

## CATALYTIC REDUCTION OF UNSATURATED KETONES IN A CONTINUOUS REACTOR.

### 1. HYDROGENATION OF 6,10,14-TRIMETHYLPENTADEC-3,5-DIEN-2-ONE ON RANEY NICKEL

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Continuous processes for the selective reduction of unsaturated carbonyl compounds are widespread in the manufacture of vitamin preparations. In particular, one of the intermediate products in the synthesis of vitamins K<sub>1</sub> and E 6,10,14-trimethylpentadecan-2-one (II), which is obtained by the catalytic hydrogenation of 6,10,14-trimethylpentadeca-3,5-dien-2-one (I). There are no literature data on carrying out this process under dynamic conditions. There is information on hydrogenation in batch reactors of substances of similar structure widely used in vitamin manufacture, perfumes, or food additives, viz., pseudoionone [1-3],  $\beta$ -ionone [4, 5], citral [6]. The reaction was usually carried out under a partial pressure of hydrogen of 0.1-2.0 MPa, temperature 30-80°C in the presence of catalysts based on Pd [1-2], Ni [3-5], Cu [6]. Modifying additives, mainly halides of potassium, sodium, or lead acetate, were often put into the reaction mixture to increase the selectivity of action of the catalyst in relation to saturation of the C=C bond [7].

One of the very early studies [8] devoted to the hydrogenation of unsaturated carbonyl-containing compounds in a flow regime was the hydrogenation, in a tubular reactor (height 500 mm, diameter 20 mm, volume flow rate  $V = 0.3 \text{ h}^{-1}$ ), of crotonic aldehyde to butyraldehyde. The mechanism found previously of 1,4-addition of hydrogen to the enone has been confirmed by the authors. In addition they established that Ni/Al<sub>2</sub>O<sub>3</sub> (20 wt. % Ni), for example, was 1.5 times less selective than Ni and was partially poisoned by cadmium or zinc oxide. A detailed study of the reaction was carried out in a similar reactor with the aim of studying comparatively a series of catalysts based on Ni, Cu, and Pd [9] on changing temperature, the volume flow rate of aldehyde, and the amount of hydrogen supplied. The high selectivity (yield of butyraldehyde 96-97%) and catalyst stability of Pd/alumina (1.8% Pd) was shown. In a pilot plant with a catalyst load of 480 liter it worked for 5000 h before regeneration.

The palladium catalyst (Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/carbon) also showed high selectivity in the hydrogenation of mesityl oxide to methyl isobutyl ketone in a continuous regime [10]. The saturated ketone was obtained in 90% yield. Mesityl oxide was also hydrogenated with the same selectivity on Raney Cu, obtained from Cu:Al (1:1) alloy [11]. A reactor has been patented in West Germany for the continuous hydrogenation of isophorone (3,5,5-trimethyl-2-cyclohexen-1-one) to trimethylcyclohexanone on Na/Al<sub>2</sub>O<sub>3</sub> catalyst (30% Ni) the construction of which provides for distillation of the resulting product in a rectification apparatus linked directly to the reactor [12]. Each system (reactor, rectification column, and settler) operates in a regime making it possible to obtain the desired product in 99% yield. Comprehensive investigations in [13] were carried out on the continuous hydrogenation of organic compounds of various classes including  $\alpha,\beta$ -unsaturated ketones.

A systematic study has been carried out in the present work on the hydrogenation of (I) on a Raney Ni catalyst varying the following parameters: temperature (T), partial pressure of hydrogen (P), rate of hydrogen supply ( $V_{\text{H}_2}$ ), and volume flow rate (V). The work was carried out in column type equipment. The reactor was a stainless steel tube Kh18NiOT (height 700 mm, internal diameter 15 mm) with a regulatable electric heater. The places for the inlet of reactants and the outlet for reaction products were fitted with corrosion resistant gratings, glass balls were placed in the mixing zone for reactants (25 cm<sup>3</sup>), and catalyst was placed in the reaction zone (100 cm<sup>3</sup>). The reactor was operated in a flow regime. The

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TABLE 1. Hydrogenation of (I) on Raney Nickel in the Flow Reactor

