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Alumina: Catalyst and Support

XXII.* Effect of Intrinsic Acidities of Aluminas in Molybdena-Alumina Catalysts upon the Hydrogenolysis and Isomerization of Alkylbenzenes

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The hydrogenolysis and isomerization of *o*-, *m*-, and *p*-xylene, ethylbenzene, *n*-propyl- and isopropylbenzene, *n*-, *sec*-, and *tert*-butyl-, and isobutylbenzene in the presence of molybdena-alumina catalysts having aluminas of various intrinsic acidities have been studied. The experiments were made under 10 atm of pressure and at temperatures ranging from 420° in the case of *t*-butylbenzene to 510° in the case of xylenes. The temperature depended on the ease of hydrogenolysis of the hydrocarbons. The molal ratio of hydrogen to hydrocarbons used was 5 to 10 moles of hydrogen per mole of hydrocarbons.

The hydrogenolysis of isopropyl-, *sec*-butyl-, and *tert*-butylbenzene to benzene and to the corresponding alkanes is facilitated by the intrinsic acidity of the aluminas used in the preparation of the catalyst.

Skeletal isomerization of *n*-butylbenzene to *sec*-butyl- and isobutylbenzene, *sec*-butylbenzene to *n*-butyl- and isobutylbenzene, and that of isobutylbenzene to *sec*- and *n*-butylbenzene increases with the acidity of the alumina.

The selectivity of the hydrogenolysis of α–β and β–γ bonds in alkylbenzenes is not influenced by the acidity of the aluminas.

In previous papers of these series it was shown that the catalytic properties of alumina depend upon its method of preparation (*2, 3*). Alumina otbained by hydrolysis of aluminum isopropoxide or by precipitation of aluminum nitrate with ammonia, and calcined at 600°, contains intrinsic acidic sites which catalyze reactions, such as skeletal isomerization of cyclohexene to methylcyclopentenes, which usually are associated with strong acids. On the other hand when the alumina is prepared by precipitation of aluminum nitrate with sodium or potassium hydroxide, the stronger acidic sites are neutralized by the sodium and potassium ions, respectively. It was thus shown that as little as 0.07 wt % of sodium in alumina can inhibit the skeletal isomerization of cyclohexene, but the catalyst may still remain active for the conversion of 3,3-dimethylbutene to 2,3-dimethylbutenes.

It was also demonstrated by us that aluminas, depending upon their method of preparation, may have an effect upon platinum-alumina catalysts for dehydromethanation and dehydroisomerization of 1,1-dimethylcyclohexane (*4*). Similar effects have been noticed in the dehydroisomerization of cyclanes (*5*) and alkanes (*6, 7*) in the presence of chromia-alumina catalysts.

The present paper deals with the effect of various aluminas in molybdena-alumina catalysts on the hydrogenolysis and isomerization of alkylbenzenes. Although ex-

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tensive research has been reported in the literature on the aromatization and isomerization of saturated hydrocarbons in the presence of alumina-molybdena (*8*), in none of the cited investigations was there an indication that aluminas *per se* may have intrinsic acidic properties which could influence the hydroisomerization characteristics of the alumina-molybdena. We have shown previously that the dehydroisomerization of naphthenes to aromatic hydrocarbons is greatly affected by the nature of the aluminas used. The extent of dehydroisomerization is most pronounced by using aluminas which do not contain either sodium or potassium ions.

The present study has been extended to investigate the effect of molybdena-alumina catalysts, having aluminas of various intrinsic acidities, upon the hydrogenolysis and isomerization of xylenes, ethylbenzene, *n*-propyl-, and isopropylbenzene and of the four butylbenzenes. It was of special interest to determine the structure of the isomers produced in order to shed light on the mechanism of isomerization, and to evaluate the relative ease of the hydrogenolysis of the various C–C bonds.

MATERIALS

Catalysts. The molybdena-alumina catalysts, having a ratio of $Mo/Al = 0.07$, were prepared by impregnating the various aluminas of 8–20 mesh size with ammonium molybdate, according to the procedure described previously (*9*).

Three types of aluminas were used:

A. Obtained from the Harshaw Chemical Company, Cleveland, Ohio; it contained 0.36% by weight of sodium ions. The catalytic behavior of the alumina is described in a previous paper (*2*).

B. This alumina was prepared from aluminum shavings of 99.99% purity. The aluminum was dissolved in an aqueous solution of potassium hydroxide. The bulk of the solution was neutralized with nitric acid and the aluminum hydroxide was precipitated with carbon dioxide. The alumina was then washed seven times with water, and after each washing the suspension was centrifuged. The detailed description of this catalyst is given in a previous paper (*2*). The properties and the catalytic behavior of Alumina B are similar to those of previously described Alumina 19c (*2*). From its catalytic behavior it is estimated that this catalyst contains 0.09% by weight of potassium ions.

C. The alumina was prepared from aluminum isopropoxide and calcined at 600° for 12 hr (*2*).

The molybdena-alumina catalysts were designated according to the alumina used.

Alkylbenzenes. Toluene, *o*-, *m*-, and *p*-xylene, ethylbenzene, *n*-propyl- and isopropylbenzene, and *t*-butylbenzene were reagent grade commercial products which were over 99% pure.

n-Butylbenzene was obtained by hydrogenation of 300 g of *n*-propyl phenyl ketone, dissolved in 300 ml of ethanol, in the presence of copper chromite at 150° and 150 atm of pressure. The carbinol thus obtained was refluxed for 6 hr with an equal volume of 20% sulfuric acid. The hydrocarbon layer was separated, washed with 5% aqueous solution of sodium carbonate, followed with water. All of the carbinol underwent dehydration.

