

STUDY OF THE HYDROGENATION OF KETONES ON METAL CATALYSTS BY AN IMPULSE-MICROREACTOR TECHNIQUE

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Hydrogenation of ketones and dehydrogenation of alcohols has been studied on thermolite-supported platinum, rhodium and palladium catalysts, in hydrogen as carrier gas, at 100–300 °C, by an impulse-microreactor technique. The platinum/thermolite and rhodium/thermolite catalysts were active, but palladium/thermolite proved inactive. Reactions accompanied by the isomerization of the carbon skeleton do not take place during the transformations of the compounds examined. As a consequence of the favourable properties of the platinum/thermolite catalyst (activity, cycle time, regenerability, lifetime), it can be employed as a catalyst in the preparation of secondary alcohols from ketones.

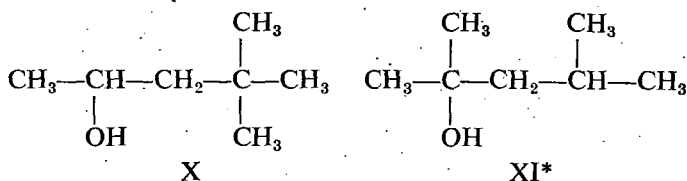
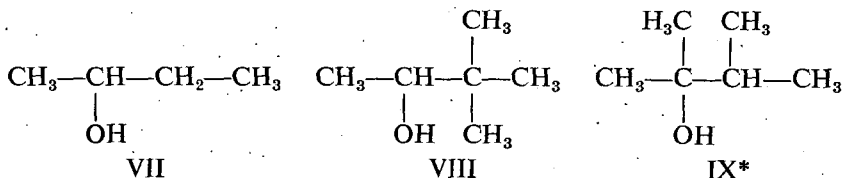
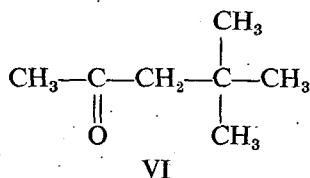
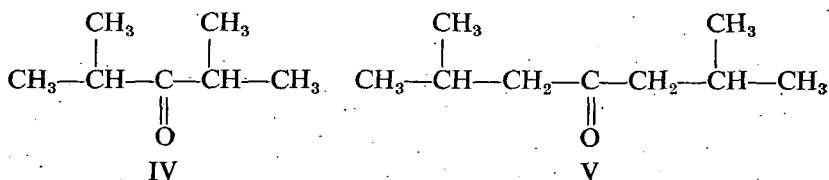
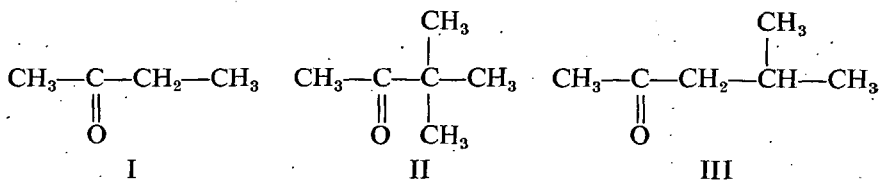
Metal catalysts active in the hydrogenation of olefins are known to catalyse the hydrogenation of the carbonyl group, too. Compared to the liquid-phase hydrogenation of oxo compounds, relatively little attention has been paid in the literature to the practical utilization of vapour-phase hydrogenation, or to the study of the mechanism of the process involved. Since our investigations were carried out on platinum, rhodium and palladium catalysts, the account given will be confined mainly to the more important literature findings regarding the catalysts. A review of the relevant literature appeared fairly recently [1]. Experimental observations unequivocally show that, when applied on various supports, most of the metals used are good catalysts of the hydrogenation of ketones [1–7]. Only palladium exhibits complete or partial inactivity [1, 5–7]. This question has not been dealt with in detail, in spite of the fact that attention has recently focused on the study of the mechanism of the hydrogenation process [1, 7–10]. At the same time it seems of interest that palladium, too, catalyses the dehydrogenation of secondary alcohols to ketones [11]. The sequence of activity in this reaction is: Pt > Pd > Rh.

