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Alumina: Catalyst and Support

XXX. Dehydrogenation and Skeletal Isomerization of Butylbenzenes over Chromia-Alumina Catalysts*,†

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The dehydrogenation of butylbenzenes at about 490° was investigated over "nonacidic" chromia-alumina B and over "acidic" chromia-alumina A catalyst. Both catalysts produced the "normal" dehydrogenation products and also their skeletal isomers.

The skeletally isomerized butenylbenzenes over chromia-alumina B were *n*-butenylbenzenes from *sec*-butylbenzene, *sec*-butenylbenzenes from *n*-butylbenzene and isobutenylbenzenes from *tert*-butylbenzene. The rearrangement can best be explained by a radical mechanism involving phenyl and/or vinyl migration.

In the presence of the acidic chromia-alumina A catalyst, the product of rearrangement consisted also of isobutenylbenzenes from either *sec*- or *n*-butylbenzene and of *sec*-butenylbenzenes from isobutylbenzene. In the presence of the acidic catalyst *tert*-butylbenzene produced substantial amounts of benzene and isobutylene, while chromia-alumina B did not form products of dealkylation. The difference in the results between the two catalysts can be ascribed to the cationic reactions occurring on chromia-alumina A.

Small amounts of methylindans and naphthalene and tetrahydronaphthalene were also produced.

INTRODUCTION

In earlier papers from this laboratory (*1*, *2*) it was shown that the catalytic properties of aluminas depend on their methods of preparation. Alumina obtained by the hydrolysis of aluminum isopropoxide or by the precipitation of aluminum nitrate with ammonia, and calcined at 600°, contains intrinsic acidic sites which catalyze reactions, such as the skeletal isomerization of cyclohexene to methylcyclopentenes, which usually are associated with strong acids. On the other hand, when alumina is prepared by the precipitation of aluminum nitrate with sodium or potassium hydroxide, the stronger acidic sites are neutralized by the sodium and potassium ions, respectively. Actually, as little as 0.07 wt % of sodium in alumina will inhibit the skeletal isomerization of 3,3-dimethylbutene to 2,3-dimethylbutenes.

It was shown that chromia-alumina catalyst which contains alumina prepared from aluminum isopropoxide has relatively strong acidic sites and that this catalyst may cause extensive cationic skeletal isomerization of the dehydrogenated product (*3*, *4*). This catalyst has been termed chromia-alumina-A. However, chromia-alumina catalyst containing alumina prepared from potassium aluminate (chromia-alumina-B) has relatively weak acidic sites

* For paper XXIX see F. G. Schappell and H. Pines, *J. Org. Chem.* **31**, 1735 (1966). Paper 2 of the series Dehydrogenation of Aromatics. For paper 1, see ref. *17*.

