steps, consistent with quantum chemical calculations, are found.

Keywords: bis(η^3-allyl)nickel complexes, kinetics, mechanism, autocatalytic effect, thermal decomposition, allyl coupling

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INTRODUCTION

The chemistry of η^3-allyl complexes of transition metals began to develop rapidly 60 years ago. This is largely associated with an outstanding achievement of I.I. Moiseev an co-workers, who synthesized and characterized the first η^3-allylic palladium complex, η^3-allylpalladium chloride [1]. Since then, this class of compounds has filled an important place in organometallic chemistry and catalysis. Nickel and palladium complexes have found the greatest use among them [2–5].

Bis(η^3-allyl)nickel complexes are precursors of many catalytic reactions [6]. They can exist only in anaerobic conditions and are thermally unstable. Their decomposition begins at the melting point and leads to the formation of metallic nickel ($\mathrm{Ni^0}$) and diallyl (Scheme 1):

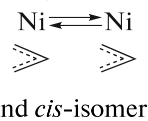
$$\mathrm{Niall_2} \rightarrow \text{all–all} + \mathrm{Ni^0}$$

$$\text{all} = \text{1-}\mathrm{CH_3C_3H_4},\ \ \mathrm{C_3H_5},\ \ \text{2-}\mathrm{CH_3C_3H_4}$$

Scheme 1. Decomposition of nickel bis(η^3-allyl) complexes.

This reaction is important for organometallic chemistry, since it models the complete breaking of two allyl–metal bonds and the generation of atomic nickel, which is an active center in many catalytic processes. Initially, this decomposition was considered a synchronous process occurring under the actions of reagents capable of displacing allyl fragments from the complex [6]. However, in 1970, Moiseev formulated the idea of a complex multi-step mechanism involving the stages of the η^3–η^1 isomerization of allyl ligands coordinated to nickel [7].

Bis(η^3-allyl)nickel complexes exist in the form *trans*- and *cis*-isomers (Scheme 2). In crystals, their ratio (possibly equilibrium) is 3 : 1 for $\mathrm{Ni(C_3H_5)_2}$ and 2.3 : 1 for $\mathrm{Ni(2\text{-}CH_3C_3H_4)_2}$ [6, 8]. The relative activity of isomers can play an important role in the implementation of regio- and stereoselective synthesis, as well as at the stages of the formation of catalytic centers.



Scheme 2. *Trans*- and *cis*-isomers of bis(η^3-allyl)nickel.

Nevertheless, the mechanisms of isomerization and thermal decomposition of bis(η^3-allyl)nickel are poorly studied. This information seems to be very useful for the formation of catalytically active complexes.

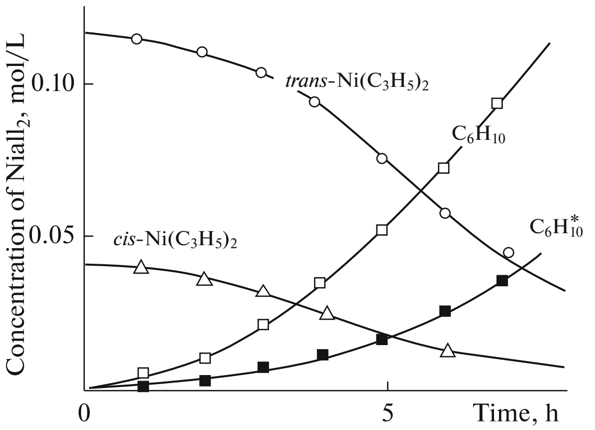


Fig. 1. Kinetic dependences of the process of thermal decomposition of $Ni(C_3H_5)_2$ isomers in C_6H_6 at 40°C; $[Niall_2] = 0.157$ mol/L; * rotating ampoule.

The charge state of the central atom and the structure of the η^3-allyl ligand is likely to affect significantly its reactivity.

The goal of this work was to study the kinetics and mechanism of thermal decomposition of bis(η^3-allyl)nickel complexes, as well as the effect of their structure and the nature of a solvent on this process.