The aims of the work described in the present paper were as follows:

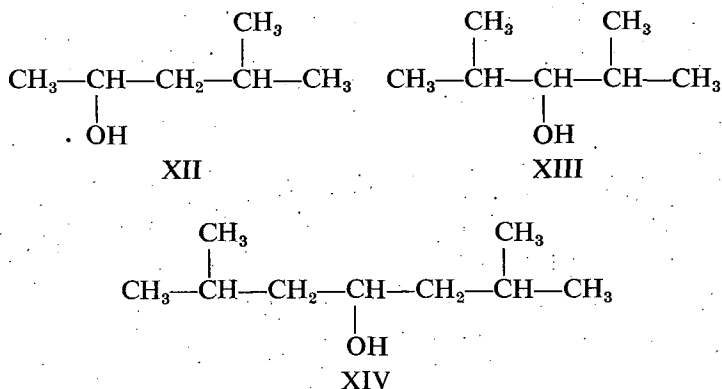
1. Study of the activities of thermolite-supported metal catalysts (in the following Pt/T, Pd/T, Rh/T) in ketone hydrogenation and alcohol dehydrogenation.
2. Examination of the applicability of the impulse-microreactor technique in the study of these two types of reaction. (Only one paper on this topic could be found in the literature [12].)

The investigations described here are of help in the study of the mechanisms of isomerization and hydrogenolysis of oxo-cycloalkanes under similar experimental conditions.

On this basis we set out to examine the transformation of the following model compounds on Pt/T, Rh/T and Pd/T catalysts:

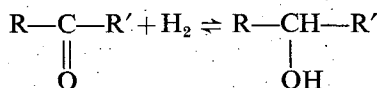


* The aim of the use of the tertiary alcohols IX and XI was to study the alcohol dehydrogenations with isomerization of the carbon skeleton.



The studies were carried out by an impulse technique in the presence of hydrogen as carrier gas, in the temperature range 90–300 °C (exact measurements were not possible at temperatures below 90 °C because of the extensive adsorption of the compounds).

It was found that the Pt/T and Rh/T catalysts possess considerable activity in the hydrogenation of ketones and the dehydrogenation of secondary alcohols:



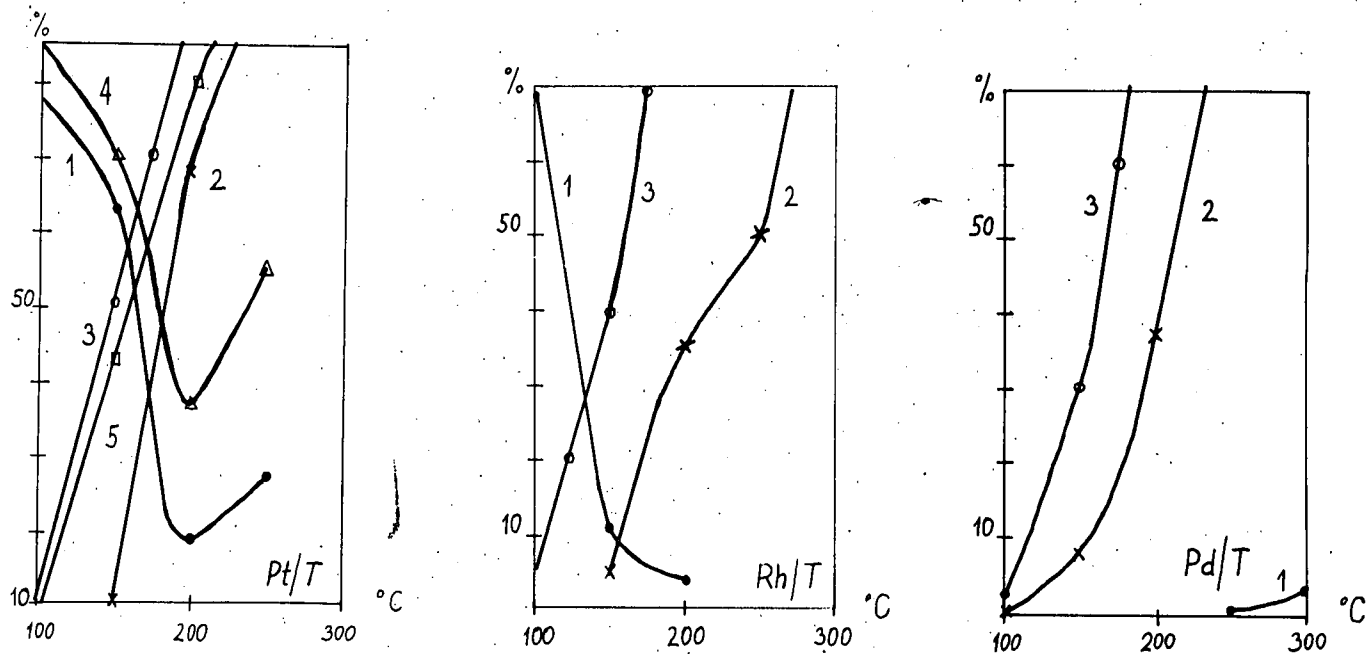
At the same time the Pd/T catalyst proved inactive in both reactions. Experimental data relating to the transformation of a number of compounds are given in Figs 1–8.

