JOURNAL OF CATALYSIS **21**, 255–262 (1971)

On the Mechanism of Contact Eliminations

XXX. The Cracking of Butyl-Benzenes over Silica-Alumina Catalysts*

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Received August 22, 1969; revised September 9, 1970

The cracking of tert-butylbenzene, sec-butylbenzene, n-butylbenzene, and cumene over silica-alumina catalysts has been studied using the microcatalytic pulse technique. The influence of catalyst composition, surface acidity, and surface area on activity have also been studied. The surface acidity increased with increasing alumina content up to a maximum of 25% Al_2O_3; further increase in alumina content resulted in lowering of surface acidity. Both acidity and activity of the catalysts varied with the method of preparation. The cracking products of sec-butylbenzene at temperatures above 400°C were benzene and the four isomeric butenes. The order of reactivities is the same as would be expected if carbonium ions were formed as reaction intermediates. A reaction mechanism is proposed in which both Brönsted and Lewis type acidic centers are involved.

INTRODUCTION

Characterization of active sites and determination of reaction mechanism has been the object of many of the studies of catalytic cracking reactions of hydrocarbons. The activity of solids, such as mixtures or combinations of silica and alumina effective as cracking catalysts, has been attributed for a long time to their surface acidity (*1–5*) of both types, i.e., Brönsted and Lewis acid centers. However, the role of the two types of acidic centers has not been established conclusively. The reason is that, in spite of the present methods available for acidity determination, the characterization of the type, strength, and distribution of the acidic sites, although recently presented and thoroughly discussed by Topchieva *et al.* (*5*) and Trambouze *et al.* (*6*), is not easily realizable. Thus, Milliken *et al.* (*7*) proposed that Lewis acid sites promote cracking by removal of hydride ions from the molecules of the reactants, giving rise to carbonium ion intermediates. The experimental evidence for this conclusion was the formation of carbonium ions from triphenylmethane, 1,1-diphenylethane and cumene, which were identified spectroscopically (*8*). Further, the presence of surface butenyl carbonium ions formed from 1-butene chemisorbed on silica-alumina catalysts was inferred by Leftin *et al.* (*9, 10*) from IR and UV spectra.

A second group of workers are of the opinion that the Brönsted sites are responsible for the activity of the catalysts. These sites promote cracking by transfer of protons to the reactant molecules (olefins or aromatic ring) giving rise to carbonium ions. Sato *et al.* (*11*) and Brouwer (*12*) showed that selective poisoning of Brönsted sites on silica-alumina with sodium ions reduces the activity for cumene cracking. Hirschler (*13*), using titrations in a nonaqueous medium with suitable indicators, concluded that protonic acidity in silica-alumina is responsible for the cracking activity. However, Hall *et al.* (*14*) and

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* Number XXIX of the series: P. Andréu, M. A. Linero and H. Noller, *J. Catal.* **21**, 349 (1971).

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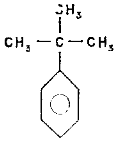
Tung *et al.* (*15*) proposed that either or both types of acidic centers, depending on the reaction conditions, might be responsible for catalytic activity. Maximum surface acidity, however, does not always correspond to a maximum activity, as other factors such as surface area and texture are effective.

In the present work, the cracking reactions of tert-butylbenzene (I), sec-butylbenzene (II), n-butylbenzene (III), and cumene (IV), have been studied over silica-alumina catalysts, in order to further our understanding of the mechanism and obtain more evidence of the influence of surface area and acidity.



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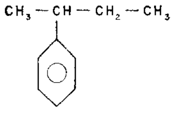

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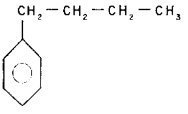

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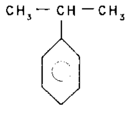

IV

EXPERIMENTAL

Conversion Measurements and Product Analysis

The microcatalytic pulse technique (*16*) was used, with a reactor previously described by one of us (*17*). Conversion of the reactants was measured for each catalyst at temperatures between 180–500°C, and the corresponding products were analyzed by gas chromatography. Activation energies were determined on the basis of first order kinetics, as described elsewhere (*18*).

