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Abstract

Full Text

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NEW DATA ON THE KINETICS OF C_5-DEHYDROCYCLIZATION OF HYDROCARBONS

(Presented by Academician B. A. Kazanskii, October 6, 1962)

Earlier, using the examples of *n*-hexane, 2,2,4-trimethylpentane (isooctane), and *n*-propylbenzene, we began the study of the kinetics of the reaction of C_5-dehydrocyclization of hydrocarbons (alkanes to homologs of cyclopentane and *n*-propylbenzene to indane) on platinized carbon. It was shown that cyclization in all three cases proceeds according to zero order. For both paraffinic hydrocarbons the activation energies proved to be practically identical (~ 20 kcal/mole), whereas for *n*-propylbenzene it was somewhat greater (27.5 kcal/mole). In order to make the picture more complete, it seemed necessary to us to determine whether the observed relationships of activation energies are typical for C_5-dehydrocyclization of paraffins and alkylbenzenes in general, or whether they characterize only the three hydrocarbons named. To solve this problem it was necessary to broaden the range of substances studied.

Fig. 1. Dependence of the yield of cyclization products of alkylbenzenes on contact time. 1 —cyclization of sec.-butylbenzene, 2 —cyclization of isobutylbenzene.

As in the preceding communication, we selected hydrocarbons that form only one product of C_5-dehydrocyclization. Such are 3-ethylpentane and isobutylbenzene, giving respectively ethylcyclopentane (^{2}) and β-methylindane (^{3}). In addition, the study of 3-ethylpentane was of interest also because, in terms of its branching, it occupies an intermediate position between the previously studied unbranched *n*-hexane and the highly branched isooctane. This interest was connected with the fact that for the latter, on a stabilized catalyst, the reaction rate was five times* greater than for the former, despite identical activation energies. At first glance this could be explained, as C. E. Rauk had already done for C_6-

dehydrocyclization (^{4}), by the statistically larger number of possibilities for the approach of the first and fifth carbon atoms in isooctane. However, inconsistent with this was the fact that, upon cyclization of the also highly branched 2,5-dimethylhexane, the yield of products of C_5-dehydrocyclization was very small (^{5}). It seemed to us that more correct results could be obtained by proceeding from the following considerations. First, to take into account our assumption that, during C_5-dehydrocyclization, the molecule of the initial hydrocarbon is adsorbed flat on the active center of the platinum catalyst (^{6}). Second, to take into account the conformational strain arising when the reacting carbon atoms in molecules of different structure approach one another, i.e., the strain of the reactive conformations; this will be described in greater detail elsewhere. From such reasoning it follows that the preexponential factor

* On a fresh catalyst —even 10 times.

(k_0) in the Arrhenius equation for the C_5-dehydrocyclization of 3-ethylpentane should occupy an intermediate position between its values for n-hexane ($1.1 \cdot 10^8$) and isooctane ($5.8 \cdot 10^8$) in the same reaction.

The present study fully confirmed our expectations. Indeed, the yields of the cyclization product isobutylbenzene as a function of contact time, as in other hydrocarbons (^{1}), obey a linear dependence

Table 1

Dependence of the yield of cyclization products of alkylbenzenes on contact time at 310°

Alkylbenzene	No. p.p.	Experiment No.	Space velocity, h^{-1}	Apparent contact time, τ	n_D^{20}	d_4^{20}	Yield of methylindanes, %
Isobutylbenzene	1	19*	0,10	112	1,4902	0,8616	10,8
Isobutylbenzene	2	16	0,22	52	1,4885	0,8579	6,0
Isobutylbenzene	3	20	0,22	52	1,4885	0,8577	6,0
Isobutylbenzene	4	17	0,36	32	1,4880	0,8569	4,6
Isobutylbenzene	5	18*	0,56	21	1,4873	0,8558	2,7
sec-Butylbenzene	1	30*	0,10	112	1,4931	0,8682	8,9
sec-Butylbenzene	2	27	0,13	87	1,4928	0,8674	8,0
sec-Butylbenzene	3	32	0,17	67	1,4922	0,8658	6,4
sec-Butylbenzene	4	28	0,20	57	1,4920	0,8653	5,8
sec-Butylbenzene	5	31	0,21	57	1,4917	0,8646	

Alkylbenzene	No. p.p.	Experiment No.	Space velocity, h^{-1}	Apparent contact time, τ	n_D^{20}	d_4^{20}	Yield of methylindanes, %
sec-Butylbenzene	6	29	0,36	32	1,4913	0,8637	4,0

* The bromine numbers of the catalysts were, respectively, 1.4 and 1.0. At higher space velocities they should evidently be still lower.