In both hydrogenation and dehydrogenation the activity of the Pt/T catalyst was higher than that of the Rh/T catalyst. The cycle-time of the latter is also substantially lower, *i.e.* its activity falls rapidly during both reactions. In accordance with the thermodynamic data, the hydrogenation is favoured by lower temperature; elevation of the temperature increases the rate of dehydrogenation of alcohols. At 90–110 °C the ketones examined were transformed to the corresponding secondary alcohols with yields of 80–90%. At lower temperatures the yields would probably be even better.

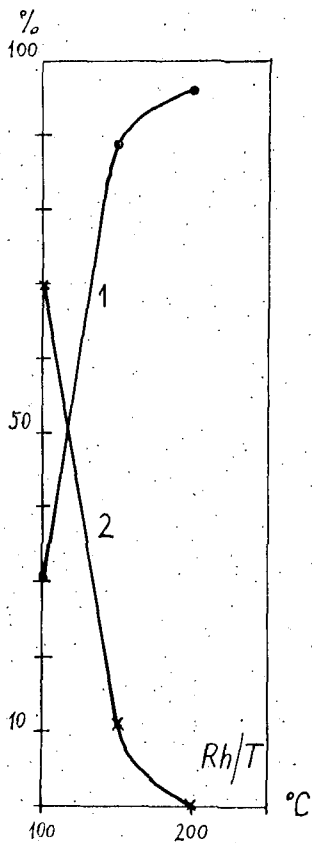
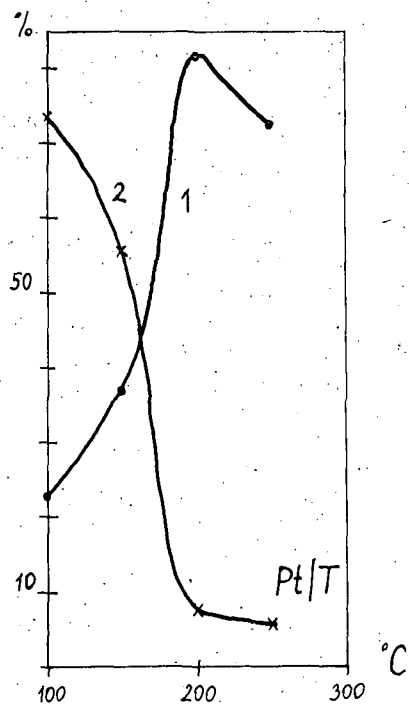
The transformation of the two tertiary alcohols (IX and XI) is faster than that of the secondary alcohols. Under the experimental conditions applied, these two compounds undergo hydrogenolysis accompanied by the loss of water, *i.e.* they are transformed to the corresponding saturated hydrocarbons. Dehydrogenation accompanied by isomerization of the carbon skeleton was not observed.

On the Pd/T catalyst both the secondary and the tertiary alcohols are transformed by means of hydrogenolysis. We did not investigate these processes in detail as our aim was the study of the hydrogenation of ketones and the dehydrogenation of alcohols.

The different behaviours of the catalysts serve as good evidence in favour of the following mechanism, proposed earlier [1, 5] for the hydrogenation of ketones:



Figs. 1—3. Variation of the conversion of individual ketones and alcohols as a function of temperature on different catalysts. (1: methyl *tert*-butyl ketone (II); 2: methyl *tert*-butyl carbinol (VIII); 3: dimethyl isopropyl carbinol (IV); 4: methyl neopentyl ketone (IV); 5: dimethyl isobutyl carbinol (XII)).



Figs. 4—5. Variation of the product composition as a function of temperature in the transformation of methyl *tert*-butyl ketone (II) (symbols as in Figs 1—3).