EXPERIMENTAL

The thermal decomposition of bis(η^3-allyl)nickel complexes, $Ni(C_3H_5)_2$ and $Ni(2\text{-}CH_3C_3H_4)_2$, was studied in sealed NMR ampoules and in 0.3 cm^3 vacuum batch reactors with a sampler. Experiments were performed in vacuum or in an argon atmosphere, thoroughly purified from oxygen impurities. The experimental conditions were as follows: the concentration of complex was 0.1–0.2 mol/L; the solvent was C_6D_6, $(C_2D_5)_2O$, CD_3CN, THF-D_8, DMFA-D_7; the temperature was 30–75°C.

The optimal method for analyzing all the components of the reaction mixture in solution, including *cis* and *trans* isomers of bis(η^3-allyl)nickel, is ^{1}H NMR spectroscopy. The concentrations of bis(η^3-allyl)nickel isomers and the products of their recombination were determined from the intensities of ^{1}H NMR signals [9]. ^{1}H and ^{13}C NMR spectra were recorded using an DPX 300 spectrometer (Bruker, Germany), using a working frequency of 300.13 MHz for nuclei ^{1}H and 75.033 MHz for nuclei ^{13}C.

Independently, the reaction was monitored by GLC using a Kristall PM-2000 chromatograph (Khromatek, Russia) with a flame ionization detector, an Agilent J&W HP-50+ capillary column (Agilent Technologies, USA). The products of decomposition were identified by gas chromatography/mass spectrometry using an Automass-120 instrument (Delsi-Nermag, France) with a CPS CP-Sil 5 CB capillary column, electron impact mode, a scanning range of $m/z = 15–300$, scanning rate of 1 scan for 300 ms, and an ionization energy of 70 eV. In analyzing and interpreting mass spectra, we used data reported in [10, 11] and standard databases.

A software package [12, 13] was used to process the kinetic data, determine the rate constants to solve the inverse kinetic problem, and perform identifiability analysis.

RESULTS AND DISCUSSION

During the reaction, the color of the solution changed from light yellow to reddish, characteristic of nickel olefin complexes. The solution loses its transparency, and by the end of the reaction, a precipitate is formed, which isolated and studied by us using elemental analysis and electron microscopy. It was a highly dispersed metallic nickel with a particle size of 0.1 to 10 μm.

The simplest scheme of the mechanism of thermal decomposition of bis(η^3-allyl)nickel complexes can be described by the following equations:

$$trans\text{-Niall}_2 \rightleftharpoons cis\text{-Niall}_2, \quad \text{(I)}$$

$$trans\text{-Niall}_2 \rightarrow \text{all–all} + \text{Ni}^0, \quad \text{(II)}$$

$$cis\text{-Niall}_2 \rightarrow \text{all–all} + \text{Ni}^0. \quad \text{(III)}$$

However, it does not take into explain a number of experimental observations: the process proceeds with an induction period, which is confirmed by the S-shaped form of the kinetic dependences of diallyl accumulation and $Ni(C_3H_5)_2$ isomer consumption (Fig. 1).

One of the possible reasons for the observed phenomenon is autocatalysis by the reaction products, hexa-1,5-diene (HD) and metallic nickel. To determine the nature of this effect, a series of comparative kinetic experiments have been carried out.

When hexa-1,5-diene is preliminarily introduced into the reaction system (the HD/$Ni(C_3H_5)_2$ molar ratio ranging from 0.1 to 2.0), the nature of the process does not change.

When Ni^0 is added, the process is substantially accelerated, and this indicates that autocatalysis is due to metallic nickel.

Another series of experiments was carried out with the rotation of the reaction ampoule in the resonator of the NMR spectrometer. Under the action of centrifugal force, metallic nickel formed during the decomposition of $Ni(C_3H_5)_2$ is deposited on the walls, and its concentration in the reaction solution decreases. At the same time, the induction period increases significantly (Fig. 1, experiment *).