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TABLE 1

DEHYDROGENATION OF *sec*-BUTYLBENZENE AND *n*-BUTYLBENZENE OVER CHROMIA-ALUMINA CATALYSTS

Alkylaromatic used:	*sec*-Butylbenzene						*n*-Butylbenzene					
Chromia-alumina:	A			B			A			B		
Temperature (°C):	492			480			482			481		
Hourly liquid space velocity:	0.57			0.74			0.58			0.80		
Cut number:	1	2	3	1	2	3	1	2	3	1	2	3
Length of cut (minutes):	11	11	10	9	11	11	10	10	11	7	9	8
Butylbenzene reacted (mole %):	77.5	59.9	54.0	47.0	40.2	36.0	59.4	52.1	48.2	41.8	24.7	18.6
	Mole % *sec*-butylbenzene converted to individual hydrocarbons						Mole % *n*-butylbenzene converted to individual hydrocarbons					
Methane	0.17	0.18	0.12	1.18	1.75	1.68	0.39	0.54	0.14	0.23	0.54	0.51
Ethane and ethylene	0.17	0.21	0.20	0.69	1.28	1.38	0.30	0.65	0.57	0.23	0.65	0.88
Propane and propylene	1.12	0.94	0.70	0.56	0.82	0.83	4.78	6.92	6.81	5.75	4.81	3.27
Isobutane and isobutylene	0.34	0.42	0.43	0.0	0.0	0.0	0.22	0.25	0.18	0.13	0.05	0.07
n-Butane	5.77	3.21	2.34	0.23	0.19	0.18	0.86	0.43	0.21	0.26	0.09	0.03
n-Butylenes	3.87	3.70	3.97	0.68	0.98	1.05	1.02	0.90	0.49	0.20	0.09	0.08
C_5 hydrocarbons	1.18	1.01	1.01	—	—	—	—	—	—	0.05	0.02	0.0
Benzene	3.94	4.57	4.44	0.07	0.05	0.03	0.22	0.29	0.21	0.42	0.22	0.14
Toluene	2.17	1.64	1.29	0.07	0.06	0.04	2.93	3.50	3.42	2.89	2.36	1.59
Ethylbenzene and styrene	4.27	3.77	3.62	1.55	1.32	1.22	4.00	3.68	3.46	2.76	2.65	2.48
Isopropylbenzene and olefin	2.61	2.41	2.06	1.67	1.42	1.42	0.25	0.11	0.07	0.0	0.0	0.0
n-Propylbenzene and olefins	2.48	1.78	1.32	0.82	0.58	0.40	1.69	1.26	1.16	3.02	1.05	0.59
n-Butylbenzene	6.31	5.41	5.65	2.03	1.08	0.99	40.56	47.92	51.81	58.23	75.28	81.43
n-Butenylbenzenes							11.24	10.81	13.16	16.24	7.56	6.24
sec-Butylbenzene	22.47	40.10	45.99	52.95	59.76	64.01						
sec-Butenylbenzenes	12.69	7.61	7.71	27.90	23.30	21.40	5.80	3.64	2.86	2.31	0.92	0.47
Isobutylbenzene and olefins	12.35	9.81	8.76	0	—	—	4.39	2.63	2.33	—	—	—
Methylindans and olefins	9.74	8.38	6.85	0.26	0.20	0.20	16.13	12.36	10.13	—	—	—
Tetrahydronaphthalene	0.51	0.38	0.27	0.17	0.12	0.08	1.53	2.77	2.37	1.85	1.91	0.68
Naphthalene	4.85	1.99	1.48	0.0	0.0	0.0	3.69	1.34	0.62	5.35	1.78	1.54
$>C_{10}$ hydrocarbons	2.99	2.48	1.79	9.17	7.09	5.09						
Total carbonaceous material		6.89			2.64			9.56			4.25	

	Distribution of Aromatic Compounds Produced											
Benzene	6.1	9.1	9.8	0.2	0.1	0.1	0.4	0.7	0.5	1.2	1.2	1.0
Toluene	3.3	3.3	2.8	0.2	0.2	0.1	5.7	8.3	8.6	8.3	12.8	11.6
Ethylbenzene and styrene	6.6	7.5	8.0	3.6	3.8	4.0	7.7	8.7	8.7	7.9	14.4	18.1
n-Propylbenzene and olefins[a]	3.8	3.5	2.9	1.9	1.7	1.3	3.3	3.0	2.9	8.7	5.7	4.3
Isopropylbenzene and olefins[a]	4.0	4.8	4.5	3.8	4.0	4.6	0.5	0.3	0.2			
n-Butylbenzene and olefins[a]	9.7	10.8	12.5	4.6	3.1	3.2	21.7[b]	25.5[b]	33.1[b]	46.6[b]	41.0[b]	45.5[b]
sec-Butenylbenzenes	19.6	15.2	17.1	63.8	66.2	69.3	11.2[c]	8.6[c]	7.2[c]	6.6[c]	5.0[c]	3.4[c]
Isobutylbenzene and olefins[a]	19.0	19.5	19.4	0.0	0.0	0.0	8.5	6.2	5.9	0.0	0.0	0.0
Methylindans and olefins[a]	15.0	16.7	15.1	0.6	0.6	0.6	31.1	29.2	25.5	0.0	0.0	0.0
Tetrahydronaphthalene	0.8	0.8	0.6	0.4	0.3	0.3	3.0	6.5	6.0	5.3	10.4	5.0
Naphthalene	7.5	4.0	3.3	0.0	0.0	0.0	7.1	3.2	1.5	5.4	9.7	11.2
$>C_{10}$ hydrocarbons	4.6	4.8	4.0	21.0	20.1	16.5						

[a] Olefins containing the same skeleton as the alkylbenzenes.
[b] *n*-Butenylbenzenes.
[c] *sec*-Butylbenzene and olefins.

and such cationic skeletal isomerization does not occur.