The β-ethylstyrene obtained was dissolved in an equal volume of *n*-hexane and hydrogenated at 125° and under 140 atm in the presence of 25 g of copper chromite. The *n*-butylbenzene produced was over 99% pure.

Isobutylbenzene was obtained by many step reactions starting with benzyl dimethyl carbinol, which was prepared from 200 g of benzyl chloride and acetone, *via* a Grignard reaction. The dimethyl benzyl carbinol was dehydrated by means of 20% sulfuric acid, and the olefins hydrogenated in the presence of copper chromite, according to the description given above. Based on the benzyl chloride used, a 45% yield of 99% pure isobutylbenzene was obtained.

sec-Butylbenzene was obtained in over 99% purity by the alkylation of benzene with butylene in the presence of 96% sulfuric acid (*10*).

EXPERIMENTAL PROCEDURE

The hydrocarbons and hydrogen were passed through a preheater and a reaction tube of 20-mm ID, made of stainless steel, and heated by means of a thermostatically controlled vertical furnace. The volume available for the catalyst was 36 ml. The catalyst was usually diluted with either Pyrex beads or quartz chips of the same size.

Before every experiment the catalyst was treated with hydrogen for 3 hr at the temperature of the reaction. After each experiment, the carbonaceous material deposited on the catalyst was burned by passing air overnight at the same temperature.

The hydrocarbons were introduced at a constant rate by means of a stainless steel, syringe type, displacement pump of 40 ml capacity. The hydrogen was supplied from a tank, the rate being measured by means of a thermoelectric flow meter. The usual duration of an experiment, which was performed at 10 atm pressure, was 80 min. The molal ratio of hydrogen introduced varied from 5 to 10 moles per mole of hydrocarbons and in this range it did not effect the conversions and the yields of products. The contact time was calculated by the equation given previously (*6*). The temperature of the experiments was adjusted in order to maintain the average conversion of the alkylbenzene used to less than 40%. This was necessary in order to minimize the extent secondary reactions.

Four samples of liquid hydrocarbons were collected from each run during the following intervals of time: (A) from 0 to 25%, (B) 25% to 50%, (C) 50% to 75%, and (D) 75% to 100%.

The gaseous products were trapped in liquid nitrogen and two samples were taken: from 0 to 50% of time elapsed (sample A-B) and from 50% to 100% (sample C-D). This procedure gave good results as far as C_2–C_4 hydrocarbons were concerned, but gave low figures for methane which was only partially condensed in the traps. On the other hand, the analysis of samples taken directly from the reaction gas gave less accurate results because of the low concentration of the hydrocarbons in the gas. For these reasons, the first procedure was always used when the concentration of methane could be calculated from other analytical data. In the other case, when the second procedure had to be used, four samples were taken at 25%, 50%, 75%, and 100% of time elapsed. The average composition of the first two samples, A-B, and the last two samples, C-D, are reported in the tables.

The butanes from the hydrogenolysis of butylbenzene were partially dissolved in the aromatic hydrocarbons forming the liquid fraction. In the analysis of these fractions the total amount of butanes was determined and added to the total amount of butanes

TABLE 1

Vapor-Phase Chromatographic Columns Used for Analysis[a]

Column:	A[b]	B[d]	C[e]	D[f]	E[h]
Liquid phase	None	33% Dimethylsulfolane	5% Benzoquinoline	30%-QF-1 6500[g]	8% Dow-Corning Silicon 550
Solid support	Silica gel[c]	Firebrick	Firebrick	Firebrick	Firebrick
Mesh size	60–200	100–120	100–120	100–120	30–60
Length (meters)	2.6	6.9	9.1	7.5	4
Temperature (°C)	90	60	85	100–125	—

[a] The VPC results were corrected on the basis of data reported by A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.* **31**, 231 (1959).

[b] For methane and ethane.

[c] Obtained from the Davison Chemical Company, Baltimore, Maryland.

[d] For ethane, propane, isobutane and *n*-butane.

[e] For ethylbenzene and *o*-, *m*-, and *p*-xylene.

[f] For isobutyl- and *sec*-butylbenzene.

[g] Obtained from Wilkens Instrument and Research Inc., Walnut Creek, California.

[h] For all the other hydrocarbons.

in the gas fraction, with the assumption that the distribution between *n*- and isobutane in the liquid sample was the same as in the gas sample. The errors involved in the calculations were very small as the quantity of butanes in the gaseous fraction was much greater than in the liquid fraction.

The liquid samples were weighed while the total amount of gaseous hydrocarbons formed in each experiment was determined from the analytical data. An assumption was made, which is well substantiated, that all the gaseous hydrocarbons were produced from the hydrogenolysis of alkyl groups and none by hydrocracking of the aromatic ring.

The composition of the gaseous and liquid hydrocarbons did not permit drawing a detailed conclusion as to the path involved in the hydrogenolysis reactions of propyl- and butylbenzenes. For that reason certain approximations had to be made to integrate the analytical data; this will be shown in the Discussion. The results of the experimental data and of the calculations relating to the splitting of carbon–carbon bonds are given in the tables. The chromatographic columns used are described in Table 1.

