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Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Abstract

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ON THE KINETICS OF C_5-DEHYDROCYCLIZATION OF *o*-ETHYLTOLUENE TO INDANE

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As is known, in the presence of platinized carbon, C_5-dehydrocyclization of paraffinic hydrocarbons leads to homologs of cyclopentane, while from alkylbenzenes hydrocarbons of the indane series are obtained in this process ([1]). Studying the kinetics of this reaction ([2,3]), we found a number of interesting regularities. It turned out that both classes of hydrocarbons reacted according to zero order. Moreover, on one sample of platinized carbon, the paraffinic hydrocarbons—*n*-hexane, 3-ethylpentane, and 2,2,4-trimethylpentane (isooctane)—underwent C_5-dehydrocyclization with practically identical apparent activation energies. Meanwhile, for the alkylbenzenes—*n*-propyl- and isobutylbenzene—these values on the same

Fig. 1. Arrhenius plots for the reaction of C_5-dehydrocyclization of the hydrocarbons studied. 1 —*o*-ethyltoluene; 2 —isooctane; 3 —*sec*-butylbenzene (right ordinate)

Fig. 2. Arrhenius plots for the reaction of C_5-dehydrocyclization of hydrocarbons, calculated from the data of Sheppard and Rooney. 1 —*n*-propylbenzene, $Q = 11.6$ kcal/mole; 2 —*o*-ethyltoluene, $Q = 5.8$ kcal/mole

catalyst sample, although not differing from one another, were noticeably greater than the values found for the paraffinic series (27.5 and 20 kcal/mole, respectively). Since these differences may be connected with the reaction mechanism, it seemed important to us to obtain some information about their causes.

Recently the viewpoint was expressed that, for C_5-dehydrocyclization on platinum, the most probable mechanism is one according to which the reaction proceeds through the formation of a cyclic transition state on the catalyst surface ([4]). According to these ideas, the five carbon atoms that form the five-membered ring in the course of the reaction are already adsorbed flat on platinum in the interstices of its lattice in the transition state. Obviously, the positions of these atoms in the transition state are not equivalent: three of them play only an

orienting role, while the other two, in addition, also directly participate in the formation of the new bond. In other words, all five atoms participate in one of the stages of the reaction—the formation of the transition state—but only two participate in the following stage, the redistribution of electron density in it, leading to the final product of the reaction. It is easy to see that, in the case of paraffinic hydrocar-

···whereas all these atoms are of the same type (sp^3-hybridized), while in alkylbenzenes two atoms out of five are characterized by sp^2-hybridization. This may in a certain way affect the conditions and energetics of formation of the transition state, which is manifested in an increase in the activation energy. However, one cannot fail to note another fact as well: in the cyclization of paraffins the new bond is formed between two sp^3-hybridized atoms, whereas in the case of monoalkylbenzenes one of these two atoms differs by having sp^2-hybridization. This too may affect the magnitude of the activation energy. It was of interest to determine which of the two above-mentioned stages of the reaction is primarily affected by the character of hybridization of the carbon atoms. In order to approach a solution of this question, it was necessary to investigate a hydrocarbon in which two sp^2-hybridized atoms would also participate in the transition state, but cyclization would occur only through interaction of sp^3-hybridized atoms. This purpose could be served by *o*-ethyltoluene:

[structural scheme: *o*-ethyltoluene → indane]

To obtain comparable results we studied, on one portion of catalyst, the kinetics of C_5-dehydrocyclization of *o*-ethyltoluene (sp^3, sp^3), isooctane (sp^3, sp^3), and sec-butylbenzene (sp^2, sp^3).

The experiments performed indicated the dominant role of the nature of the reacting atoms. Indeed, the apparent activation energy of C_5-dehydrocyclization of the first two of the hydrocarbons listed proved to be the same (14 kcal/mole*), whereas for the third a substantially larger value was found (29 kcal/mole). This is clearly seen in Fig. 1.

It is interesting to note that, in a recent paper by Sheppard and Rooney ([6]), in studying transformations of aromatic hydrocarbons of composition C_9 in the presence of platinized alumina (0.5% Pt), similar results were obtained. Indeed, a calculation we made on the basis of the experimental data of these authors showed that the conversion of *n*-propylbenzene to indane requires approximately twice as large an activation energy as the analogous conversion of *o*-ethyltoluene (in these calculations it was taken into account that in both cases part of the indane formed was dehydrogenated to indene). The corresponding Arrhenius straight lines are shown, for greater clarity, in Fig. 2.

Thus, on two platinum catalysts (0.5% Pt/Al_2O_3 and 20% Pt/C), which differ substantially in their catalytic properties, similar regularities appear in the case under consideration.