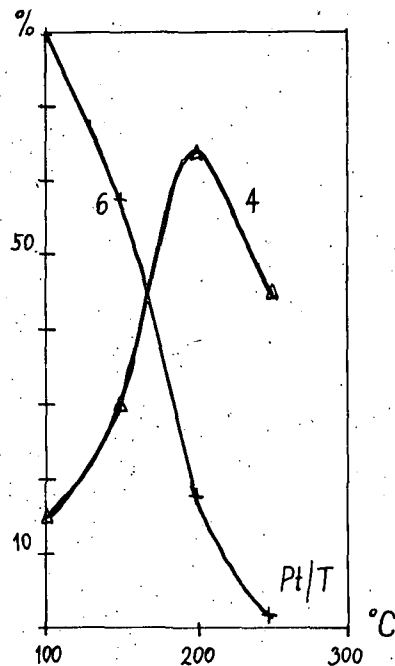
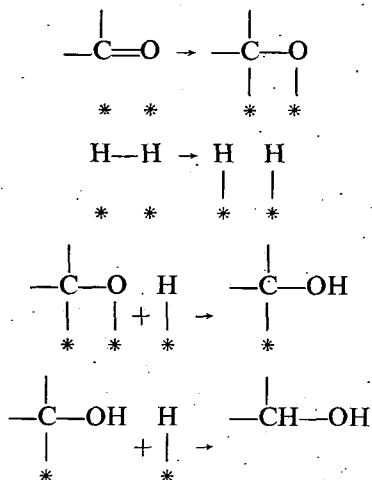
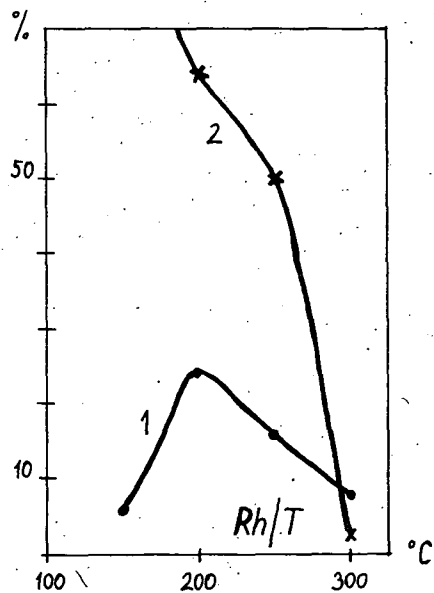
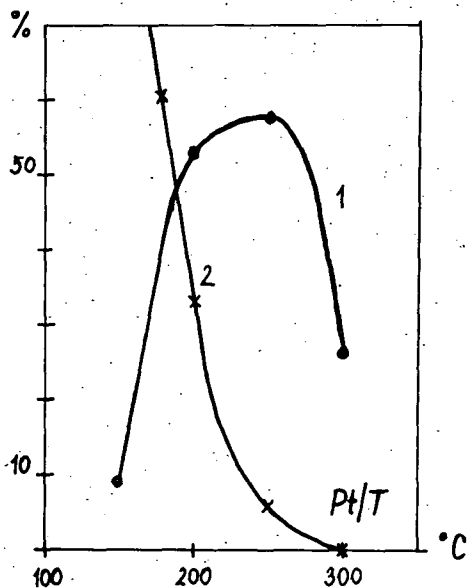


Fig. 6. Variation of the product composition as a function of temperature in the transformation of methyl neopentyl ketone (VI) (symbols: 4: methyl neopentyl ketone (VI); 6: methyl neopentyl carbinol (V))



In our view, palladium is not capable of activating the C=O bond. This finding is confirmed by experimental data on the hydrogenation of α, β -unsaturated ketones in the presence of deuterated methanol [10]. The opinion can also be found in the literature that the reason for the inactivity of palladium is the strong adsorption of the ketones [5, 6].



Figs 7—8. Variation of the product composition as a function of temperature in the transformation of methyl *tert*-butyl carbinol (VIII) (symbols as in Figs 1—3).

In the course of the experimental work we give further evidence that palladium catalysts on various supports (silica gel, kieselguhr, active carbon) are inactive in the hydrogenation of ketones, and the inactivity is thus a characteristic of the palladium itself. Detailed, complex investigations are necessary to establish which of the properties of palladium can be most closely correlated with this phenomenon. An intensive study of this problem may lead to conclusions of great importance. Our preliminary experiments in this respect strongly suggest the conclusion that the hydrogenation of ketones and olefins takes place on various centres of the metal catalysts.