RESULTS

Toluene

The reactions with toluene were carried out at 500–510° over molybdena-alumina A and C catalysts; at lower temperature practically no reaction occurred. From the data presented in Table 2 it can be seen that the variation in the aluminas used in the preparation of the catalyst had little effect on the extent of hydrogenolysis.

The hydrogenolysis reaction, leading to benzene, was accompanied by the formation of small amount of C_8 hydrocarbons consisting of some ethylbenzene and of a mixture of xylenes. The steps leading to ethylbenzene are most probably due to a free radical type reaction. It was reported by one of us that *p*-cymene at this temperature in the absence of a catalyst but at elevated pressures forms *p*-ethylisopropylbenzene (*11*).

The transalkylation reaction resulting in xylene formation can be attributed to an acid-type reaction since thermal reactions of such type were not encountered previously (*11*).

Xylenes

The experiments were made at 507° using as catalysts Molybdena-Alumina A and C and in the case of *p*-xylene also Catalyst B (Table 3). At the beginning of the reaction, as indicated by Cut 1, the extent of hydrogenolysis is much greater than in the succeeding cuts. This might be due to a large initial adsorption of hydrogen in the catalyst.

The hydrogenolysis is the main reaction and it does not seem to be affected by the acidity of the alumina. It is of interest to note that at a given rate of conversion the

TABLE 2
HYDROGENOLYSIS OF TOLUENE

	Experiment[a]							
	1				2			
Molybdena-Alumina:	A				C			
Temperature (°C):	506°				510°			
Cut:	1	2	3	4	1	2	3	4
Hydrogenolysis (benzene) (mole %)	10	8	7	5	17	11	6	5
Transmethylation	2.3	1.7	1.3	1.1	2.6	2	1	1.2
Composition of C_8H_{10}:								
Ethylbenzene	9	—	—	9	8	—	—	8
o-Xylene	24	—	—	26	26	—	—	26
m-Xylene	57	—	—	56	53	—	—	53
p-Xylene	10	—	—	9	13	—	—	13

[a] In each experiment 7 ml of catalyst was used, diluted with 29 ml of pyrex beads of the same mesh size. The contact time was 17 sec.

TABLE 3

HYDROGENOLYSIS AND HYDROISOMERIZATION OF XYLENES[a]

Experiment:	3				4				5			6			7			8			9			10		
Xylene used:	*o*-Xylene				*o*-Xylene				*o*-Xylene			*m*-Xylene			*m*-Xylene			*p*-Xylene			*p*-Xylene			*p*-Xylene		
MoO_3-Al_2O_3:	A				C				Al_2O_3-C			A			C			A			B			C		
Cut:	1	2	3	4	1	2	3	4	1	2	4	1	2	4	1	2	4	1	2	4	1	2	3	1	2	4
Hydrogenolysis (%)	45	23	18	13	49	26	19	16	9	4	2	36	15	14	53	30	16	31	26	24	40	29	23	58	34	27
Benzene (%)	28	19	17	13	26	17	12	11	21	18	18	7	5	3	10	6	4	5	4	4	7	5	4	11	8	6
Toluene (%)	72	81	83	87	74	83	88	89	79	82	82	93	95	97	90	94	96	95	96	96	93	95	96	89	92	94
Isomerization	4.3	3.1	2.9	2.6	—	9.1	8.4	7.5	3	2	2	4.1	2.4	2.1	9.1	10	9.3	6	5	4	11.5	10	10	14.4	12.8	11.5
Ethylbenzene	—	20	20	18	—	5	5	7	7	4	1	—	—	—	2	2	—	—	—	—	—	—	—	—	—	—
o-Xylene	—	—	—	—	—	—	—	—	—	—	—	49	61	62	52	44	49	12	12	11	17	17	14	20	16	15
m-Xylene	—	60	65	69	—	80	82	78	80	84	88	—	—	—	—	—	—	88	88	89	83	83	86	80	84	85
p-Xylene	—	20	15	13	—	15	13	15	13	12	11	51	39	38	46	54	51	—	—	—	—	—	—	—	—	—
Transalkylation	2.1	1.9	1.7	1.4		3.3	2.9	2.6	1.3	—	0.2	1.6	1.3	1.1	1.9	2.2	1.8	1.2	1.1	0.9	2.2	1.7	2.2	1.7	2.2	1.7

[a] Experimental conditions: temperature 507 ± 4°C; contact time 97–100 sec. All experiments were performed on 36 ml of catalyst, without any diluent.

ratio of benzene to toluene produced is greater in the case of *o*-xylene than in *m*- and *p*-xylene. It is possible that owing to steric hindrance, the *o*-xylene is not as readily adsorbed on the catalyst as toluene and therefore the latter undergoes further hydrogenolysis to benzene and methane. The extent of the positional isomerization of the xylenes increases with the acidity of the aluminas and it seems to proceed stepwise inasmuch as the ratio of *m*-/*p*- and *m*-/*o*- xylenes starting from *o*- and *p*-xylene, respectively, is greater than the equilibrium ratio. This stepwise isomerization from *o*- to *m*- to *p*- is in agreement with the results obtained using aluminum chloride as a catalyst (*12*).

The mechanism of the formation of the small amounts of ethylbenzene from *o*-xylene and practically none from *m*- and *p*-xylene is difficult to explain with the data on hand.

