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O. K. BOGDANOVA, Academician A. A. BALANDIN, and I. P. BELOMESTNYKH

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Abstract

Full Text

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ON THE INFLUENCE OF CONJUGATION ENERGY ON THE RATE OF CATALYTIC DEHYDROGENATION OF ALKYLAROMATIC AND ALKYLHEXAHYDROAROMATIC HYDROCARBONS

Catalytic dehydrogenation of alkylaromatic hydrocarbons with the formation of a conjugated bond with the benzene ring proceeds at a considerable rate, depending on the structure of the alkyl radical. Thus, in a previous work ([1]) it was shown that ethylbenzene and isopropylbenzene are readily dehydrogenated on a mixed oxide catalyst, and the rate constant for dehydrogenation of isopropylbenzene with a branched alkyl radical is twice as high as the rate constant for dehydrogenation of ethylbenzene (see Table 1). It was of interest to determine whether the alkyl radical of a hexahydroaromatic ring would undergo dehydrogenation. For this purpose, on the same catalyst, the dehydrogenation of ethylcyclohexane and isopropylcyclohexane was studied.

Table 1

Rate constants for dehydrogenation of alkylaromatic and alkylhexahydroaromatic hydrocarbons,
$k_c \cdot 10^2$ g • min • ml

T, °C	Ethylbenzene	Isopropylbenzene	Ethylcyclohexane*	Isopropylcyclohexane*
520	0.285	0.776	–	–
540	0.5096	1.226	–	0.0333
550	0.783	1.572	0.04	–
560	1.055	–	–	0.0666
570	–	–	0.075	–

* In view of the small percentages of conversion, the yield in the same units was taken as k_c.

Hexahydroaromatic hydrocarbons, as is known ([2]), are smoothly dehydrogenated on metals according to the sextet scheme ([3]). In work ([4]) it was

shown that over chromium oxide cyclohexane is dehydrogenated to benzene by a rib mechanism. On an alumina–chromium catalyst ([5]) at 440° cyclohexane is dehydrogenated to benzene by 50%; when ethylcyclohexane was passed over this catalyst at 400–450°, as the authors showed, the reaction proceeds stepwise through successive dehydrogenation of the ring to ethylbenzene and of ethylbenzene to styrene. When ethylcyclohexane was passed over mixed alumina–chromium–molybdenum and alumina–chromium–vanadium catalysts ([6]), styrene was obtained, and the supposition was expressed that the reaction proceeds in two stages through ethylbenzene. In experiments carried out by us with cyclohexane, it was found that on the catalyst on which the dehydrogenation of alkylbenzenes was carried out, cyclohexane is not dehydrogenated and passes through unchanged.

Results of the experiments and their discussion

The apparatus and procedure for carrying out the experiments are described in the work on the dehydrogenation of isopropylbenzene ([1]). The experiments, as before, were carried out with 10 ml of catalyst in the temperature range 550–600° at a hydrocarbon feed rate of···

hydrocarbons: 0.5 ml in 3 min (which corresponds to a space velocity of 1000 ml/l · h), and with dilution by steam in a ratio of 1 : 2.7–3.0 by weight. After each experiment the catalyst was purged with a steam–air mixture and with air. The experiments were carried out with cyclohexane, b.p. 81°, d_4^{20} 0.7783, n_D^{20} 1.4263; ethylcyclohexane, b.p. 129–130°, d_4^{20} 0.7854, n_D^{20} 1.4327; and isopropylcyclohexane, b.p. 153°, d_4^{20} 0.7939, n_D^{20} 1.4410. The catalyzate was analyzed for unsaturated compounds by bromometric titration according to Rosenmund ([7]).

As was stated above, cyclohexane is not dehydrogenated under these conditions. The constants of the catalyzate were the same as those of the original cyclohexane (n_D^{20}1.4264). Ethylcyclohexane and isopropylcyclohexane are dehydrogenated only slightly. When ethylcyclohexane was passed over the catalyst at 550°, vinylcyclohexane was detected in an amount of 1%; when isopropylcyclohexane was passed, about 2% isopropylidenecyclohexane was formed. With an increase in temperature to 600°, the content of unsaturated compounds in the catalyzate increases to 3.8% and 6.7%, respectively, for the two hydrocarbons studied. At this temperature cracking of the hydrocarbons is also observed, with formation of methylcyclohexane and light hydrocarbons (methane, ethane, and unsaturated hydrocarbons).

Vinylcyclohexane was isolated from the catalyzate and characterized as an insoluble adduct with mercuric acetate, m.p. 218–220°. A mixed sample with an adduct prepared from synthesized vinylcyclohexane showed no depression of the melting point. Table 1 gives comparative data on the rates of dehydrogenation of alkylaromatic and alkylhexahydroaromatic hydrocarbons.

The results obtained show that the rate of catalytic dehydrogenation depends on the structure of the starting hydrocarbons, their alkyl radicals, and chiefly

on the possibility of forming a conjugated bond with the aromatic ring. Dehydrogenation of the alkyl group of the hexahydroaromatic ring is hindered.

Institute of Organic Chemistry
im. N. D. Zelinskii
Academy of Sciences of the USSR

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CITED LITERATURE

[1] O. K. Bogdanova, A. A. Balandin, I. P. Belomestnykh, DAN, **132**, No. 2 (1960).
[2] N. D. Zelinskii, ZhRKhO, **34**, 1220 (1911); **44**, 274 (1912).
[3] A. A. Balandin, ZhRKhO, **61**, 909 (1929); Usp. khim., **4**, 1004 (1935).
[4] A. A. Balandin, I. I. Brusov, ZhOKh, **69**, 18 (1937).
[5] E. G. Herington, E. R. Rideal, Proc. Roy. Soc., A. **193**, 1022 (1947).
[6] N. I. Shuikin, I. I. Levitskii, Izv. AN SSSR, OKhN, **1953**, No. 5, 1003.
[7] K. W. Rosenmund, W. Kuhnhenn, Zs. f. Untersuch. d. Nahrungs.-u. Genussmittel, **46**, 154 (1923).

Note: Figure translations are in progress. See original paper for figures.