KINETIC REGULARITIES OF HYDROGENATION OF 6,10-DIMETHYL-3,5,9-UNDECATRIEN-

2-ONE AT ELEVATED HYDROGEN PRESSURE.

III. HYDROGENATION IN OPEN SYSTEM

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Production of chemical compounds can be considerably increased if the processes are carried out in open systems. Thus, the hydrogenation of 6,1--dimethy1-3,5,9-undecatrien 2-one [pseudoionone, (I)] to 6,10-dimethylundecan-2-one [hexahydropseudoionone, (II)], an intermediate in the synthesis of vitamin E, was studied in a flow-type displaceable reactor on Raney nickel catalyst [1]. The influence of temperature (T), partial hydrogen vapor pressure (P_{H_2}) , feed rate of hydrogen ($V_{H_{2}}$), and volumetric feed rate (V), on the rate of reaction were investigated. The best results were obtained for the catalytic reduction of a 10% solution of (I) in isopropanol at a temperature of 50°C in the reaction zone, partial hydrogen pressure of 2 MPa, bubbling of hydrogen at a flow rate of 0.15 liter/min, and feed rate of the solution of 1-2.1 h⁻¹, whereby the yield of (II) was 87.8%. Up to 3.2% of 6,10-dimethylundecan-2-ol were measured in the catalyzate. We should note that under static conditions, when the saturation of the double bond in (I) was carried out on a Raney nickel catalyst, a carbinol was also isolated [6]. In accordance with previous publications, the hydrogenation of (I) on palladium deposited on the activated charcoal in a static system proceeds selectively. The authors of [6] studied the hydrogeneration of crotonaldehyde into butyraldehyde in a tubular reactor, in particular, in a palladium catalyst (Pd/aluminum oxide) by varying the temperature, volumetric feeding rate of the aldehyde, and rate of hydrogen bubbling. This catalyst (1.8% Pd) was used on a pilot plant apparatus for 5000 h before being regenerated, with a 96-97% selectivity with respect to the desired end product.

In the reduction of mesityl oxide under dynamic conditions on Pd/Al_2O_3 and Pd/C catalysts, the yield of methyl isobutyl ketone was 90% [2].

It should be noted that the authors of the above-mentioned publications did not observe the formation of a saturated alcohol. It was therefore desirable to study the behavior of (I) in the hydrogenation reaction on Pd/C in an open system. The hydrogenation of (I) was studied on Pd/C under dynamic conditions, on an apparatus described in [1]. Glass balls (25 cm³) were placed in the mixing zone of the reagents, and the Pd/C catalyst with grain size of 1-2 mm was introduced into the reaction zone (60 cm³). The catalyzate samples were analyzed by the GLC method on a "Chrom-4" apparatus. In the experiments, the concentration of (I) (C_I) at the inlet to the reactor was varied from 5 to 20%, the temperature (T) from 30 to 70°C, and volumetric feed rate of hydrogen (V_{H₂}) from 1.25 to 6 liters/h.

Table 1 shows that in the hydrogenation of a 5% solution of (I) in a flow-type system, the process proceeds nonselectively: 11.1% of a saturated alcohol III is formed. Increase in the concentration of (I) to 20% leads to a more selective process course. The content of the desired end product in the catalyzate increases from 88.9 (at 5% C_I) to 95.3% (at 20% C_I). In the subsequent experiments, a 20% solution of (I) underwent conversion. Increase in the temperature from 30 to 50°C promotes the accumulation of (II) in the catalyzate; further increase in the temperature to 70°C leads to an increase in the content of (II) in the catalyzate. Variation of the feed rate also leads to a dependence of the content of (II) in the catalyzate on the feed rate that passes through a maximum. It is probable that with decrease in the feed rate, i.e., with increase in the time of contact of the reacting compounds with the catalyst, diffusional inhibition begins to play a role; this decreases the selectivity with respect to (II). From the dependence of the accumulation of (II) and (III) in the reaction mixture on the feed rate, we can calculate the apparent energy of activation of the formation process of (II) and (III) at medium degrees of conversion of (I) and (III), respectively, under condi-

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Experimental conditions	Parameter measured	Composition of catalyst		
		I	L I I	II!
$V = 2.0 \text{ h}^{-1}$ $P_{\text{H}_{a}} = 2.0 \text{ MPa}$	C1. %	None	88,9	11.(
$V_{\rm H_s} = 4.0$ liter/min	10	»	92,1	7,9
$T = 50 ^{\circ}\text{C}$ $V = 2.0 \text{h}^{-1}$	20 T, C	»	95,3	4,7
$V_{\rm H_s} = 4.0$ liter/min	30	4,6	92,7	2,7 .
$P_{\rm H_a} = 2,0$ MPa	50	None	95,3	4,7
$C_{\rm I} = 20.0 \%$ $T = 30 ^{\circ}{\rm C}$	70 V, h ⁻¹	»	92,4	7,6
$V_{\rm H_a} = 4.0$ liter/min	0,4	None	80,2	19,8
$P_{\rm H_s} = 2,0$ MPa	1	»	95,3	4,7
$C_{\rm I} = 20,0 \%$	2 3 4 7 12	4,6 10,9 18,6 36,8 67,3	92,7 87,6 81,4 63,2 32,7	2,7 1,5 None
$V = 2.0 h^{-1}$	V _H	,-		
$T = 50 \circ C$ $P_{H_{g}} = 2,0 MPa$ $C_{I} = 20,0 \%$	1,25 2,5 4,0 6,0	6,3 4,2 None *	92,7 93,7 96,4 96,3	1,0 2,1 3,6 3,7
	1	1		

TABLE 1. Hydrogenation of (I) in Open System

tions at which the formation of (II) and (III) proceeds at a maximal rate.