The hydroisomerization was accompanied by a transmethylation reaction, which was only very slightly affected by the acidity of the alumina in the catalyst.

In the case of *o*-xylene the acidic Alumina C as such was used as the catalyst (Expt. 3). The extent of hydrogenolysis and hydroisomerization is only a fraction of what occurs in the presence of Molybdena-Alumina C (Expt. 2).

Ethylbenzene

The acidity of the alumina in the catalyst seems to have little effect upon the course of the hydrogenolysis reaction (Table 4). The rupture of α–β bond in the side chain proceeds three times faster than the cleavage of the phenyl–carbon bond.

Pyrex beads of about 1½ mm diameter which were used as catalyst diluent were practically catalytically inert.

n-Propylbenzene

The experimental results are summarized in Table 5. The concentration of propane in the gases is greater when an acidic alumina is used for the preparation of the catalyst. The extent of isomerization to isopropylbenzene is difficult to establish because the latter once formed may undergo a rapid dealkylation reaction. It is interesting to note that the preferential hydrogenolysis of the side chain occurs at the β–γ carbon–carbon bond.

Isopropylbenzene

Three catalysts with increasing acidity of alumina were used. The contact time and

TABLE 4

HYDROGENOLYSIS AND HYDROISOMERIZATION OF ETHYLBENZENE[a]

Experiment:	11			12			13	
MoO_3-Al_2O_3:	A			C			Pyrex beads	
Cut:	1	2	4	1	2	4	1	3
Hydrogenolysis (%)	32	23	17	53	31	18	5	1
Benzene (mole %)	38	39	40	43	41	44	33	64
Toluene (mole %)	62	61	60	57	59	56	67	36
Isomerization (%)	1.1	n.d.[b]	0.4	1.6	0.9	n.d.	None	
o-Xylene (mole %)	41	42	46	25	36	43		
m-Xylene (mole %)	40	41	36	48	44	34		
p-Xylene (mole %)	19	17	18	27	20	23		
Transalkylation	1.4	1.4	1.1	1.3	1.2	1	None	
Composition of gases								
Methane (mole %)		81	78		83	78		
Ethane (mole %)		19	22		17	22		
Cleavage								
Ring–α		23	25		21	26		
α–β		77	75		79	74		

[a] The experiments were made at 501–507° with a contact time of 19–20 sec using 7 ml of catalyst, diluted with 29 ml of pyrex beads of the same size.

[b] Not determined.

TABLE 5

Hydrogenolysis and Hydroisomerization of *n*-Propylbenzene

Experiment:[a]	14				15			
Molybdena-alumina:	A				C			
Temperature (°C):	495°				489°			
Cut:	1	2	3	4	1	2	3	4
Hydrogenolysis (%)	19	10	8	7	32	21	16	15
Benzene (mole %)	17	20	20	21	24	25	24	23
Toluene (mole %)	43	40	38	37	36	33	32	33
Ethylbenzene (mole %)	40	40	42	42	40	42	44	44
Isopropylbenzene (%)	1.5	1.2	1	1	2.7	2.8	2.5	2.3
Isopropylbenzene (%)[b]	7	11	11	13	7	11	13	12
Transalkylation	n.d.[c]	n.d.	n.d.	n.d.	1.8	1.4	1.4	1.4
Composition of gases								
Methane (mole %)	72		72		62		66	
Ethane (mole %)	17		18		22		19	
Propane (mole %)	11		10		16		15	
Cleavage								
Ring–α	13.8		13.5		18.7		17.4	
α–β	17		16.2		20.7		17.3	
β–γ	69.2		70.3		60.6		65.3	

[a] The reaction tube was filled with 7 ml of catalyst and 29 ml of pyrex beads of the same size as the catalyst. The contact time was 23 sec.

[b] The calculation was based on *n*-propylbenzene which underwent reaction.

[c] Not determined.

experimental conditions were similar to those applied to *n*-propylbenzene but the temperature of the reaction was about 35° lower.

The experimental data (Table 6) show that the ease of hydrogenolysis, as indicated by benzene and propane formation, is much greater than in the case of *n*-propylbenzene, and that the depropylation reaction is greatly influenced by the acidity of the alumina. These data indicate that the removal of an isopropyl group is an acid-catalyzed reaction and that the mechanism of this reaction is similar to the dealkylation reactions occurring over silica-alumina catalysts (*13a,b*).

The isomerization of isopropyl- to *n*-propylbenzene may be ascribed to an acid-type reaction, although a free radical isomerization at this temperature cannot be ignored (*11*).

n-Butylbenzene

The experiments were made using Molybdena-Alumina A and C as catalysts and as catalyst diluents Pyrex beads and quartz chips (Table 7). The extent of isomerization is greater when the acidic alumina is used. The isomerization leads to the formation of *sec*- and isobutylbenzene, the ratio of *sec*- to *iso* isomers being greater when the less acidic alumina is used, which can be interpreted that the reaction proceeds stepwise.

The hydrogenolysis reaction is very little affected by the change of the acidity of the catalyst; the cleavage of β–γ bond is the predominant one.