The gas chromatograph used was made in our laboratory; it was provided with a Gow-Mac gas-density-balance detector with nitrogen as the carrier gas. For separation of butylbenzenes, benzene, and butenes, the following column and conditions were used: Column: 20% beta, beta′-oxidipropionitrile on sterchamol 60/80 mesh, .635 cm o.d. and 1 m length; temperature, 90°C; carrier gas, nitrogen 40 ml/min. The separation of the four isomeric butenes was carried out as follows: Column: 37% propylenecarbonate on Chromosorb P 30/60 mesh acid washed, .635 cm o.d. and 14 m length; temperature, 26°C; carrier gas, nitrogen 40 ml/min. The peaks were identified by comparing their retention times with those of standards supplied by Air Products and Chemicals (USA).

The amount of catalyst employed was 0.6 g. 0.4 μl of reactant was injected to obtain the conversion curves, and 5 μl were injected to study the reaction product distribution. The contact time over the catalyst was about 0.1 sec.

Reactants

Tert-butylbenzene, sec-butylbenzene, n-butylbenzene and cumene were obtained from Fluka AG (Buchs, Switzerland). The degree of purity was Fluka Puriss.; all the reactants were used without further purification.

Catalysts

The catalysts were prepared by the two methods described below using the following materials:

Aerosil: SiO_2, aerosol type, particle size 100–200 Å, Degussa (Hanau, Germany).

Alon C: γ-Al_2O_3, aerosol type, Godfrey L. Cabot Co. (Boston, USA).

Aluminium nitrate: $Al(NO_3)_3 \cdot 9H_2O$, Merck (Darmstadt, Germany) (pro analysis).

Method A

A measured volume of aluminium nitrate solution was added to a known weight of Aerosil. The mixture was left standing for 22 hr and then dried slowly on a hot plate. The dry gel was then calcined at 700°C for 16 hr. The concentration of the aluminium nitrate solution was 0.0107 g Al_2O_3/ml. The alumina content in the catalyst was estimated from the volume of solution employed.

Method B

Aerosil was mixed with 10% by weight of Alon C and 20 ml of distilled H_2O. The mixture was dried and calcined as in method A. Maximum activity of all catalysts was obtained by heating them at 400°C for at least 30 min in the reactor in a nitrogen stream.

Determination of Acidity

The method used was that described earlier by Tamele (*19*). It consists of titrating the solid, suspended in benzene, with n-butylamine using p-dimethylaminoazobenzene as indicator. Acidity determinations were carried out on samples of catalysts weighing 0.1 g, after calcining at 500°C for 2 hr. For conversion experiments fresh catalysts were employed.

Surface Area Measurements

The surface areas of the catalysts were measured using the dynamic method (*20–21*). The sorptometer was constructed in our laboratory. The samples of catalysts (about 0.2 g) were subjected to the already indicated pretreatment to obtain maximum activity.

RESULTS AND DISCUSSION

Homogeneous Reaction

Because no evidence of thermal cracking was observed with tert-butylbenzene up to 450°C, thermolysis could be ruled out for all the reactants, on the basis of this compound being the most reactive one.

Catalytic Reactions

The extent of conversion at the respective reaction temperatures as well as the activation energies for each catalyst and reactant are listed in Table 1. The components of the catalysts, Aerosil and Alon C, singly used, showed no activity in cracking. Simple mixtures of silica gel and acid alumina made in a mortar, however, showed some activity.

As can be seen in Fig. 1, the order of decreasing reactivity found for the reactants is: tert-butylbenzene > sec-butylbenzene > cumene > n-butylbenzene. Cracking of tert-butylbenzene gave only benzene and isobutylene. No isomerization of this olefin was observed. With Catalysts 1–5 (see Table 1), the reaction products of sec-butylbenzene cracking are benzene and the four isomeric butenes. Figure 2 represents the product distribution obtained using Catalyst 2. Reaction products from cumene cracking are benzene and propylene. n-Butylbenzene was cracked to benzene and butenes with great difficulty. At 520°C only 12% conversion was obtained with Catalyst 1. Due to its low reactivity, the reaction product distribution of this reactant could not be determined.