Table 1. Rate and equilibrium constants of individual steps of the thermal decomposition of bis(η^3-allyl)nickel complexes

Solvent*	ε^{25}	T, °C	$k_1 \times 10^5$, s^{-1}	$k_2 \times 10^5$, $mol^{-1}\, L\, s^{-1}$	$k_3 \times 10^4$, $mol^{-1}\, L\, s^{-1}$	$k_4 \times 10^5$, $mol^{-1}\, L\, s^{-1}$	$K_1 \times 10$
$Ni(C_3H_5)_2$							
Benzene	2.28	30	3.6 ± 1.0	1.3 ± 0.1	2.5 ± 2.2	2.2 ± 0.3	3.0 ± 0.2
		40	7.0 ± 2.1	1.1 ± 0.1	3.2 ± 2.9	5.2 ± 0.8	3.4 ± 0.2
		50	16 ± 4.7	10.0 ± 1.3	6.3 ± 5.7	7.3 ± 1.1	4.2 ± 0.3
Diethyl ether	4.27	30	7.9 ± 2.3	2.5 ± 0.3	5.3 ± 4.8	4.0 ± 0.6	3.1 ± 0.2
THF	7.58	30	5.1 ± 1.5	17.0 ± 2.2	15.0 ± 13.5	6.9 ± 1.0	3.7 ± 0.2
Acetonitrile	36.0	30	15 ± 4.6	21 ± 2.7	18 ± 16	8.3 ± 1.2	3.1 ± 0.2
DMFA	36.7	30	9.3 ± 2.8	37 ± 4.8	32 ± 28	9.4 ± 1.4	3.7 ± 0.2
$Ni(2\text{-}CH_3C_3H_4)_2$							
Benzene		50	4.3 ± 1.9	3.9 ± 0.5	0.6 ± 0.1	3.6 ± 0.7	4.3 ± 1.3
	2.28	60	0.8 ± 0.3	11 ± 1.6	5.4 ± 1.0	16 ± 0.3	2.3 ± 0.7
		75	1.0 ± 0.4	18 ± 2.7	13 ± 2.6	47 ± 0.9	2.4 ± 0.7

* In all experiments, a deuterated solvent was used. ε^{25} is the dielectric constant of the solvent at 25°C.

Based on the results obtained, the reaction mechanism was supplemented by the following steps of catalytic decomposition of each of the $Niall_2$ isomers:

$$trans\text{-}NiaIl_2 + Ni^0 \rightarrow \text{all–all} + 2Ni^0, \qquad (IV)$$

$$cis\text{-}NiaIl_2 + Ni^0 \rightarrow \text{all–all} + 2Ni^0. \qquad (V)$$

These additional steps significantly improve the description of the experimental data by the kinetic model (the standard deviation is reduced to 4.8%). However, this variant is also unacceptable because of the systematic error observed at the initial stage of the reaction. An adequate description is achieved for a mechanism (Scheme 3), in which the initiation stage is bimolecular, and the activity of the *cis* and *trans* isomers in it is practically indistinguishable (deviation 4.5%). Metallic nickel catalyzes the decomposition of both $Niall_2$ isomers.

Step **I** $trans\text{-}Niall_2 \rightleftarrows cis\text{-}Niall_2\ \ k_1, K_1.$

Step **II** $Niall_2 + Niall_2 \rightarrow 2\text{all–all} + 2Ni^0\ \ k_2$

Step **III** $trans\text{-}Niall_2 + Ni^0 \rightarrow \text{all–all} + 2Ni^0\ \ k_3$

Step **IV** $cis\text{-}Niall_2 + Ni^0 \rightarrow \text{all–all} + 2Ni^0\ \ k_4,$

k_i is the rate constant step **I**

K_1 is the equilibrium constant of step **I**

Scheme 3. Mechanism of thermal decomposition of bis(η^3-allyl)nickel.

According to Scheme 3, the kinetic description of the process can be as follows:

- rate of *trans–cis* isomerization of the complex:

$$W_1 = k_1(C_{trans} - C_{cis}/K_1);$$

- the rate of initiation step has the second order in the complex:

$$W_2 = k_2(C_{trans}^2 + C_{trans}C_{cis} + C_{cis}^2);$$

- the rates of *trans* and *cis* isomer decomposition are the second-order equations, the first order in each reactant:

$$W_3 = k_3C_{trans}C_{Ni}^0 = k_3C_{trans}C_d,$$

$$W_4 = k_4C_{cis}C_{Ni}^0 = k_4C_{cis}C_d,$$

where C_{trans}, C_{cis}, C_{Ni}^0, C_d are the concentrations of *trans* and *cis* isomers of $Ni(C_3H_5)_2$, metallic nickel and diallyl, respectively.