The substitution of pyrex beads by quartz chips, as catalyst diluent, does not seem to influence the selectivity of the reaction.

sec-Butylbenzene

The hydrogenolysis of *sec*-butylbenzene may produce as the primary products *n*-propylbenzene, isopropylbenzene, ethylbenzene, and benzene. The calculation of the data had to be based on various assumptions. It is sound to suppose that ethylbenzene, once formed, will not undergo ring–α-carbon splitting under the experimental conditions used. It is also sound to suppose that any three- or four-step reactions (as three-step demethylation to

TABLE 6
Hydrogenolysis and Hydroisomerization of Isopropylbenzene

Experiment:[a]	16				17				18			
Molybdena-alumina:	A				B				C			
Temperature (°C):	463°				455°				448°			
Cut:	1	2	3	4	1	2	3	4	1	2	3	4
Hydrogenolysis (%)	47	35	29	25	24	18	15	13	34	26	23	20
Benzene (mole %)	33	45	50	52	46	56	58	59	61	71	73	72
Toluene (mole %)	26	18	14	12	12	8	7	6	10	6	5	4
Ethylbenzene (mole %)	41	37	36	36	42	36	35	35	29	23	22	24
n-Propylbenzene (%)	1.5	1.7	—	1.7	1.4	1.3	1.2	1.3	2.0	1.8	1.9	2.0
n-Propylbenzene (%)[b]	3.0	4.4	—	6.2	5.2	6.6	7.4	8.0	5.5	6.4	7.7	9.1
Transalkylation	1.7	1.4	1.2	0.9	0.7	0.5	0.4	0.4	0.6	0.5	0.4	0.4
Composition of gases												
Methane (mole %)	67		57		55		48		39		35	
Ethane (mole %)	6		5		8		4		9		5	
Propane (mole %)	27		38		37		48		52		60	
Cleavage												
Ring–α	34.6		44.6		43.8		53.8		60		66.2	
α–β[c]	32.7		27.7		28.1		23.1		20		16.9	

[a] In each experiment 7 ml of catalyst was used, diluted with 29 ml of pyrex beads of the same mesh. The contact time was 23 sec.

[b] The calculation was based on isopropylbenzene reacted.

[c] Refers to each of the two α–β carbon–carbon bonds.

TABLE 7

HYDROGENOLYSIS AND HYDROISOMERIZATION OF *n*-BUTYLBENZENE

Experiment[a]	19				20				21				22			
Molybdena-alumina:	A				C				A				C			
Catalyst diluent:	Pyrex				Pyrex				Quartz				Quartz			
Temperature (°C):	502°				484°				504°				489°			
Cut:	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Hydrogenolysis (%)	41	23	19	17	14	14	13	12	64	31	23	21	45	21	17	15
Benzene (mole %)	14	15	15	14	22	21	21	19	17	15	15	14	19	19	19	17
Toluene	40	38	39	37	33	33	32	34	42	39	39	38	30	31	32	32
Ethylbenzene	35	36	36	38	36	37	37	39	33	36	36	38	42	41	40	42
n-Propylbenzene	11	11	10	11	9	9	10	8	8	10	10	10	9	9	9	9
Isomerization (%)[b]	n.d.	3.4	4.1	3.1	8.1	7.2	n.d.	7.5	3.1	2.8	n.d.	2.5	7.1	6.8	n.d.	8.1
sec-Butylbenzene (%)[c]	—	8.7	11.9	10.3	18.0	16.7	—	18.7	3.3	5.9	—	7.8	7.6	12.9	—	16.7
Isobutylbenzene (%)[c]	—	4.2	6.2	5.1	18.5	17.5	—	19.2	1.3	2.4	—	3.0	6.2	11.4	—	18.0
Composition of gases (mole %)																
Methane	18		17		16		13		19		16		12		14	
Ethane	44		45		50		50		44		44		48		48	
Propane	26		27		21		24		25		29		25		24	
n-Butane	12		11		11		12		12		11		14		13	
Isobutane	0		0		2		1		0		0		1		1	
Cleavage																
Ring-α	13		12		16		14		14		13		16		15	
α-β	29		30		24		27		28		31		27		26	
β-γ	47		47		51		50		48		46		49		50	
γ-δ	22		11		9		9		10		10		8		9	

[a] In each experiment 7 ml of catalyst was used which was dispersed with either 29 ml of pyrex beads or quartz chips of approximately the same size as the catalyst. The experiments were made with a contact time of 25 sec.

[b] The calculation was based on the *n*-butylbenzene charged.

[c] The calculation was based on *n*-butylbenzene reacted.