(Fig. 1 and Table 1). For greater completeness, sec-butylbenzene, which gives α-methylindan ([3]), was also studied; an analogous result was obtained (Fig. 1 and Table 1).

Thus, the zero order of the C_5-dehydrocyclization reaction is apparently realized under the conditions studied in all cases. Examination of the dependence of the rate of this reaction on temperature showed that the activation energies for

Table 2

Dependence of the yield of cyclization products on temperature (space velocity 0.2 h^{-1})

Hydrocarbon	Experiment No.	Temp., °C	n_D^{20} before chromatography	n_D^{20} after chromatography	Yield of cyclization products, %
3-Ethylpentane	25	280	1,3948	1,3947	4,9
3-Ethylpentane	24	290	1,3953	1,3952	6,8
3-Ethylpentane	23	300	1,3962	1,3959	9,5
3-Ethylpentane	22	310	1,3970	1,3966	12,2
3-Ethylpentane	26	310	1,3969	1,3966	12,1
Isobutylbenzene	32	280	1,4880	–	4,0
Isobutylbenzene	35	280	1,4880	–	4,0
Isobutylbenzene	31	290	1,4890	–	6,7
Isobutylbenzene	30	300	1,4899	–	9,2
Isobutylbenzene	29	310	1,4920	–	14,8
Isobutylbenzene	33	310	1,4909	–	11,9
Isobutylbenzene	34	310	1,4918	–	14,3

Figure 2

Figure 2: Figure 2

hydrocarbons of one class are indeed identical or very close and are characteristic for each such class (Figs. 2 and 3 and Table 2). Thus, for 3-ethylpentane a value of 20 ± 1 kcal/mol was found, and for isobutylbenzene 27.5 ± 1 kcal/mol was obtained. This is in good agreement with what we observed earlier (1). Thus, the statement advanced by us was once again confirmed: differences in the structure of hydrocarbons of one class have practically no effect on the magnitude of the activation energy. As for the value of k_0 in the Arrhenius equation for the C_5-dehydrocyclization of 3-ethylpentane, it proved to be $4.0 \cdot 10^8$, i.e., as we expected, lying between the values of this quantity for *n*-hexane and isooctane. The value of k_0 for isobutylbenzene ($3.1 \cdot 10^{11}$) is somewhat greater than for *n*-propylbenzene ($1.1 \cdot 10^{11}$), and substantially greater than for paraffinic hydrocarbons.

To come closer to understanding the reaction mechanism, it seemed interesting to verify experimentally the proposition we had expressed earlier (1) concerning the substantially stronger adsorption of aromatic compounds on the active centers of platinized carbon, which cause C_5-dehydrocyclization, as compared with paraffinic hydrocarbons. Indeed, it is easy to imagine that the benzene ring serves, as it were, as a magnet drawing the entire molecule of the aromatic hydrocarbon onto the catalyst surface. In the case of paraffinic hydrocarbons there is no such "magnet," and their adsorbability will be substantially lower.

Fig. 2. Straight lines of the Arrhenius equation for C_5-dehydrocyclization of paraffinic hydrocarbons: 1—3-ethylpentane, 2—iso-octane

By passing an equimolecular mixture of iso-octane with isobutylbenzene over a fresh catalyst, we were able to show that, at the moment of reaction, the entire active surface of the catalyst is occupied only by the aromatic hydrocarbon. As a result of the stronger adsorption of isobutylbenzene, in comparison with iso-octane, the catalyst obtained consisted only of the initial hydrocarbons and ~7% β-methylindane, and contained absolutely no product of iso-octane cyclization —1,1,3-trimethylcyclopentane. Meanwhile, under the experimental conditions, iso-octane in pure form cyclizes significantly faster than isobutylbenzene. Consequently, iso-octane is indeed displaced by isobutylbenzene from the catalyst surface.