The processing of kinetic data using the software package [12] made it possible to calculate the values of the rate constants and equilibria of all stages for different temperatures (Table 1).

The nature of a solvent has a significant effect on the process. With an increase in its polarity, thermal decomposition of bis(η^3-allyl)nickel accelerates.

At a moderate temperature (30–50°C) in C_6D_6, the values of the rate constants of steps **I**, **II**, and **IV** were determined with a high accuracy (Table 1), which points to the realization of a route related to *trans* → *cis* isomerization and catalytic decomposition of *cis*-$Ni(C_3H_5)_2$ under this conditions. On the contrary, the value of the rate constant k_3 of the step of *trans*-$Ni(C_3H_5)_2$ decomposition is uncertain. It was determined with a high error (up to 90%) because of the low contribution of this step to the overall rate of the process. However, at a high temperature (60–75°C), bimolecular decomposition (step **II**) begins to be dominating over the catalytic one. This is evident from

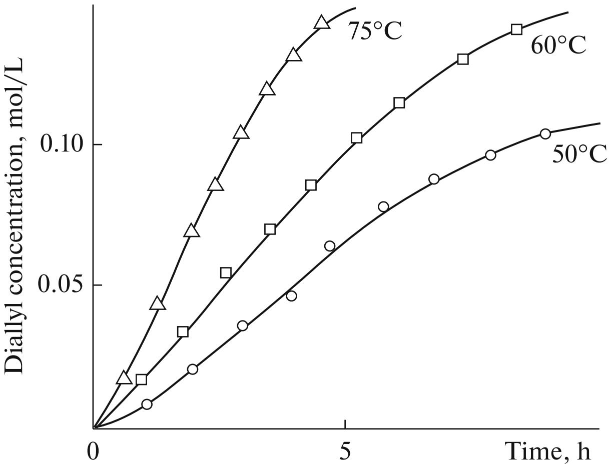
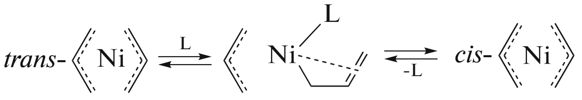


Fig. 2. Kinetic curves of accumulation of 2,5-dimethylhexa-1,5-diene in the thermal decomposition of Ni(2-$CH_3C_3H_4)_2$. Solvent: C_6D_6.

the disappearance of the induction period on the kinetic curves (Fig. 2).

Based on the obtained values of the rate constants, we calculated the activation parameters for the stages, whose contribution to the main route of thermal decomposition is the most significant (Table 2). Analysis of the data obtained for these stages indicates the complex nature of their occurrence.

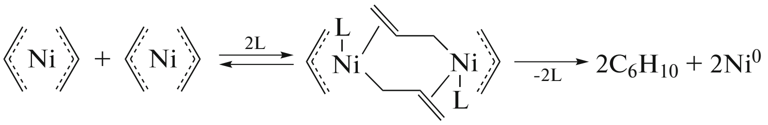
One may assume that, in step **I** the $\eta^3 \rightarrow \eta^1$ isomerization takes place with one of the allyl ligands (L is the solvent) (Scheme 4):



Scheme 4.

The reverse transition $\eta^1 \rightarrow \eta^3$ leads to the formation of both *trans*- and *cis*-$Ni(C_3H_5)_2$. The activation energy of this step (~60 kJ/mol) is mostly related with $\eta^3 \rightarrow \eta^1$ isomerization of an allyl ligand. Its intramolecular nature is confirmed by a low value of activation entropy $\Delta S^{\neq}$. It is likely that the polar solvent is favorable for $\eta^3 \rightarrow \eta^1$ isomerization of an allyl ligand and stabilizes the intermediate species formed.

The initiation step **II** is characterized by the second-order rate equation with respect to $Ni(C_3H_5)_2$, and isomers are not distinguishable in it. Step **II** is likely to proceed through the formation of a binuclear intermediate **1**, in which allyl ligands play the role of bridges between nickel atoms (Scheme 5). At this stage, the reaction is facilitated by the solvent.