The conversion curves of tert-butylbenzene on Catalysts 2 and 6 (see Fig. 1), although both have the same alumina content, show different catalytic activity because of the difference in the method of preparation. The higher activity of Catalyst 2, prepared according to method A, is assigned to its higher acidity.

Acidity and Surface Area

The values of surface area and specific acidity for each catalyst are listed in Table 1. As can be seen, the maximum acidity was obtained with about 25% alumina, while the catalyst with 18% alumina showed minimum surface area. It was not possible to differentiate between Brönsted and Lewis sites, due to the method used to determine the acidity.

Catalytic Activity

For a discussion of the relative influence of acidity and surface area on the catalytic activity of silica-alumina as cracking catalysts, we consider the two factors separately.

Figure 3 represents the specific rate of cracking at a given contact time for sec- and tert-butylbenzenes at different temperatures as a function of the acidity of the catalysts. Although the dispersion of the experimental points is greater than might be desired, the following trends can be seen: In the case of sec-butylbenzene, the reaction rate increases with the acidity, while with tert-butylbenzene it is practically independent of this parameter.

TABLE 1
Catalysts and Reactions Parameters

					Tert-butylbenzene			Sec-butylbenzene			Cumene		
Catalyst No.	Method of preparation	% Al_2O_3	Surface area (m^2/g)	Acidity (meq/ m^2) · 10^3	T°C	% conversion[a]	E_a (kcal/ mole)	T°C	% conversion	E_a (kcal/ mole)	T°C	% conversion	E_a (kcal/ mole)
1	A	5	190 ± 0.7%	0.66 ± 0.3%	180	45	5	340	37	12	—	—	—
					280	92		380	54				
					320	100		460	82				
								480	86				
2	A	10	89 ± 4.5%	1.53 ± 0.4%	200	53	4	360	52	9	380	20	12
					280	83		380	58		500	67	
					340	95		430	75				
					360	100		460	86				
3	A	18	87 ± 5%	2.48 ± 0.2%	220	63	4	320	50	9	—	—	—
					280	78		380	64				
					320	87		430	76				
					340	88		460	91				
					400	95							
4	A	25	92 ± 7.5%	2.61 ± 0.1%	220	64	4	380	65	9	—	—	—
					280	83		430	83				
					320	89		460	89				
					340	91							
					400	100							
5	A	50	140 ± 7%	1.56 ± 0.2%	250	71	5	340	48	9	—	—	—
					280	83		380	57				
					320	91		430	78				
					340	94		460	84				
					360	100		480	88				
6	B	10	125	0.80 ± 0.3%	260	11	11	—	—	—	—	—	—
					280	21							
					460	87							
7 Alon C	—	100	105	—	450	0	—	—	—	—	—	—	—
8 Aerosil	—	0	177 ± 4%	0.09 ± 6%	450	0	—	—	—	—	—	—	—

[a] The conversion values lie within ± 2%.