This can, in our opinion, serve as the basis for explaining the fact that alkylbenzenes, despite having a considerably greater activation energy than paraffinic hydrocarbons, have a C_5-dehydrocyclization rate comparable with the latter. Indeed, a difference of 7.5 kcal/mol, all other conditions being equal, should have reduced the reaction rate by approximately 600-fold. However, the greater adsorbability of the benzene ring creates an inequality of conditions. We believe that, for this reason, the benzene ring is immediately adsorbed flat on the

Figure 3

Figure 3: Figure 3

active center; therefore, in the same plane the first atom of the side chain must also be located. It remains only for the second and third atoms of this chain to be adsorbed on the plane (in the required conformation) for the reaction to become possible. Meanwhile, in paraffinic hydrocarbons, in which the adsorbability of all carbon atoms is approximately the same, a substantial portion of the molecules is adsorbed by fewer than five carbon atoms (one, two, etc.) and cannot participate in the reaction. All this is manifested in considerably larger values of the pre-exponential terms of the Arrhenius equation for alkylbenzenes as compared with paraffins.

Fig. 3. Straight lines of the Arrhenius equation for C_5-dehydrocyclization of alkylbenzenes. 1—propylbenzene, 2—isobutylbenzene

Experimental Part

Starting hydrocarbons and catalyst. Iso-octane and sec.-butylbenzene were isolated from commercial preparations by chromato-

by chromatography on silica gel and rectification on high-efficiency columns. The preparation of isobutylbenzene and 3-ethylpentane has already been described by us earlier ([3], [7]). The constants of the starting hydrocarbons, which practically do not differ from the most reliable literature data ([8]), are presented in Table 3. The catalyst was platinized carbon (20% Pt), prepared according to the prescription of N. D. Zelinskii and M. B. Turova-Polyak ([9]) and stabilized by passing isooctane over it for 30 h. All experiments were carried out in a flow system over one and the same portion of catalyst (10 ml).

Kinetics of C_5 dehydrocyclization. The method of the experiment and of determining the yields of the products of C_5 dehydrocyclization was described earlier ([1]). The dependence of the yields of indane hydrocarbons from alkylbenzenes on contact time was studied at 310°. The dependence of the rate of C_5 dehydrocyclization of 3-ethylpentane and isobutylbenzene was determined in the temperature interval 280–310°. The data obtained are summarized in Tables 1 and 2 and presented in Figs. 1 and 2.

Table 3

Physical properties of the starting hydrocarbons

Hydrocarbon	B.p., °C/mm	n_D^{20}	d_4^{20}
3-Ethylpentane	93.2/760	1.3933	0.6979
Isooctane	99.3/760	1.3914	0.6919
Isobutylbenzene	113.3/132	1.4865	0.8532

Hydrocarbon	B.p., °C/mm	n_D^{20}	d_4^{20}
sec-Butylbenzene	113.1/130	1.4900	0.8613

Study of the relative adsorbability of paraffinic and aromatic hydrocarbons on the active centers of the platinum catalyst. An equimolecular mixture of isooctane with isobutylbenzene (n_D^{20} 1.4438) was passed at 310° and a space velocity of 0.2 h^{-1} over a highly active catalyst (on a separate portion of this catalyst sample, isooctane was cyclized under the same conditions by 38%). The resulting catalyzate (5.3 ml with n_D^{20} 1.4447) was chromatographed on silica gel to separate the paraffinic-naphthenic portion from the aromatic portion. The paraffinic-naphthenic portion should have contained only the initial isooctane and the product of its C_6 dehydrocyclization, 1,1,3-trimethylcyclopentane ([10]). However, the fractions isolated in the course of chromatography (fr. I (2.1 ml) n_D^{20} 1.3914; fr. II (0.5 ml) n_D^{20} 1.3914–1.4172; fr. III (1.0 ml) n_D^{20} 1.4172–1.4880; fr. IV (1.2 ml) n_D^{20} 1.4880–1.5090) showed that the paraffinic-naphthenic portion—fraction I—was pure isooctane and contained absolutely no 1,1,3-trimethylcyclopentane. Fraction IV was a mixture of isobutylbenzene and β-methylindane ([3]); fractions II and III were intermediate fractions evidently containing isooctane, isobutylbenzene, and traces of β-methylindane.

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