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KINETIC PRINCIPLES OF THE HYDROGENATION OF 6,10-DIMETHYL-UNDECA-3,5,9-TRIEN-2-ONE ON RANEY NICKEL

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Both palladium catalysts on supports with various percentages of the active phase (0.5-5% Pd) [3, 8, 10, 11] and nickel catalysts [9] are used as catalysts for the hydrogenation of unsaturated ketones, including 6,10-dimethylundeca-3,5,9-trien-2-one (I). However, nickel catalysts have not yet found extensive application in these processes, despite their obvious merits (the simplicity of their preparation and activation, their stability, and their relatively low cost). The hydrogenation of I on various nickel catalysts was described in [7, 8]; the formation of a product of saturation of the C=0 group of I is not noted in either of the indicated publications. We have previously observed [4] that the hydrogenation of I on nickel catalysts is accompanied by the formation of 6,10-dimethylundecanol (V), the presence of which was confirmed by IR spectroscopy [1].

The aim of the present communication was to discuss the results of the hydrogenation of I on a selectively acting nickel catalyst specially prepared from Ni-Al alloy (30:70).

EXPERIMENTAL

The process was carried out in a reactor with vigorous stirring in the líquid phase at a hydrogen partial pressure of 2-13.2 MPa at 20-50°C; the concentration of I in isopropyl alcohol was 10%, and the concentration of the catalyst was 15% Ni with respect to mass based on I. The selectivity of the reaction was evaluated by the method in [2]. The catalysate was analyzed in accordance with [1].

Under the selected conditions the reaction rate was quite high, and only products of hydrogenation of I, viz., 6,10-dimethylundeca-3,9-dien-2-one (II), 6,10-dimethyl-undeca-9-en-2-one (III), and 6,10-dimethylundecan-2-one (IV), were detected in the reaction medium 5 min from the start of the process.

The experimental "catalysate composition-reaction time" curves for various reaction temperatures and a hydrogen partial pressure of 8.1 MPa are presented in Fig. 1.

It is apparent from the results presented that an increase in the temperature leads to an increase in the rate of hydrogenation of all of the double bonds of I (see Fig. 1) and, correspondingly, a decrease in the selectivity of the process relative to the ethylene bonds of I (see Fig. 1). Over the investigated temperature range II was no longer detected 30 min from the start of the reaction. The maximum selectivity of the process was observed at 20°C and was 97%.

Kalinin Polytechnical Institute. Translated from Khimiko-farmatsevticheskii Zhurnal, Vol. 22, No. 1, pp. 70-73, January, 1988. Original article submitted April 14, 1986.

Temp., °C	Hydrogen pressure, MPa	Specific rate constants of the steps, min ⁻¹			Selectivity
		K2·104	Ks · 104	K4-104	tion, S
30 25 30 50 30 50 50 50 50 50 50 50 50	8,1 8,1 8,1 10,1 10,1 2,0 4,0 6,0 8,1 10,1 13,1	10,49 12,94 16,62 31,54 31,96 6,35 10,42 22,28 31,54 31,96 31,74	$\begin{array}{c} 3.70\\ 4.53\\ 6.75\\ 15.69\\ 16.38\\ 3.08\\ 6.52\\ 9.05\\ 15.69\\ 16.38\\ 15.82\\ \end{array}$	0.034 0.045 0.068 0.189 0.231 0.204 0.219 0.213 0.213 0.231 0.231 0.231	0,97 0,96 0,95 0,95 0,94 0,94 0,94 0,94 0,95 0,95 0,95 0,94
E _i , kJ/mole		30	<u> </u> 41	47	

TABLE 1. Effect of the Temperature and Pressure on the Hydrogenation of I in the Presence of Raney Ni

<u>Note</u>. In connection with the high initial rate of the process a reliable value of the rate constant for hydrogenation of the ethylene bond in the 5,6 position could not be obtained.

Similar principles were noted at a hydrogen partial pressure of 10.1 MPa.

Let us note that an increase in the temperature at this pressure promoted the hydrogenation of the C=O group of the ketone to a greater degree than at 8.1 MPa (see Table 1).

At gas-reagent pressures of 2.0-8.1 MPa the reaction rate increases almost proportionally with respect to the increase in the hydrogen pressure (Fig. 2) and reaches its maximum value at 8.1 MPa, after which it remained virtually unchanged (up to 13.2 MPa).

It should be noted that the selectivity of the process, evaluated by the method in [2], remained virtually unchanged over the entire investigated range of gas pressures (see Table 1). The maximum selectivity of the saturation of the ethylene bonds was attained at a hydrogen pressure of 8.1 MPa. The percentage of III was high over the entire temperature range (65-70%); in the opinion of Frank-Kamenetskii [6], this constitutes evidence that the process takes place under kinetic conditions.

The experimental results were processed in conformity with a consecutive reaction scheme with the use of the algorithm for searching for constants described in [5].

The values of the observed specific rate constants for saturation of the 3,4 (K_2) and 9,10 (K_3) bonds and the C=O group (K_4) and the apparent energies of activation of these steps (E_2 , E_3 , and E_4 , respectively) are presented in Table 1.

An analysis of the data presented above shows that an increase in the temperature from 20°C to 50°C accelerates the addition of hydrogen to all of the unsaturated bonds of I. The rate constants increase proportionally with respect to an increase in the temperature; this confirms the assumption advanced that the reaction takes place under kinetic conditions.

The values of the apparent energies of activation of the steps in the hydrogenation of I (see Table 1) calculated from the Arrhenius equation at 20-50°C also attest to this.

The K_2 and K_3 constants increase with an increase in the hydrogen pressure to 8.1 MPa (see Table 1); this constitutes evidence for the existence of extradiffusion inhibition of the process with respect to the gas-reagent. The order in hydrogen for the step involving the hydrogenation of the 3,4 bond is 0.94, as compared with 0.81 for the step involving the hydrogenation of the 9,10 bond. Above 8.1 MPa the order in the gas-reagent is close to zero. Let us note that the hydrogenation of the carbonyl group of the ketone is virtually independent of the pressure and proceeds via a zero-order scheme.

In comparing the results obtained with respect to the hydrogenation of I on Raney Ni with those obtained on Pd/C [5] it may be noted that on the first catalyst the reduction of I proceeds at a higher rate in the step involving the hydrogenation of the 5,6 bond, while



Fig. 1. Dependence of the catalysate composition on the temperature: 1), 5), 9), 13) 20°C; 2), 6), 10), 14) 25°C; 3), 7), 11), 15) 30°C; 4), 8), 12), 16) 50°C; 1), 2), 3), 4) III; 5), 6), 7), 8) II; 9), 10), 11), 12), IV; 13), 14), 15), 16) 6,10-dimethyl-2-undecanol. The time (in minutes) is plotted along the abscissa, and the catalysate composition (in percent) is plotted along the oridinate.

Fig. 2. Dependence of the rate of hydrogenation of I on the hydrogen partial pressure. Pressure P (in MPa) is plotted along the abscissa, and $\Delta V/\Delta \tau$ (in ml/min) is plotted along the ordinates.

the formation of III occurs at a lower rate, whereas its consumption, on the other hand, occurs a higher rate. The hydrogenation process was limited by saturation of the carbonyl group.

In contrast to Pd/C [9], zero order in the gas on Raney Ni for the 3,4 and 9,10 bonds of the ketone is achieved at the same pressure, viz., 8.1 MPa.

The data presented above make it possible to conclude that the reaction must be carried out at 8.1 MPa to realize the selective hydrogenation of I in the kinetic region on Raney Ni; the maximum selectivity of the process is also achieved at the same hydrogen pressure.

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