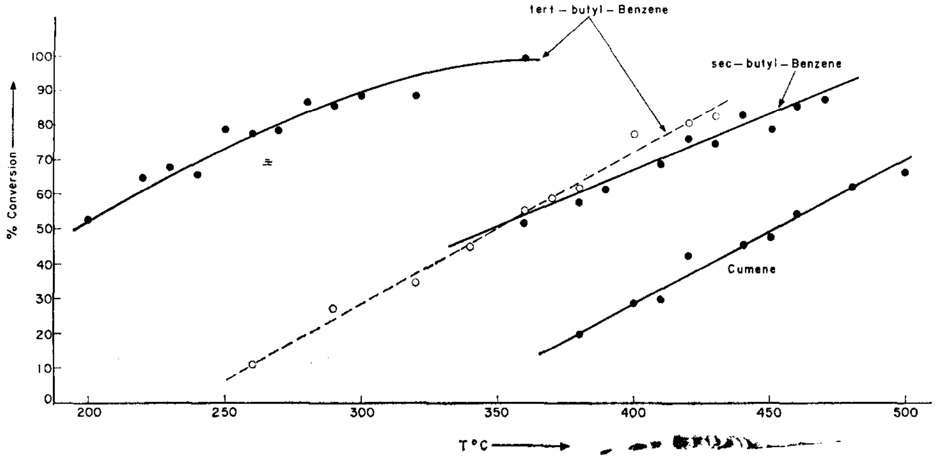

FIG. 1. Temperature dependence of conversion in percent of cracking. Catalysts: ● No. 2; ○ No. 6.

These trends can be interpreted by considering the acid sites of the catalysts as polarizing centers, their function being the polarization of the reactant leading to the formation of the reaction intermediate. With sec-butylbenzene the correlation obtained is probably due to the interaction between the acid sites and the reactant molecules. With tert-butylbenzene, the molecule seems to be sufficiently polarized at the working temperatures to be able to react without the further polarization effect of relatively strong acid sites. This behavior is therefore a consequence of reactant structure; the structure of tert-butylbenzene permits it to stabilize the reaction intermediate better, enabling it to react on weaker acid sites, whereas sec-butylbenzene can be adequately polarized to the reaction state only on stronger acid sites.

Considering the dependence of the reaction rate, at a given contact time, on the surface area (both calculated per unit of acidity) of the different catalysts (see Fig. 4), we find that tert-butylbenzene in-

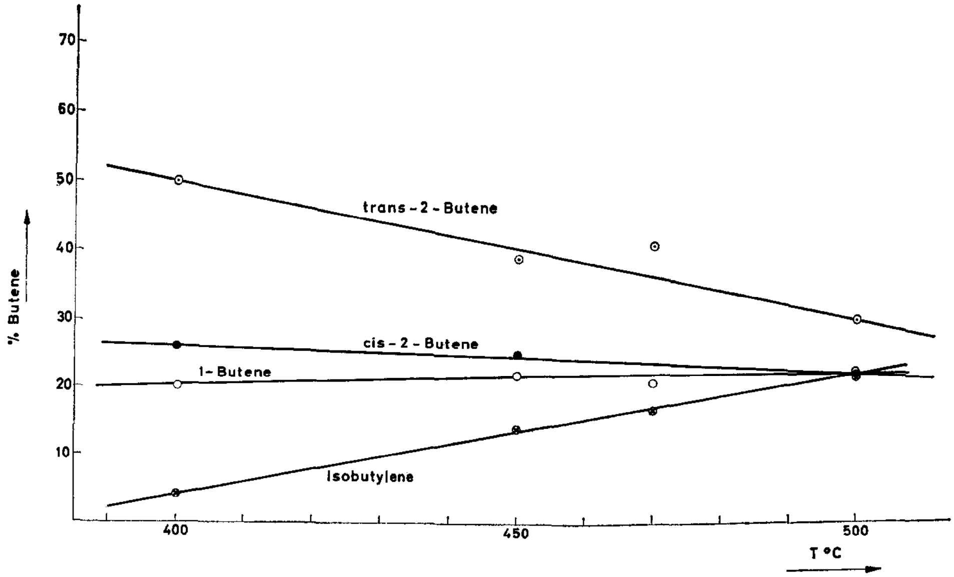

FIG. 2. Distribution of cracking products (butenes) as a function of temperature. Reactant: sec-butylbenzene. Catalysts: No. 2 [SiO_2 (90%)-Al_2O_3 (10%)].