Experimental conditions	Measured parameter	Catalysate composition, * %		
		I	II	III
$T=30^{\circ}\text{C}$ , $V_{\text{H}_2}=0.15$ liter/min, $P=2.0$ MPa	$V, \text{h}^{-1}$ :			
	0.6	None	47.3	52.7
	1.2	"	70.6	29.4
	1.8	"	89.6	10.4
	2.1	3.6	94.5	1.9
	2.4	6.7	91.1	2.2
$V=2.1 \text{ h}^{-1}$ , $V_{\text{H}_2}=0.15$ liter/min: $T=30^{\circ}\text{C}$	$P, \text{MPa}$ :			
	0.5	19.2	80.8	None
	1.0	8.2	91.8	"
	2.0	None	94.6	4.5
	3.0	"	87.1	12.9
	4.0	"	81.2	18.8
$V=2.1 \text{ h}^{-1}$ , $V_{\text{H}_2}=0.15$ liter/min, $P=2.0$ MPa	$T, ^{\circ}\text{C}$ :			
	20	3.0	94.2	2.8
	30	None	96.8	3.2
	40	"	94.9	5.1
	50	"	93.7	6.3
	60	"	92.4	7.6
$V=2.1 \text{ h}^{-1}$ , $P=2.0$ MPa, $T=30^{\circ}\text{C}$	$V_{\text{H}_2}, \text{liter/min}$ :			
	0.05	7.9	92.1	None
	0.10	3.6	96.4	"
	0.15	None	96.8	3.2
	0.50	"	95.4	4.6
	1.50	2.2	93.9	3.9
	2.50	5.4	92.7	1.9

\*Mean analysis of three test samples for each regime of operating the reactor.

catalyst was Raney Ni with particle size 4-6 mm leached out directly in the reactor to 10% (degree of leaching out was determined from the volume of isolated hydrogen). The mass of catalyst before the first leaching out was 180 g. Test samples were taken after placing the equipment in the given regime of temperature, pressure, and flow through the reactor of a quantity of solution being hydrogenated equal to three times the free volume of the reactor and supply lines. At least three test samples were taken for each given regime at time intervals appropriate for the volume flow rate. Analysis of the catalysate was carried out by GLC on a Khrom-4 instrument [14].

A 10% solution of (I) in isopropyl alcohol was subjected to hydrogenation. The results obtained are given in Table 1.

The influence of the volume flow rate (contact time) was studied at a hydrogen pressure of 2.0 MPa, temperature  $30^{\circ}\text{C}$ , bubbling hydrogen with  $V_{\text{H}_2} = 0.15$  liter/min. On feeding the solution being hydrogenated at a rate  $V = 0.6 \text{ h}^{-1}$  the catalysate consisted of saturated ketone (II) and the product of hydrogenation of its carbonyl group, viz., 6,10,14-trimethylpentadecan-2-ol (III), in approximately equal amounts (47.3 and 52.7% respectively). An increase in the rate of feeding (reduction of contact time) led to a gradual fall in the amount of (III) in the catalysate and a corresponding increase in the content of (I). On feeding at  $2.1 \text{ h}^{-1}$  the content of (III) reached a minimum (1.9%), simultaneously accumulation of unreacted (I) in the catalysate began. A further increase in the rate of feeding led to disappearance of (III) and a fairly rapid growth of the content of (I). Consequently at a rate of  $2.1 \text{ h}^{-1}$  there was a clearly marked maximum content of (II) (94.5%) corresponding to the efficiency of the catalyst saturating the C=C bond under the given conditions. It should be noted that at each of the studied intervals of supply rate there was none of the product of hydrogenation of one C=C bond, viz., 6,10,14-trimethylpentadeca-5-en-2-one (IV), present in the catalysates.

The influence of the partial pressure of hydrogen was studied at constant volume flow rate  $2.1 \text{ h}^{-1}$ , bubbling hydrogen at 0.15 liter/min, and a temperature of  $30^{\circ}\text{C}$ . At 0.5 MPa the catalysate consisted of (I) (19.2%) and (II) (80.8%). Compounds (III) and (IV) were absent.

An increase in pressure led initially to the disappearance of (I) from the catalysate and then to the appearance of (III). The maximum content of (II) (94.6%) was in the region of 2.0 MPa pressure, it was less marked than in the previous case.

The influence of temperature was investigated in the range 20-60°C at the optimum pressure and volume flow rate found previously (2.0 MPa and 2.1 h<sup>-1</sup> respectively). At 20°C (I) was still present in the catalysate, although there was also 3.0% (III). Beginning at 30°C there was no initial ketone (I) in the hydrogenation product but it did occur insignificantly.

The influence of the supply rate (bubbling) of hydrogen was studied at a pressure, temperature, and volume flow rate of (I) equal to 2.0 MPa, 30°C, and 2.1 h<sup>-1</sup> respectively. An increase in bubbling from 0.05 to 1.5-2.0 liter/min led to rapid disappearance of (I) from the catalysate. A further increase in hydrogen supply rate to 2.5 liter/min led to the appearance of an insignificant amount of (III). At higher flow rates, evidently because of carry-away, unreacted (I) appeared in the catalysate.

On the basis of the work carried out on the catalytic hydrogenation of (I) in a column type reactor in a flow regime, the following optimum parameters are proposed for carrying out the process with the aim of maximum yield (95-97%) of (II) on a nickel catalyst: volume flow rate of 10% solution of (I) in isopropanol 2.1 h<sup>-1</sup>, temperature in reaction zone 30°C, partial pressure of hydrogen 2.0 MPa, hydrogen supply rate 0.15 liter/min.

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