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Abstract

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DEALKYLATION OF ALKYLAROMATIC HYDROCARBONS AND THEIR DERIVATIVES IN THE PRESENCE OF AN ALUMINOSILICATE CATALYST

The dealkylation of alkylaromatic hydrocarbons in the presence of aluminosilicate catalysts of catalytic cracking has been the subject of a number of studies. Thus, Thomas, Hekstra, and Pinkston, as early as 1944 ([1]), studied the dealkylation of ethylbenzene, cumene, *n*-butylbenzene, and a mixture of amylbenzenes in the presence of synthetic aluminosilicates at 400–500°; they found that the nature of the alkyl chain affects the extent of the reaction; of the hydrocarbons listed, ethylbenzene is dealkylated with the greatest difficulty, while cumene is dealkylated most readily—with formation of the corresponding olefins and benzene. Greensfelder, Voge, and Good ([2]) made a special study of the influence of the length and structure of the side alkyl chain on the rate of dealkylation at 500° in the presence of an aluminosilicate catalyst promoted with zirconium oxide.

In the work of Moldavsky and Bezdel' ([3]), the influence of different positions of the CH_3 group and chlorine on the extent of propylene cleavage from *o*-, *m*-, and *p*-cymenes and *p*-chlorocumene at 410° was studied. Later, the influence of the nature and different orientation of substituents was studied, using as examples *p*-chlorocumene, 1,3-dimethyl-5-isopropylbenzene, *p*-cymene, and 1,3-dimethyl-4-isopropylbenzene, by Roberts and Good ([4]). The rates, calculated theoretically by them, of electrophilic substitution of the isopropyl group by hydrogen in the presence of differently oriented substituents for the above-listed compounds were in good agreement with the experimental data found for the extent of dealkylation. In the authors' opinion, this circumstance may serve as evidence in favor of the carbonium-ion mechanism of the dealkylation reaction of alkylaromatic hydrocarbons in the presence of aluminosilicate catalysts.

Without dwelling in greater detail on certain other works on the dealkylation of alkylbenzenes in the presence of catalytic-cracking catalysts, we note that, in them, as in those mentioned above, there are only qualitative data on the influence of the nature and structure of the alkyls being cleaved, and also of the orientation of alkyl and other substituents simultaneously present in a given aromatic compound, on the rate and extent of its catalytic cracking. Moreover, these data were obtained by different authors under different experimental conditions for different catalysts, differing both in composition and in method of

preparation.

One of the simplest and best-studied cases of dealkylation of an alkylaromatic hydrocarbon in the presence of an aluminosilicate catalyst is the dealkylation of cumene, which, within a certain temperature range and at a definite duration of contact with the catalyst, leads practically to the formation of only two compounds—benzene and propylene.

The kinetics of this reaction has been studied repeatedly, and sufficiently reliable and clear kinetic parameters of this reaction are given in the literature ([5–8]). This and similar reactions are often interpreted as reactions of electrophilic substitution of an alkyl by a proton of the aluminosilicate catalyst, which has an acidic character. The formation of a carbonium ion corresponding to the given alkyl is allowed as a very short-lived intermediate stage; this takes place on the surface of the catalyst, and the carbonium ion rapidly returns a proton to it, turning into an olefinic hydrocarbon. From this point of view, the dealkylation reaction may be represented by the following scheme:

$$C_6H_5{-}CH(CH_3)R + H^+A^- \longrightarrow C_6H_6 + [\,^+CH(CH_3)R\,]A^- \longrightarrow H^+A^- + CH_2{=}CHR$$

The rate of dealkylation will depend on the relative ease of formation of the carbonium ion, or on the ability of the C–C bond between the benzene nucleus and the alkyl to become polarized on the surface of the catalyst, as well as on the structure of the alkyl substituent. It is assumed that alkyls possessing a tertiary carbon atom are most capable of intermediate formation of a carbonium ion with an electron sextet at the tertiary atom, while alkyls with primary carbon atoms are least capable. Ethyl and especially methyl form carbonium ions with greater difficulty.

If an aromatic compound is subjected to catalytic dealkylation in which, in addition to a more or less readily cleaved alkyl group, there is also a substituent more firmly bound to the benzene nucleus, possessing clearly expressed electron-donor or electron-acceptor properties and oriented in the corresponding manner with respect to the first substituent, as was the case, for example, in the above-mentioned work of Moldavskii and Roberts and of Guda, then the extent and rate of dealkylation change. If the ionic mechanism of dealkylation in the presence of aluminosilicates is correct, this change may be related to a change in the electron density of the benzene nucleus as a whole and to its redistribution depending on the nature and orientation of the second substituent.

It seemed timely to us to carry out a more systematic study than had been done up to now, under comparable conditions and with one and the same catalyst, of the rate of dealkylation of a series of alkylaromatic hydrocarbons and some of their derivatives. This would make it possible to obtain quantities (rate constants and apparent activation energies of the dealkylation reaction) that would help to characterize quantitatively the influence of the chain length and

structure of the cleaved alkyl on the reaction rate, and also to give an idea of the role of the second substituent, which is not cleaved under the reaction conditions.

For this purpose we prepared and subjected to catalytic dealkylation the following 11 compounds, whose properties are given in Table 1.