Considerable work has been done on the dehydrogenation of nonaromatic hydrocarbons over these catalysts. Although skeletal rearrangements via carbonium ion mechanisms are not observed over chromia-alumina-B catalyst, skeletal rearrangements via other mechanisms are possible (*5*). Surprisingly, however, very little work has been centered on the dehydrogenation of alkylbenzenes. Yet, with such a study may lie the means of detecting the ionic species associated with the hydrocarbon and catalytic site. Phenyl migrations have been observed during high-pressure thermal reactions of alkylbenzenes (*6, 7, 8*) during the decomposition of peroxides in alkylbenzenes (*9*), and finally during the hydrogenolysis studies over molybdena-alumina catalysts (*10*). In the first four cases, the phenyl migrations are strictly associated with the free radical mechanism. However, in the last case, the degree of phenyl migration appears to parallel the acidity of the catalyst.

The present study of the dehydrogenation of butylbenzenes over chromia-alumina catalysts was undertaken to observe phenyl migrations, if any, during the course of the reaction. From the results, deductions could possibly be made as to the type of mechanism participating during the rearrangement and dehydrogenation.

Procedure

a. Apparatus and technique. The apparatus and procedure were the same as described previously (*11, 12*). The amount of catalyst used was 20 ml (24.2 g) of chromia-alumina-B. All experiments were made at atmospheric pressure. The products were collected at Dry Ice–acetone temperature. In this manner, all the liquid and gaseous products were trapped together, with the exception of a small amount of methane; the latter was collected in a liquid nitrogen trap while the hydrogen was measured in a wet test meter. Collecting the product at this low temperature simplified the analytical procedure since practically all the gaseous products were dissolved in the liquid. A dehydrogenation experiment consisted of three cuts. The liquid samples were withdrawn from the Dry Ice-acetone trap into a vial cooled to Dry Ice temperature at the end of each cut and kept at this temperature until the analysis for the gases was complete.

b. Analytical procedure. The products were analyzed by gas chromatography using an F and M Model 300 Programmed Temperature Gas Chromatograph with the following columns: silica gel "950," 60–200 mesh, 8 ft—for C_1–C_2 compounds; 35% dimethylsulfolane on 100/120 mesh firebrick, 10 ft—for C_3–C_6 aliphatics; 15% diethylene glycol succinate on 60/80 mesh chromsorb W, 20 ft—for aromatic compounds.

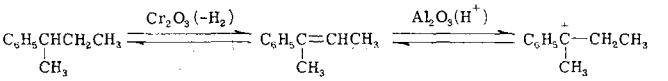
Chromatograms of each cut were taken using 30 μl samples for the gas analysis and 3 μl samples for nongaseous products. After such an analysis of the reaction products, each cut was selectively hydrogenated on a microhydrogenation apparatus at room temperature and atmospheric pressure using 5% palladium-on-charcoal catalyst, and analyzed by gas chromatography. Only the olefinic double bonds underwent hydrogenation while the aromatic ring remained intact.

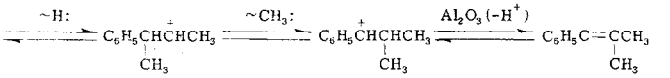
c. Reagents. Isobutylbenzene was obtained in over 99% purity by the purification of commercial isobutylbenzene by preparative gas chromatography. *sec*-Butylbenzene was prepared in over 99% purity by the alkylation of benzene with butylene in the presence of 96% sulfuric acid (*13*). *n*-Butylbenzene and *tert*-butylbenzene were pure grade commercial products of over 99% purity.

Discussion of Results

a. *sec*-Butylbenzene. The experimental results and reaction conditions are summarized in Table 1. With the acidic chromia-alumina-A extensive skeletal isomerization of *sec*-butylbenzene to isobutylbenzene and to its corresponding olefins took place. Part of the *sec*-butylbenzene was also converted to *n*-butylbenzene and to its olefins. The other main products were benzene and methylindans. However, over

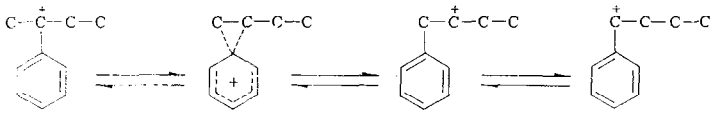
the nonacidic chromia-alumina-B the main reaction was dehydrogenation to *sec*-butenylbenzenes. Some *n*-butenylbenzenes were also produced; however, practically no benzene, isobutylbenzene, or methylindans were formed. The reaction products obtained from the experiment with chromia-alumina A can best be explained by a carbonium ion mechanism. Chromia catalyzes the dehydrogenation of the *sec*-butylbenzene to butenylbenzenes, while the intrinsic acidic sites of the alumina are responsible for the rearrangement of the cations formed, e.g.,



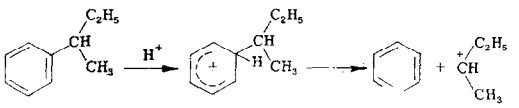


The reversible skeletal isomerization of *sec*- to isobutylbenzene was encountered until recently only in the presence of strong acid catalysts such as aluminum chloride (*14, 15*). Alumina in the absence of chromia, under comparable conditions, causes only little reaction.