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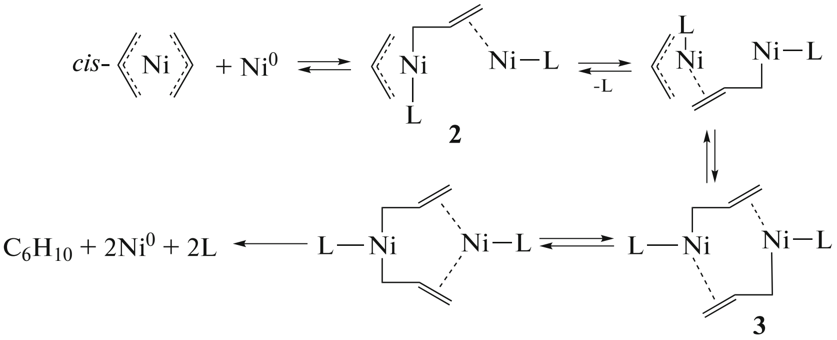
Scheme 5.

Certain analogies between steps **I** and **II** are confirmed by the close values of the activation energies (E^a). A somewhat lower value of E_2^a may be associated with the formation of dimeric complex **1**. It has a fairly ordered structure as evidenced by the small value of the entropy of activation.

It is likely that the decomposition of the *cis* isomer (step **IV**) also involves the consecutive $\eta^3 \rightarrow \eta^1$ isomerization of allyl ligands and the coordination of the double bond of one of them to a nickel atom, which plays the role of a catalyst (Scheme 6).



Scheme 6.

Table 2. Values of the activation parameters of the stages of the thermal decomposition process of nickel bis-η^3-allyl complexes in C_6D_6

Step	E^a, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
$Ni(C_3H_5)_2$			
I	62 ± 22	59 ± 22	−136 ± 51
II	67 ± 10	62 ± 9.8	−336 ± 59
III	43 ± 12	38 ± 12	−390 ± 46
$Ni(2\text{-}CH_3C_3H_4)_2$			
II	70 ± 9	55 ± 9	−340 ± 40

A further restructuring of complex **2** is related to the participation of the second allyl ligand and migration of a double bond. The formation of the binuclear center similar to **3** substantially decrease the activation energy of this step. Taking into account the assumption of the necessary and synchronous $\eta^3 \rightarrow \eta^1$ isomerization of two allyl ligands, we may expect that E_3^a will two times higher than E_1^a. However, its value is three times lower than expected (≈40 kJ/mol).

The activation energy of the initiation step increases when switching from the unsubstituted allyl to 2-methyl-η^3-allyl, which agrees with the results of quantum chemical studies. The values of Mulliken charges at the nickel atoms in $Ni(C_3H_5)_2$ and $Ni(2\text{-}CH_3C_3H_4)_2$, calculated by the DFT-PBE/TZ2P method are +0.329 and +0.305, respectively. The bond of 2-methyl-η^3-allyl ligand with nickel has a less ionic character. Therefore, its $\eta^3 \rightarrow \eta^1$ isomerization is more difficult compared to the unsubstituted η^3-allyl.

The equilibrium constant of the *trans-cis* $Ni(C_3H_5)_2$ isomerization step is practically independent of temperature in the studied range, which also agrees with literature data [14]. The value of the Gibbs energy calculated on the basis of the equilibrium constant is approximately 3 kJ/mol.

CONCLUSIONS

We studied the thermal decomposition of bis(η^3-allyl)nickel complexes in a solution at 30–75°C. The reaction products are diallyl and metallic nickel. The higher polarity of the solvent and the higher effective positive charge on a nickel atom lead to the acceleration of the process.

^{1}H NMR spectroscopy and GLC were used to study the reaction kinetics. It was found that the decomposition bis(η^3-allyl)nickel complexes occurs with autocatalysis. It was shown that the catalyst is metallic nickel formed during the reaction. The values of activation parameters of individual steps of thermal decomposition of $Niall_2$ were determined. The activation energies were estimated for the $\eta^3 \rightarrow \eta^1$ isomerization of the allyl ligand for C_3H_5 and $2\text{-}CH_3C_3H_4$ allyls. These are in agreement with quantum chemical calculations.

A mechanism of thermal decomposition was proposed, which includes the *trans–cis* isomerization of $Niall_2$ and the catalytic decomposition of the *cis* isomer. With increasing temperature, bimolecular decomposition begins to prevail over catalytic.

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