On the basis of our experimental work it can be stated that, among the thermolite-supported catalysts, Pt/T is suitable for the vapour-phase hydrogenation of ketones for preparative purposes, too. It was also found that the impulse technique is a satisfactory means of studying the hydrogenation and dehydrogenation of various types of compounds.

Experimental

Of the compounds examined, methyl ethyl ketone (I), methyl isobutyl ketone (III), diisopropyl ketone (IV), diisobutyl ketone (V), 2-butanol (VII), methyl isobutyl carbinol (XII), diisopropyl carbinol (XIII) and diisobutyl carbinol (XIV) were commercial products of FLUKA.

The other compounds were prepared by methods described in the literature: methyl *tert*-butyl ketone (II) [13, 14]; methyl neopentyl ketone (VI) [15]; methyl *tert*-butyl carbinol (XIII) [14]; dimethyl isopropyl carbinol (IX) [16]; methyl neopentyl carbinol (X) [17]; dimethyl isobutyl carbinol (XI) [16].

The starting compounds were purified by fractional distillation, and their purity was checked on the basis of their physical constants, gas-chromatograms and IR spectra.

Some properties of compounds I—XIV are listed in the Table I.

Table I

Compound	Boiling point at		n_D^{20}	Gas-chromatographic retention time (min)
	°C	Hg/mm		
I	80	760	1.3814 ¹⁵	0.7
II	105	746	1.3956 ²⁰	0.9
III	116	760	1.3967 ²⁰	1.2
IV	125	742	1.4007 ²⁰	1.1
V	164	741	1.4120 ²¹	2.6
VI	124	760	1.4041 ²⁰	1.1
VII	100	760	1.3995 ¹⁵	1.1
VIII	120	746	1.4148 ²⁰	1.6
IX	119	759	1.4176 ²⁰	1.4
X	137	736	1.4188 ²⁰	2.2
XI	132	760	1.4166 ²⁰	2.0
XII	131	740	1.4122 ²⁰	2.0
XIII	136	746	1.4250 ²⁰	2.3
XIV	81	18	1.4230 ²¹	5.1

Catalysts. Pt/T, Rh/T and Pd/T catalysts (metal content 10%) were prepared by described methods [18, 19]. The Cu/Al catalyst was prepared from an alloy containing 30% active metal (particle size 0.2—0.4 mm) [20]. The activities of the catalysts were checked with crotyl alcohol, under the same experimental conditions as in the catalytic studies [21].

Description of experimental method. The examinations were carried out by an impulse-microreactor technique. The method described earlier [18] was modified in so far as the material selected for the microreactor was rasotherm glass, and the internal diameter of the microreactor was 6 mm. 1 ml, T-supported catalysts and 0.2 ml Cu/Al catalyst were employed. The active metal contents of the catalysts were approximately the same. The microreactor was built onto a Carlo Erba GV gas-chromatograph. The gas-chromatographic conditions were as follows: Column: A glass column, 1.5 m long and of 4 mm internal diameter, containing 15% rheoplex on silanized kieselguhr of 0.2—0.3 mm particle size. Thermostat temperature: 120 °C. Carrier gas: 60 ml hydrogen/min. Detector current: 150 mA. Amount of sample injected: 5 µl.

The peaks on the chromatograms were identified with the aid of appropriate reference substances, and evaluated quantitatively by reference to standard calibration curves.

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ИССЛЕДОВАНИЕ ГИДРОГЕНИЗАЦИИ КЕТОНОВ НА МЕТАЛЛИЧЕСКИХ КАТАЛИЗТОРАХ МЕТОДОМ ИМПУЛЬСНОГО РЕАКТОРА

М. Барток

Изучена гидрогенизация кетонов (I—VI) и дегидрогенизация спиртов (VII—XIV) на платиновом, родиевом и палладиевом катализаторах с термолитными носителями, в интервале температур 100—300 °С, используя водород в качестве газа-носителя, методом импульсного реактора. Катализаторы платина и родий были активными, а палладий оказался неактивным. При превращениях изученных веществ не происходили реакции изомеризации углеродных остовов молекул. Платиновый катализатор, вследствие своих подходящих свойств (активность, время цикла, регенерационная способность, долговечность), может быть рекомендован в качестве катализатора при синтезе вторичных спиртов и кетонов.