TABLE 8

HYDROGENOLYSIS AND HYDROISOMERIZATION OF *sec*-BUTYLBENZENE

Experiment:	23				24				25				26				27				28			29	30		
Molybdena-alumina:	A^a				B^a				C^a				A^a				C^a				$Al_2O_3C^a$						
Catalyst diluent:	Pyrex				Pyrex				Pyrex				Quartz				Quartz				None			Quartz	Pyrex		
Temperature (°C):	454°				460°				446°				457°				447°				452°			465°	458°		
Cut:	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3		1	2	3
Hydrogenolysis (%)	25	18	15	14	55	46	32	28	26	25	23	22	38	25	25	24	42	30	26	23	3.4	2.1	1.5	None	20	11	8
Benzene (mole %)	27	32	35	36	39	44	46	47	63	51	52	56	38	42	44	44	52	55	57	55	22	34	46		9	9	9
Toluene (mole %)	10	8	7	6	16	11	8	6	6	6	5	4	11	7	7	6	4	4	3	3	9	10	8		19	16	15
Ethylbenzene (mole %)	25	24	23	26	20	19	17	17	11	15	14	14	24	23	22	24	18	18	16	17	27	23	23		27	27	27
i-Propylbenzene (mole %)	13	14	15	14	12	13	17	19	8	10	11	10	11	14	13	13	16	13	13	14	11	11	7		13	16	17
n-Propylbenzene (mole %)	25	22	20	18	13	13	12	11	12	18	18	16	16	14	14	13	10	10	11	11	32	22	16		32	32	32
Isomerization (%)^b	2.3	2.3	2.2	2.3	3.9	4.4	n.d.	3.6	9.4	12.5	n.d.	10.5	Not determined				Not determined				1.6	1.5	1.5	None	<0.7		
n-Butylbenzene (%)^c	2.9	3.9	4.1	4.4	2.7	3.6	—	4.4	4.7	5.6	—	6.5									8	9	10				
i-Butylbenzene (%)^c	5.5	6.5	8.7	9.2	3.9	5.2	—	7.0	21.5	27.7	—	26.2									24	27	40				
Composition of gases (mole %)																											
Methane	65		58		53		46		49		43		48		42		33		34								
Ethane	11		13		14		15		7		9		18		20		19		16								
Propane	2		3		5		5		4		4		4		5		6		5								
n-Butane	20		25		27		33		39		43		30		33		42		45								
Isobutane	2		<1		<1		<1		1		1		—		—		—		—								
Cleavage																											
Ring–α	28.3		32.3		36.6		40.3		49.2		51.2		36.3		39		47.3		50.4								
α–β (methyl)	22.2		18.9		12.6		11.4		17.2		16.1		14.3		13		10.3		10.9								
α–β (ethyl)	5.6		9.6		6.9		10.6		2.6		6.6		14.1		17		16.8		14.4								
β–γ	13.7		14.4		13.3		17.6		9.2		10.2		13.1		13.3		13.8		13.9								
C_3	3.3		3.3		7.0		6.3		4.7		5		5.5		5.3		7		5.3								
Ethylbenzene	18.4		14.9		12.2		6.6		11.1		7.3		9		5.9		0.8		2								
Toluene	8.5		6.6		11.4		7.2		6		3.6		7.7		6.5		4		3.1								

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[a] Footnote *a*, Table 7.

[b] Footnote *b*, Table 7.

[c] Footnote *c*, Table 7.

toluene and four-step demethylation to benzene) will not occur to a great extent.

However, the propane found in the reaction products can be derived both from *n*- and isopropylbenzene, the contribution of the latter being probably more important. Ethylbenzene is partially formed in a primary process, through a splitting of an ethyl group from *sec*-butylbenzene. The excess of ethylbenzene probably resulted from a two-step reaction involving the intermediate formation of *iso*- and *n*-propylbenzene. Finally, toluene was formed by a two-stage hydrogenolysis, which involved intermediate formation of ethyl- and/or *n*-propylbenzene.

In view of the above, it is not possible to assign definite values for the relative cleavages of the various C–C bonds. In Table 8 separate figures for the formation of propane, of excess ethylbenzene, and of toluene are given.

The reaction with *sec*-butylbenzene was made with Molybdena-Alumina A, B, and C, having aluminas of progressively higher acidity. For the purpose of comparison both pyrex and quartz were used as catalyst diluents. Check experiments were also made using as contacting medium Alumina C, quartz chips, and pyrex beads, respectively. The experimental data are summarized in Table 8.

The cleavage of *sec*-butylbenzene to benzene and butane is the predominant reaction when the most acidic Molybdena-Alumina C is used. The isomerization to *n*- and isobutylbenzene increases with the acidity of the catalyst. In the presence of quartz alone *sec*-butylbenzene undergoes neither hydrogenolysis nor hydroisomerization while in the presence of pyrex beads hydrogenolysis of butylbenzene occurs leading mostly to ethyl- and *n*-propylbenzene; benzene is produced to a small extent only. Alumina C as such causes very little hydrogenolysis and only some isomerization, isobutylbenzene being the main product.

The concentration of isobutane in the gases is very small, in most cases less than 1%, which shows that the butyl group *which splits off does not* undergo isomerization and that isobutylbenzene produced in the reaction does not dealkylate.

Isobutylbenzene and t-Butylbenzene

The greatest catalytic effect of the acidity of molybdena-alumina catalysts was noticed in the case of isobutylbenzene. With Catalyst C 69% of the reacted isobutylbenzene was isomerized to *n*- and *sec*-butylbenzene, the latter being the predominant isomer. The hydrocarbon gases obtained from the reaction contained *n*-butane, which was most probably formed from the hydrogenolysis of the *sec*-butylbenzene. If we then recalculate the total amount of *sec*-butylbenzene produced, then the extent of isomerization of isobutylbenzene will be much greater than actually recorded, as indicated in Table 9 in parentheses under "Isomerization."

The predominant hydrogenolysis reaction is the β–γ cleavage, which amounts to about 30% for each carbon–methyl group.

In the case of *tert*-butylbenzene the main reaction is splitting of the *tert*-butyl group with the formation of isobutane and benzene. This reaction is slightly more predominant when acidic catalyst is used and it occurs already at 419°. The skeletal isomerization of *t*-butylbenzene was negligible.