The cleavage of butylbenzene to benzene and butenes is an acid-type reaction and depends on the type of butyl group present and the acidity of the catalyst. The necessary sigma complex intermediate is produced by protonation of the aromatic ring;



the complex is then decomposed to form benzene and *sec*-butyl carbonium ion.



The alkyl carbonium ion can lose a proton and be converted to an olefin, which then may react with the hydrogen produced from the dehydrogenation of the butylbenzene. The *sec*-butyl carbonium ion can also undergo skeletal isomerization to form *tert*-butyl carbonium ion.

The formation of methylindans can be explained by an acid-catalyzed cyclization of the butenylbenzene produced (*16*). Tetrahydronaphthalene and its dehydrogenation product, naphthalene, are products of skeletal isomerization of *sec*-butylbenzene and must have been produced by a noncationic mechanism, because large yields of these hydrocarbons were also formed from the dehydrogenation of *n*-butylbenzene over the nonacidic chromia-alumina-B (Table 1).

The presence of *n*-butylbenzene and of its corresponding olefins can be interpreted by a radical mechanism in the case of catalyst B and/or by a cationic mechanism in the case of catalyst A. The free radical mechanism may involve a vinyl migration of the intermediate 3-phenylbutene-1 (methyl–carbon insertion) and/or a phenyl migration. From the study of 2-phenylbutane-2-C^{14} it was found that both types of migrations participate to an equal degree (*17*).

The reversible cationic isomerization of *sec*-butylbenzene to *n*-butylbenzene can be presented as follows:

b. *n*-Butylbenzene. Over both catalysts A and B the formation of benzene and C_4 hydrocarbons is very low (Table 1). This is expected, even with the acidic chromia-alumina A, due to the instability of the primary butyl carbonium ion which would have to be produced. The isopropylbenzene formed over catalyst A probably arises as a cracking product of the *sec*-butylbenzene formed.

The isomerization products over catalyst A can be explained by carbonium ion inter-

TABLE 2

DEHYDROGENATION OF ISOBUTYLBENZENE AND *tert*-BUTYLBENZENE OVER CHROMIA-ALUMINA CATALYSTS

Alkylaromatic used:	Isobutylbenzene						*tert*-Butylbenzene				
Chromia-alumina:	A			B			A			B	
Temperature (°C):	482			486			488			481	
Hourly liquid space velocity:	0.56			0.82			0.56			0.77	
Cut number:	1	2	3	1	2	3	1	2	3	1	2
Length of cut (minutes):	10	9	10	10	10	11	9	7	9	11	11
Butylbenzene reacted (mole %):	74.5	66.1	60.9	48.4	42.2	37.5	79.44	68.90	61.55	10.30	5.44
	Mole % of isobutylbenzene converted to individual hydrocarbons						Mole % of *tert*-butylbenzene converted to individual hydrocarbons				
Methane	0.77	0.11	0.04	1.42	0.93	0.53	0.74	0.63	0.50	0.0	0.0
Ethane and ethylene	0.23	0.18	0.18	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Propane and propene	7.00	6.51	5.68	3.24	1.69	1.09	0.57	0.48	0.38	0.02	0.01
n-Butane and butylenes	3.90	1.91	1.01	0.0	0.0	0.0	5.80	4.35	2.30	<0.01	0.0
Isobutane	1.21	0.22	1.37	0.63	0.72	1.32	13.13	7.13	7.22	<0.01	<0.01
Isobutylene	0.60	0.69	0.53	—	—	—	18.09	19.40	17.55	<0.01	<0.01
Benzene	1.16	0.67	0.46	0.20	0.23	0.21	32.90	26.05	22.45	0.02	0.01
Toluene	4.54	3.49	3.00	2.65	2.75	2.69	1.51	1.39	1.15	0.02	0.01
Ethylbenzene and styrene	1.98	1.23	0.92	0.10	0.09	0.07	0.86	0.86	0.68	—	—
n-Propylbenzene and olefins	4.74	3.18	2.46	3.79	2.81	2.83	1.28	1.37	1.20	—	—
Isopropylbenzene and olefins	1.29	1.05	0.94	0.30	0.25	0.26	1.77	2.43	2.53	—	—
n-Butylbenzene and olefins	5.78	4.63	3.48	0.0	0.0	0.0	—	—	—	—	—
sec-Butylbenzene and olefins	20.17	21.40	19.86	0.0	0.0	0.0	—	—	—	—	—
Isobutylbenzene	25.50	33.86	39.08	51.61	57.77	62.47	1.60	2.71	2.98	3.12	1.09
Isobutenylbenzenes	9.11	12.07	13.19	31.84	29.84	25.22	1.18	2.10	2.71	7.10[a]	4.29[b]
tert-Butylbenzene	0.0	0.0	0.0	0.0	0.0	0.0	20.56	31.10	38.45	89.70	94.56
Methylindans and olefins	7.15	6.47	7.13	2.53	1.23	1.07	—	—	—	—	—
Tetrahydronaphthalene	2.26	1.52	1.19	—	—	—	—	—	—	—	—
Naphthalene	1.49	0.63	0.48	—	—	—	—	—	—	—	—
>C_{10}-hydrocarbons	1.12	0.18	0.0	—	—	—	—	—	—	—	—
Total carbonaceous material		9.87			2.88			8.2		0.52	