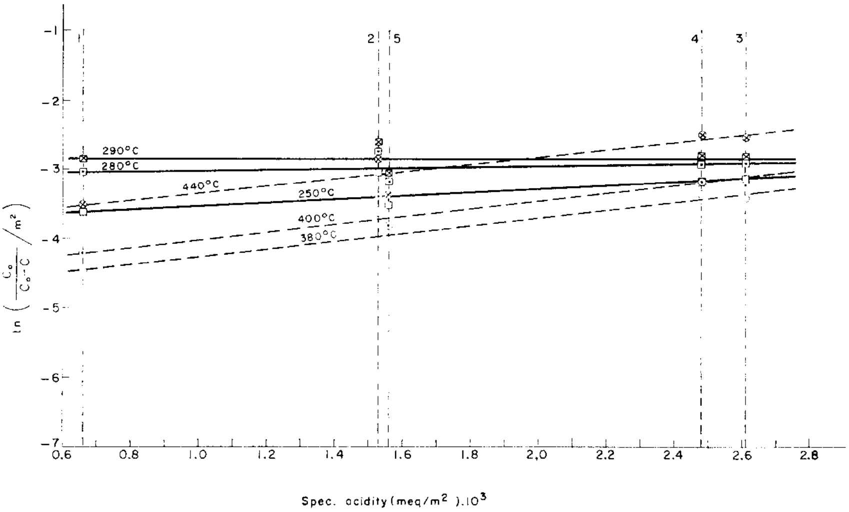

FIG. 3. Reaction rate curves as a function of the acidity of the catalysts (numbering according to Table 1) calculated for unit surface, for different temperatures. ○ --- sec-butylbenzene; □ — tert-butylbenzene.

creases its rate with the surface area steeper than sec-butylbenzene. It should be pointed out here that the surface area plotted refers to unit acid site and therefore, signifies the density of acid sites on the catalyst surface. This increase can be understood as a change in the nature of the acid sites with their density and/or due to steric hindrance of the reacting molecules.

Thus, it can be concluded that an increase in surface area of the catalyst favors the cracking of tert-butylbenzene, whereas sec-butylbenzene cracking is favored by increasing the catalyst acidity.

Reactivity and Mechanism

The reactivity sequence found for the reactants studied (see Fig. 1) as well as the product distribution from sec-butylbenzene (see Fig. 2) can be explained assuming a carbonium ion mechanism, similar to that proposed by Pines (*22*). Accordingly, the necessary σ-complex intermediate for the E1 mechanism can be produced on Brönsted sites by protonation of the aromatic ring as shown in Fig. 5. This complex decomposes subsequently to benzene and a carbonium ion, which then loses a proton to form the olefins. The

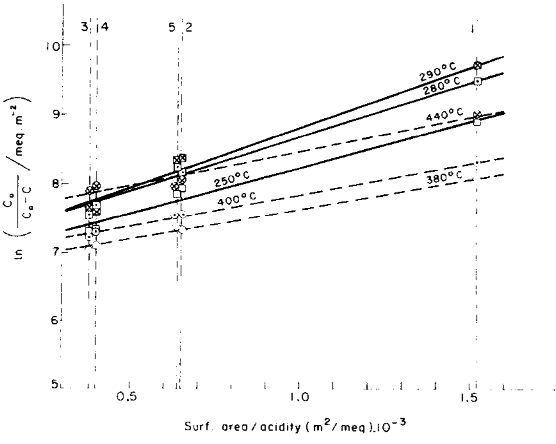

FIG. 4. Reaction rate curves as a function of the surface area of the catalysts (numbering according to Table 1) calculated per unit of acidity, for different temperatures. ○ --- sec-butylbenzene; □ — tert-butylbenzene.