Table 1

Compound	B.p., °C	Pressure, mm Hg	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.
Ethylbenzene	136.1	760	1.4960	0.8670	35.78	35.54
n-Propylbenzene	76.9	50	1.4920	0.8618	40.46	40.16
Isopropylbenzene (cumene)	152.5	760	1.4915	0.8625	40.39	40.16
n-Butylbenzene	97.0	50	1.4900	0.8602	45.10	44.78
sec-Butylbenzene	82.3	40	1.4901	0.8601	45.11	44.78
tert-Butylbenzene	84.8	50	1.4926	0.8668	44.95	44.78
o-Cymene	93.0	50	1.5013	0.8799	44.85	44.78
m-Cymene	90.0	50	1.4930	0.8608	45.30	44.78
p-Cymene	91.3	50	1.4911	0.8570	45.35	44.78
o-Chlorocumene	68.0	9	1.5170	1.0339	45.19	44.94
p-Chlorocumene	75.5–76.5	9	1.5140	1.0225	45.50	44.94

The properties of the compounds used by us for dealkylation are in good agreement with the most reliable literature data.

The rate of dealkylation was studied in the presence of 10 cm³ of an industrial aluminosilicate catalyst, formed as cylinders (4 × 4 mm). Its activity was determined from the yield of benzene from cumene or from the rate of propylene evolution in an experiment carried out at 450° and a space velocity for passing cumene of 1.60 hr^{-1}. The activity characteristics based on benzene and on propylene coincided. After each experiment the catalyst was regenerated with air, and its activity was fully restored.

Table 2

Compounds	E_{app}, kcal/mole	Compounds	E_{app}, kcal/mole
Ethylbenzene	50000	*o*-Cymene	12000
n-Propylbenzene	34000	*m*-Cymene	14000
Isopropylbenzene	17500	*p*-Cymene	13000
sec-Butylbenzene	19000	*o*-Chlorocumene	21500
n-Butylbenzene	33000	*p*-Chlorocumene	24200
tert-Butylbenzene	12700		

The experiments were carried out in a quartz tube placed in an electric furnace with a thermoregulator. The temperature was measured by a thermocouple in the center of the catalyst bed with an accuracy to 1°. The feed of liquid substance to the reactor was automated and proceeded at a constant rate. The gases formed were collected in a Patrikeev gas meter, and their volume was automatically recorded and written down. The liquid reaction products were fractionated on a sufficiently efficient laboratory column; the gaseous products were liquefied and rectified on "TsIATIM 51-U,"1954, or "TsIATIM-52,"1954, apparatuses. Individual fractions were analyzed by ordinary absorption methods and by combustion. The reaction rate was determined both from the composition of the gaseous products and from that of the liquid products. In a number of cases convergent figures were obtained, since side reactions occurred only to an insignificant extent. At higher temperatures or with longer contact times, cracking phenomena and the formation of methane in the gases were observed. In such cases preference was given to the results of rectification of the liquid reaction products.

The experiments were carried out at temperatures from 370 to 490° and with space velocities from 0.8 to 4.00 volumes of liquid substance per 1 volume of catalyst per hour. In the case of compounds reacting especially rapidly or especially slowly, it was necessary to make deviations both toward lower and toward higher temperatures.

The results of the experiments were treated by Frost' s equation ([9,10]) for monomolecular heterogeneous reactions in a flow system inhibited by the transformation products:

$$v_0 \ln \frac{1}{1-y} = \alpha + \beta v_0 y,$$

where v_0 is the volume of liquid substance fed into the reaction space per unit time, y is the degree of conversion of the initial substance, and α and β are

constants depending on the experimental conditions, the nature of the catalyst, and the reacting substance.

The apparent reaction-rate constants were calculated, and from them, graphically, the apparent activation energies, whose values are given in Table 2.

In considering the data presented in Table 2, attention is drawn to the very large value of the apparent activation energy for dealkylation of ethylbenzene. Apparently, this should be attributed to the fact that the reaction proceeded not only catalytically, but partly also as a thermal process; this is supported by the composition of the gases obtained and the higher temperatures of the experiments to which it was necessary to resort because of the small conversions.

It should be noted that for monoalkylbenzenes of composition $C_3H_7 \cdot C_6H_5$ and $C_4H_9 \cdot C_6H_5$, the structure of the alkyl group has a strong effect on the rate of the dealkylation reaction: E for the dealkylation of isopropylbenzene decreases almost twofold in comparison with E for the dealkylation of *n*-propylbenzene; E for the dealkylation of tert-butylbenzene is more than 2.5 times lower than the value of E for *n*-butylbenzene.

The substituents CH_3 and Cl, which do not participate in the dealkylation reaction, also have a clear effect on the magnitude of the activation energy. If the values of E for the dealkylation of isopropylbenzene, isomeric cymenes, and chlorocumenes are compared, the activating effect of methyl and the passivating effect of chlorine become evident. It seems to us that the comparable data obtained by us may be regarded as further evidence in favor of the ionic mechanism of the catalytic dealkylation of alkylbenzenes and some of their derivatives.

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CITED LITERATURE

1. C. L. Thomas, I. Hoekstra, J. T. Pinkston, *J. Am. Chem. Soc.*, **66**, 1694 (1944).

2. B. S. Greensfelder, H. H. Voge, G. M. Good, *Ind. and Eng. Chem.*, **41**, 2573 (1949).

3. B. L. Moldavskii, L. S. Bezdel, *ZhOKh*, **16**, 6133 (1956).

4. R. H. Roberts, G. M. Good, *J. Am. Chem. Soc.*, **73**, 1320 (1951).

5. K. V. Topchieva, G. M. Panchenkov, *DAN*, **74**, 1109 (1950).

6. R. D. Obolentsev, N. N. Grachev, *ZhOKh*, **21**, 860 (1951).

7. A. V. Frost, A. P. Balod, E. K. Mikhailash, D. I. Orochko, *Tr. VNIGI*, issue 4, 116 (1952).

8. H. F. Rase, R. S. Kirk, *Eng. Progr.*, **50**, No. 1, 35 (1954).

9. A. V. Frost, *Vestn. MGU*, No. 3–4, 111 (1946).

10. T. V. Antipina, A. V. Frost, *Usp. Khim.*, **19**, 342 (1950).

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