To obtain the activation energy, the dependence of $\ln v$ on 1/T is plotted (see Fig. 1). By comparing the values of the activation energies obtained with those given in [1], it can be stated that in an open system, the process proceeds with intradiffusional inhibition. The apparent activation energy of the conversion of (I) into (II) (E_{I+II}) is equal to 27 kJ/mole under dynamic conditions and 41 kJ/mole under static conditions; the activation energy of the conversion of (II) into (III) into (III) (E_{I+II}) is form of the kinetic equations in the internal diffusion region [5] shows a weaker temperature dependence than in the kinetic region.

The activation energy in the internal-diffusional region is $E^* > 0.5E$ in the present reaction, which shows that the process proceeds in the internal transition region, for which $0.5E < E^* < E_{bp}$. In this region the regime for the course of the reaction is intermediate between kinetic and internal-diffusional.

The influence of hydrogen bubbling was studied at a temperature of 50° C, a partial pressure of 2 MPa, 20% concentration of (I) in isopropanol, and a volumetric feed rate of 2 h⁻¹. Increase in the hydrogen bubbling from 1.25 to 4 liters/min leads to a decrease in the content of (I) in the catalyzate and increase in the content of (II) and (III). The subsequent increase in the rate of hydrogen bubbling to 6 liters/min does not appreciably influence the process.

Thus, from the investigations that were carried out, the following optimal conditions for carrying out the hydrogenation of (I) on Pd/C in an open system have been established: temperature 50°C, partial hydrogen pressure 2 MPa, hydrogen bubbling 4 liters/min, 20% solution of (I) in isopropanol, feed rate $3.5 h^{-1}$. As the result, the content of (II) in the catalyzate is 97.7%, and that of (III) 2.3%.

As has already been noted, no indications of the possibility of the hydrogenation of the C=O group in (II) on the Pd/C catalyst can be found in the literature. It is possible that this is due to the fact that the hydrogenation was interrupted immediately after the saturation of the C=C bonds, so that the hydrogenation of the C=O group, for which a considerable contact time is required, did not take place.

We carried out an orbital analysis of the hydrogenation of (I) and (II) by a noncomputer variant of perturbations theory [4]. The process is broken up into several elementary events. The intermediate stage has a low energy barrier if the principles of the structural and energetic matching of the partners orbitals are obeyed. The orbitals of the transition states of all stages should satisfy the rules of orbital symmetry, minimum movement of the orbitals, and charge bonding.

The hydrogenation reaction of a dienic system begins with the activation event of hydrogen. According to [3], hydrogen is activated by means of oxidative addition. Regarding the



Fig. 1. Dependence of $\ln \tau$ on 1/T for hydrogenation of (I) (dark circles) and II (light circles) on Pd/C. On abscissa — reciprocal temperature $1/T \cdot 10^3$ in ${}^{\circ}K^{-1}$; on ordinate — logarithm of reaction rate (ln τ).

symmetry, the occupied p_{π} -orbital has the most appropriate symmetry for the oxidative addition of a hydrogen molecule. Since the hydrogen atom has an s-orbital only, the greatest overlap can be achieved if the partner uses an s-orbital. Therefore, the optimal hydrogenation catalyst should have a low energy of sp_{π} -symmetry promotion. Metals of the VIIIth group of the periodic system, including palladium, satisfy these conditions. Palladium belongs to the class of catalysts with high s-character and a tendency to undergo an orbital interaction, which is symbatic with the redox potential.

We shall now consider the consecutive addition of hydrogen to the 3-4, 5-6, and 9-10 bonds and the C=O group of compound (I). During the saturation of the 5-6 bond, unpopulated s-orbitals operate on the Pd/C, whereby the antibonding orbitals used are not of the two-atomic fragments,

but of a four-atomic fragment of the diene system C=C-C=C' system. The 3-4 bond also be-

comes saturated by the interaction of empty s-orbitals of Pd/C with the tetraatomic enone fragment. With the progressing hydrogenation of the 5-6 bond of (I), the π -acceptor properties of the substrate decrease, the splitting of the d-orbitals of the catalyst is decreased, and hence the spm-protonation is facilitated and the d-character of the unoccupied orbital of Pd/C increases. The hydrogenation of alkenes to alkanes proceeds preferably on d-catalysts, with preference for the orbital bonding [3], i.e., the 9-10 bond becomes saturated by the π -mechanism on the d-catalysts. As the result of internal diffusional inhibition, the concentration of the substrate deep in the pores is less than on the external surface of the contact, and hence the modification of the latter due to a decrease in the π -acceptor properties of the substrate is less as the hydrogenation progresses, i.e., free s-orbitals are active in the catalyst pores. Moreover, under the influence of the hydrocarbon chains of (II), the proportion of the chargecontrolled binding increases, which causes an O-coordination of (II). The hydrogenation of the carbonyl group is thus made possible and is realized in a flow-type reactor when the contact time is increased.

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