The skeletal isomerization of isobutylbenzene to *sec*-butylbenzene and *n*-butylbenzene can be considered as an acid-type reaction and it is similar to the reaction described by Roberts and co-workers who used aluminum chloride as catalyst (*14*). The formation of *n*-butylbenzene from isobutylbenzene was not reported previously and it probably occurred through the isomerization of *sec*-butylbenzene produced in the reaction. The mechanism of the skeletal isomerization of butylbenzenes can be interpreted by a cationic mechanism similar to the ones proposed by Schmerling (*15*) and Roberts (*14*) in the case of skeletal isomerization occurring with acid catalysts.

The phenyl butyl carbonium ions which are required for the skeletal rearrangement to occur could have been produced either by hydride removal by the Lewis acid sites of the catalysts or by protonation of alkenylbenzenes formed by a dehydrogenation reaction.

TABLE 9

HYDROGENOLYSIS AND HYDROISOMERIZATION OF ISOBUTYLBENZENE AND *tert*-BUTYLBENZENE

Experiment:	31				32				33			34		
Hydrocarbon charged:	Isobutylbenzene				Isobutylbenzene				*t*-Butylbenzene			*t*-Butylbenzene		
Molybdena-alumina:[a]	A				C				A			C		
Temperature (°C):	490°				Not determined				435°			419°		
Cut:	1	2	3	4	1	2	3	4	1	2	3	1	2	3
Hydrogenolysis (%)	32	27	22	17	21	11	9	7	11	10	9	18	17	17
Benzene (mole %)	16	17	18	18	19	27	32	34	67	73	76	83	79	81
Toluene	47	45	43	44	28	27	26	26	3	2	2	2	2	2
Ethylbenzene	7	7	6	5	10	7	7	6	4	3	2	2	2	2
n-Propylbenzene	30	31	33	33	43	39	35	34	—	—	—	—	—	—
Isopropylbenzene	—	—	—	—	—	—	—	—	26	22	20	13	17	15
Isomerization (%)[b]	5.3	4.7	—	3.8	18.4	17.8	—	16.7	<1.5			<1.5		
n-Butylbenzene (%)[c]	3.8	4.1	—	3.8	7.9	9.3	—	12.8	—			0		
sec-Butylbenzene (%)[c]	9.7	10.2	—	13.8	39.2	52.1	—	56.5	—			<2		
	(11.3)	(11.8)	—	(15.7)	(56.0)	(57.0)	—	(63.0)	—			—		
t-Butylbenzene (%)[c]	0.8	0.6	—	0.5	0	0	—	0	—			—		
Isobutylbenzene (%)[c]	—	—	—	—	—	—	—	—	—			<5		
Composition of gases (mole %)														
Methane	51		49		58		51		41	33		28	26	
Ethane	13		10		10		8		5	2		0	0	
Propane	24		27		15		17		3	2		4	4	
n-Butane	2		2		11		16		3	3		4	3	
Isobutane	10		12		7		8		48	60		64	67	
Cleavage (%)														
Ring–α	15		17		21		29		63	70		75	77	
α–β[d]	28		31		16		17		12	10		8	8	
β–γ[e]	28		26		12		17							

[a,b,c] See footnotes Table VII.

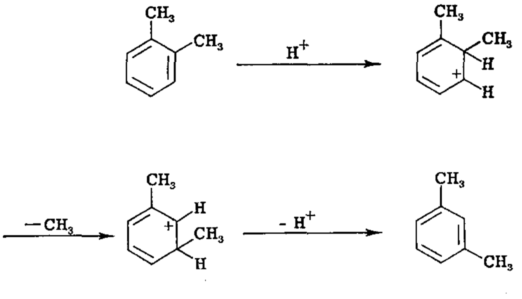
[d] For each methyl group in the case of *tert*-butylbenzene.

[e] For each methyl group in the case of isobutylbenzene.

Discussion of Results

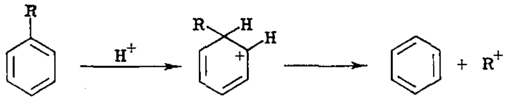
It is well known that the positional isomerization of xylenes (*12*), the skeletal isomerization of *sec*-butylbenzene (*14, 16*), and the cleavage of phenyl–alkyl group in alkylbenzenes (*17*) are acid-catalyzed reactions. The cleavage of isopropylbenzene to benzene and propylene is used to evaluate the activity of silica-alumina catalysts, which are known to have strong acidic properties. In the present study these reactions were used to evaluate the relative acidities of three molybdena-alumina catalysts which were prepared from aluminas having acidic sites of different strengths. The composition of the primary products from the reactions were the best indicators of the acidic character of the catalyst. It was therefore necessary to maintain the conversion at below 40% in order to avoid excessive secondary reactions. For that reason the temperature of the reactions was adjusted accordingly, while other parameters were maintained constant.

The positional isomerization of xylenes can be accomplished at less than 100° in the presence of strong acids such as aluminum chloride–hydrogen chloride or boron fluoride–hydrogen fluoride (*18, 19*). In the presence of silica-alumina catalyst a temperature of about 550° is required (*20*). The mechanism of the isomerization is best explained by the addition of proton at the ring carbon atom holding the alkyl group to form a sigma complex (*18, 19*). The methyl group being less firmly held can then move intramolecularly by a 1,2 shift



It was found that in the presence of molybdena-alumina catalysts the extent of isomerization increases with the increase in intrinsic acidity of the aluminas. The isomerization proceeds intramolecularly as in the case of aluminum chloride catalyzed isomerization. It was also found that molybdena-alumina catalyst is much more effective for isomerization than alumina *per se* (Expts. 4 and 5, Table 3). This indicates that either molybdena-alumina, being a mixed oxide, has stronger acidic sites than alumina, or that molybdena-alumina can dissociate hydrogen heterolytically to form protons required for the formation of the sigma complexes.