Experimental Part

Methyl-*o*-tolylcarbinol. Grignard reagent, obtained in the usual way at 36–40° from isomer-free *o*-bromotoluene**, gave, with acetaldehyde, methyl *o*-tolylcarbinol (yield 75% of theory), b.p. 83–83.5°/2 mm, n_D^{20} 1.5298. Literature data ([7]): b.p. 106°/10 mm.

***o*-Ethyltoluene** was obtained from methyl-*o*-tolylcarbinol by the previously described method ([8]), by passing it over platinized charcoal (20% Pt)

* A certain difference of this value from that found earlier ([2]) is apparently connected with subtle and as yet unexplained differences in the preparation of the catalyst. We have already encountered this phenomenon previously in studying the C_5-dehydrocyclization of paraffinic hydrocarbons ([5]). It should be emphasized, however, that although the activation energies of indane differed for different catalyst samples, within the limits of each sample all alkanes studied on it always gave mutually identical values of the activation energy.

** The synthetic preparation of *o*-bromotoluene, distilled on an efficient column, with b.p. 73.5–73.6°/19 mm, n_D^{20} 1.5570 and d_4^{20} 1.4238, was kindly provided to us by T. V. Vasina, for which the authors express their gratitude to her.

in a stream of hydrogen at 280° and a space velocity of 0.25–0.30 hr^{-1}. After additional purification by chromatography on silica gel and distillation on a column with an efficiency of 100 theoretical plates, practically pure *o*-ethyltoluene had the following properties: b.p. 165.3°/760 mm; n_D^{20} 1.5048; d_4^{20} 0.8807. According to the most reliable literature data [(9)], the properties of *o*-ethyltoluene are as follows: b.p. 165–153°/760 mm, n_D^{20} 1.50456; d_4^{20} 0.88069.

The preparation and properties of the isooctane and *tert*-butylbenzene used in the present work were described earlier [(3)].

Experimental procedure. The experiments were carried out in a flow system at a space velocity of 0.2 hr^{-1} over platinized carbon (20% Pt), prepared according to the procedure of N. D. Zelinskii and M. B. Turova-Polyak [(10)].

The freshly prepared catalyst was preliminarily stabilized by passing isooctane over it for 25–30 hr. The yields of reaction products were determined by gas-liquid chromatography with thermal-conductivity detection (instrument of the Special Design Bureau of the Institute of Organic Chemistry, Academy of Sciences of the USSR). Silicone oil (20% by weight), grade PFMS-4, deposited on diatomaceous brick, was used as the stationary liquid phase. In other respects the method of investigation did not differ from that used earlier [(2)].

Table 1

Dependence of the rate of C_5-dehydrocyclization of hydrocarbons on temperature

Hydrocarbon	No. of experiment	Temp., °C	Yield of cyclization products, %
o-Ethyltoluene	1	280	7.7
o-Ethyltoluene	5	280	9.1
o-Ethyltoluene	9	280	8.4
o-Ethyltoluene	10	280	8.5
o-Ethyltoluene	7	290	9.3
o-Ethyltoluene	8	290	9.7
o-Ethyltoluene	2	300	11.5
o-Ethyltoluene	6	300	12.9
o-Ethyltoluene	3	310	15.2
o-Ethyltoluene	4	310	13.4
o-Ethyltoluene	11	310	13.4
o-Ethyltoluene	12	310	15.4
o-Ethyltoluene	13	310	14.8
tert-Butylbenzene	10	280	2.5
tert-Butylbenzene	12	280	2.1
tert-Butylbenzene	7	290	3.8
tert-Butylbenzene	8	290	4.1
tert-Butylbenzene	5	300	5.7
tert-Butylbenzene	6	300	7.2
tert-Butylbenzene	11	300	4.7
tert-Butylbenzene	3	310	8.4

Hydrocarbon	No. of experiment	Temp., °C	Yield of cyclization products, %
tert-Butylbenzene	4	310	7.3
tert-Butylbenzene	9	310	8.2
Isooctane	1	280	10.8
Isooctane	6	280	10.8
Isooctane	10	280	11.0
Isooctane	13	280	11.2
Isooctane	2	290	13.6
Isooctane	4	290	11.7
Isooctane	12	290	13.5
Isooctane	5	300	15.0
Isooctane	9	300	17.7
Isooctane	11	300	16.9
Isooctane	3	310	18.0
Isooctane	7	310	20.6
Isooctane	8	310	20.2
Isooctane	14	310	21.0

The results of the investigation are given in Table 1 and in Fig. 1.

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