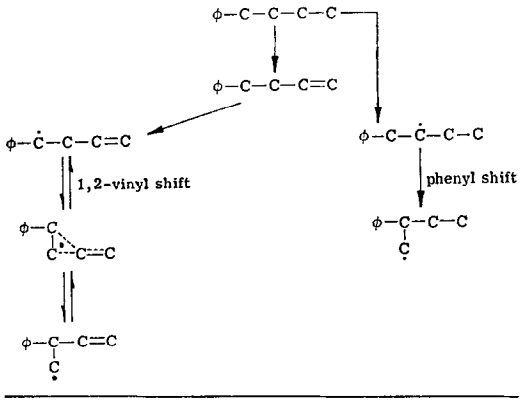
	Distribution of Aromatic Compounds Produced										
Benzene	1.91	1.2	0.9	0.5	0.6	0.7	80.0	70.6	66.6	0.2	0.2
Toluene	7.7	6.2	5.7	6.4	7.4	8.3	3.7	3.8	3.4	0.2	0.3
Ethylbenzene and styrene	3.3	2.2	1.7	0.2	0.2	0.2	2.1	2.1	2.0		
n-Propylbenzene and olefins[e]	7.8	5.6	4.6	9.2	7.6	8.7	3.1	3.7	3.6		
Isopropylbenzene and olefin	2.1	1.9	1.8	0.7	0.7	0.8	4.3	6.6	7.5		
n-Butylbenzene and olefins[e]	9.5	8.2	6.5	0.0	0.0	0.0					
sec-Butylbenzene and olefins[e]	33.2	37.9	37.4	0.0	0.0	0.0					
Isobutylbenzene							3.9	7.3	8.8	30.1	20.2
Isobutenylbenzenes	15.0	21.3	24.8	76.9	80.2	78.0	2.9	5.7	8.1	69.5[c]	79.3[d]
Methylindans	11.8	11.5	13.4	6.1	3.3	3.3					
Tetrahydronaphthalene	3.7	2.7	2.2								
Naphthalene	2.5	1.1	0.9								
$>C_{10}$-hydrocarbons	1.8	0.3	0.0								

[a] 1-Phenyl-2-methylpropene, 5.04%; 3-phenyl-2-methylpropene, 2.97%.
[b] 1-Phenyl-2-methylpropene, 2.97%; 3-phenyl-2-methylpropene, 1.32%.
[c] 1-Phenyl-2-methylpropene, 48.9%; 3-phenyl-2-methylpropene, 20.6%.
[d] 1-Phenyl-2-methylpropene 54.9%; 3-phenyl-2-methylpropene, 24.4%.
[e] Olefins containing the same skeleton as the alkylbenzenes.

mediates. The lack of isobutylbenzene in the reaction product when catalyst B is employed is reasonable if a free radical intermediate is assumed, since methyl migrations have not been reported to occur under free radical conditions (*18, 19*). However, the *sec*-butylbenzene formed is a reasonable product of a free radical reaction. A phenyl and/or 1,2-vinyl migration (*17*) are possible under free radical conditions (Chart I).