The hydrogenolysis of alkylbenzenes to benzene and to the corresponding alkanes depends on the nature of the alkyl groups and on the acidity of the molybdena-aluminas. The mechanism of the cleavage reaction is similar to the positional isomerization reaction. A sigma complex intermediate is produced by protonation of the aromatic ring and the complex is then decomposed to form benzene and an alkyl carbonium ion

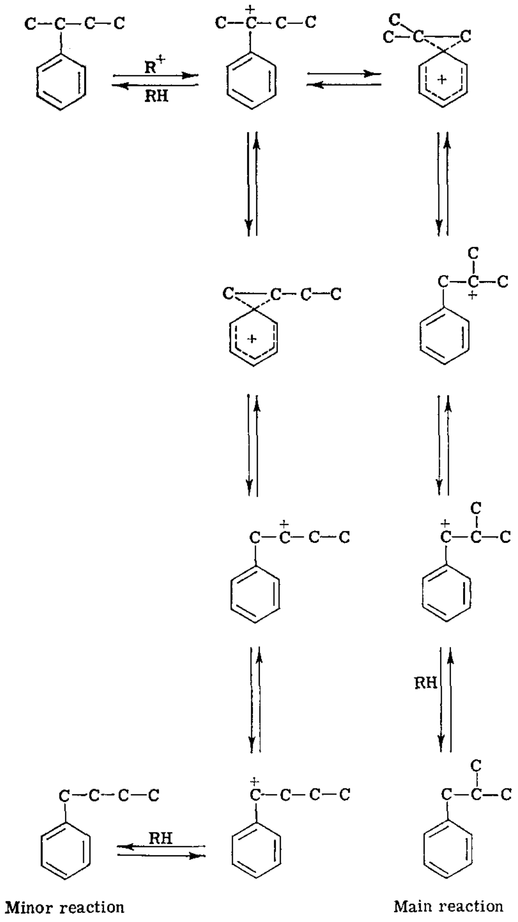


The alkyl carbonium ion can either lose a proton and be converted to an olefin which then reacts with hydrogen in the presence of the molybdena-alumina catalyst. The carbonium ion may also react directly with hydrogen to form the corresponding alkane and generate a proton as in the case of reactions catalyzed by aluminum chloride.

The ease of the cleavage of alkyl groups to form carbonium ions will depend on the stability of the ions. Since tertiary alkyl carbonium ions are more stable than secondary and the latter more than primary, it is not surprising that the cleavage of the *tert*-butylbenzene occurs more readily than that of *sec*-butylbenzene. This will also explain the reason for the lower temperatures required for the hydrogenolysis of *tert*-butylbenzene than for the other alkylbenzenes.

The greater resistance of *n*-alkylbenzenes to form an alkane and benzene (*n*-propylbenzene vs isopropylbenzene and *n*-butylbenzene vs *sec*-butylbenzene) is in accordance with the discussed mechanism.

Another reaction which is influenced by the acidity of molybdena-alumina catalyst is the skeletal isomerization of butylbenzenes. Reversible isomerization of butylbenzenes was encountered until now only in the presence of strong acid catalysts, such as aluminum chloride (*22*), and the mechanism of the reaction can be presented as follows:



RH = Butylbenzene

The experiments in the presence of molybdena-alumina catalysts show that the reversible isomerization of isobutylbenzene to *sec*-butylbenzene is the main reaction and it is influenced by the acidity of the aluminas. This reaction could be served as an indicator of the acidic sites of the molybdena-alumina catalysts.

The various aluminas have only a slight effect upon the hydrogenolysis of toluene, xylenes, ethylbenzene, and *n*-propylbenzene. This is not surprising because the cleavage of a primary alkyl group via a carbonium ion mechanism is an unfavorable reaction on account of the very low stability of their alkyl carbonium ions.

The somewhat larger extent of hydrogenolysis of *n*-propylbenzene in the presence of the more acidic Molybdena-Alumina C (Table 5) can be interpreted by the more ready isomerization of *n*-propylbenzene to isopropylbenzene in the presence of this catalyst, and the subsequent cleavage of the isopropylbenzene to propane and benzene. This interpretation is in agreement with the results obtained with isobutylbenzene in which the *sec*-butylbenzene produced in the reaction, and not the isobutylbenzene charged, was cleaved to benzene and *n*-butane.

The selectivity of the hydrogenolysis of α–β and β–γ bonds is not influenced by the acidity of the molybdena-alumina catalysts inasmuch as these reactions do not take place via a carbonium ion mechanism.

The molybdena-alumina catalysts have different catalytic sites which undergo deactivation at variable rates. The catalyst activity towards hydrogenolysis decreases sharply at the beginning of the experiment and more slowly later. The first sample collected after 25% of time elapsed actually corresponds to the product of the very first minutes because of the liquid remaining in the reactor. The isomerization properties of the catalyst seem to be only little affected with time.

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