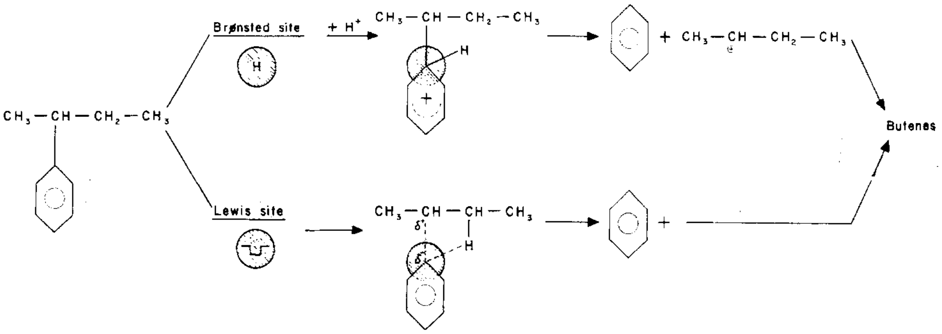

FIG. 5. The reaction scheme.

greater reactivity of sec-butylbenzene as compared with that of cumene may be explained considering that the induction effect of the ethyl group leads to a greater stabilization of the reaction intermediate.

It is interesting to compare the distribution of the four isomeric butenes obtained by cracking of sec-butylbenzene (Fig. 2) with the equilibrium distribution calculated from thermodynamic data (*23*). The values are listed in Table 2. From these values it is obvious that the experimental distribution does not correspond to thermodynamic equilibrium. By increasing the temperature, the equilibrium concentration of *trans*-2-butene remains constant, while according to our results the obtained concentration of this isomer decreases with increasing temperature. It can be also noted that the amount of the isobutene formed with increasing temperature comes closer to that of equilibrium. Similar results were reported by Tung and Mcininch (*15*) for 1-butene isomerization over alumina. Using a commercial silica-alumina catalyst with 13% alumina, they observed that the skeletal isomerization of 1-butene began at 310°C, and at 370°C the concentration of isobutene had increased to about 5%.

In order to explain the predominance of the *trans*-2-butene in the cracking of sec-butylbenzene at lower temperatures, we may assume a contribution from the concerted mechanism in this temperature range, due probably to Lewis acid sites.

TABLE 2
EXPERIMENTAL AND EQUILIBRIUM DISTRIBUTION OF THE FOUR ISOMERIC BUTENES

Experimental Values

T°C	% 1-butene	% isobutene	% *trans*-2-butene	% *cis*-2-butene
400	20	4	50	26
450	22	14	39	25
470	21	17	41	21
500	23	23	31	23

Equilibrium Values

T°C	% 1-butene	% isobutene	% *trans*-2-butene	% *cis*-2-butene
327	12	44	28	16
427	17	40	26	17
527	21	36	26	17
627	25	33	26	16

The *trans* isomer is favored because the conformation with the lowest energy in both *cis* and *trans* concerted mechanisms leads to this olefin. The scheme for this mechanism is also shown on Fig. 5. Here the reactant molecule should be adsorbed at its steric site of highest electron density. A corresponding characterization of the nature of the acid sites would be helpful to clarify this point.

At temperatures above 400°C, the sec-butylbenzene cracking follows a pure carbonium ion mechanism. Here the sec-butyl carbonium ion rearranges to the more

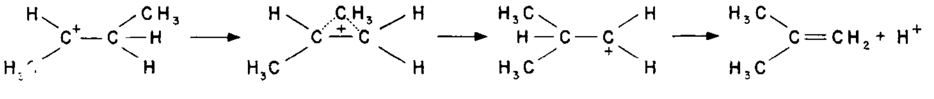

FIG. 6. Scheme of the skeletal isomerization of 2-butene.

stable tertiary butyl carbonium ions, leading to an increase of isobutene. The mechanism of the rearrangement of sec-butyl carbonium ion (Fig. 6), has been proposed previously (*24*) to explain methyl group migration, and its molecular orbital description (*25*) has also been attempted. In the case of tert-butylbenzene, the E1 mechanism is even more favored than in the former case since a tertiary carbonium ion is involved.

ACKNOWLEDGMENTS

The authors express their gratitude to Dr. H. Knözinger, Institute of Physical Chemistry, University of Munich, Germany, for helpful discussions of this work and to Dr. S. Prakash, Facultad de Ingeniería, Universidad Central de Venezuela, for a critical study of the manuscript.

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