CHART I

FREE RADICAL MECHANISMS FOR THE ISOMERIZATION OF *n*-BUTYLBENZENE TO *sec*-BUTYLBENZENE.



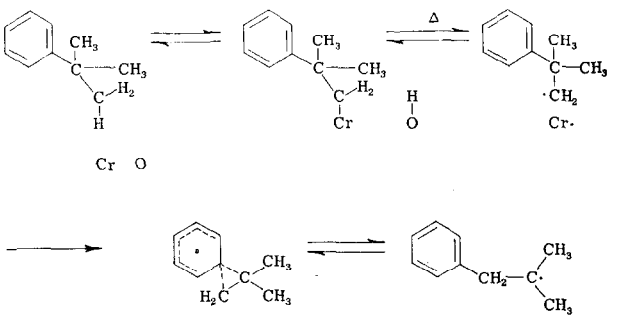
The presence of substantial amounts of methylindans in the products from the reaction over catalyst A and none from over catalyst B is a further confirmation that the indans were formed through a cationic mechanism, and most probably through the cycloalkylation of *n*-butenylbenzenes. The formation, however, of naphthalene and tetrahydronaphthalene is a non-cationic-type cyclization.

c. Isobutylbenzene. The experimental data are given in Table 2. As in the case of *n*- and *sec*-butylbenzene there is a great difference between the products obtained from isobutylbenzene over the two chromia-alumina catalysts. About 80% of the aromatics produced by the nonacidic chromia-alumina-B consisted of isobutenylbenzenes, the remainder being toluene and propylbenzene. Catalyst A, on the other hand, yielded products of skeletal rearrangement, namely *n*- and *sec*-butylbenzene, and the corresponding olefins.

d. *tert*-Butylbenzene. The experimental conditions and results are given in Table 2. Dealkylation was the main reaction when chromia-alumina-A was used. The products were benzene and C_4 hydrocarbons, which is not surprising since the stable *tert*-butyl carbonium ion would be formed as an intermediate. The *n*-butenes and *n*-butane present are the products of the skeletal isomerization of the *tert*-butyl carbonium ion. The yield of isobutyl- and isobutenylbenzene produced, based on the reacted *tert*-butylbenzene, was about 7% to 17%, depending on the length of the experiment.

There is a significant difference between the activity of chromia-alumina-A and B. In the presence of catalyst A, under similar experimental conditions, 69% to 79% of the *tert*-butylbenzene reacted, while in the presence of catalyst B only 5% to 11% reacted. Unlike catalyst A, catalyst B causes only skeletal isomerization of *tert*-butylbenzene. The formation of isobutylbenzene and of its olefins, which are the only rearranged products present, demonstrates that the reactions proceed via a free radical mechanism since acid-type reactions do not cause rearrangement of *tert*-butylbenzene.

Chromia is a vital part of the chromia-alumina catalyst since the nonacidic alumina B *per se* has no catalytic effect upon *tert*-butylbenzene. The interaction of chromia with *tert*-butylbenzene can be presented according to a mechanism proposed by Burwell for the reaction of hydrocarbons with deuterium (*20*). Chromium(II) atom and an adjacent oxygen atom form a pair of sites and the monoadsorbed *tert*-butylbenzene is attached to chromium. The adsorbed species can then decompose pyrolytically to form phenyl-*tert*-butyl free radical, which can rearrange according to the mechanism presented previously (*9*). The amount of carbonaceous material deposited on catalyst A was much greater than that on catalyst B. This is not too unexpected since on the acidic catalyst the butenylbenzene produced can undergo conversion to polycyclic hydrocarbons. The



latter seem to promote a free radical reaction, since the yield of isobutylbenzene and of its olefins increases with the duration of the experiment.

Conclusion

This study has shown that phenyl migrations do occur during the dehydrogenation of butylbenzenes over both chromia-alumina-A and -B catalysts. With the acidic chromia-alumina-A catalyst, the products formed through phenyl migrations are easily explained via cationic mechanisms. However, over chromia-alumina-B catalyst, the products formed through phenyl migration can best be explained by assuming free radical intermediates. This is shown most strikingly by the sole rearrangement of *tert*-butylbenzene to isobutylbenzene, a process known to be free radical in character.

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