

sodium hydroxide when necessary. After 28 hr. when the oxidant was consumed, the mixture was deionized by means of both cation and anion exchange resins in the manner described above and was concentrated to 100 ml. A 50-ml. aliquot was concentrated further and chromatographed on a carbon-Celite column. The first 300 ml. of aqueous effluent contained both D-glucose and D-arabinose in small amounts. The next 100 ml. contained a very small amount of D-glucose and some disaccharide. The remaining disaccharide was then removed from the column with 700 ml. of 5% ethanol. This fraction was concentrated to a sirup and triturated with absolute ethanol to give 0.260 g. (16.6% of the theoretical amount) of amorphous powder ($R_{\text{glucose}} 0.52$) which yielded only D-glucose and D-arabinose on hydrolysis. The phenylsazone, m.p. 196–200°, showed no change in melting point on admixture with 3-O- α -D-glucopyranosyl- α -D-arabinose obtained by the oxidation of maltose.

Oxidation of D-mannonic acid. D-Mannono- γ -lactone was prepared from D-mannose by oxidation with bromine,²² m.p. 151°. After hydrolysis of 1.78 g. (0.01 mole) of D-mannono- γ -lactone by boiling with 100 ml. of 0.1N sodium hydroxide solution for 10 min., the solution was adjusted to pH 5 with hydrochloric acid, and 100 ml. of 0.418N sodium hypochlorite (2 moles per mole of D-mannonic acid) at pH 5 were added. The solution was kept at 25° in the dark and the pH was maintained at 4.5–5.0 by the addition of sodium hydroxide solution. After about 30 hr. when the oxidant was consumed, the reaction mixture was deionized with ion exchange resins and found to contain D-arabinose in 48.7% of the theoretical amount when analyzed by the Willstätter-

Schudel method.²³ Crystalline β -D-arabinose was obtained in the yield of 0.53 g. (35.3% of the theoretical amount); $[\alpha]_D^{25} -175^\circ \rightarrow -105^\circ$ (c, 1.0 in water), m.p. 156–157°, undepressed on admixture with authentic D-arabinose.

Oxidation of D-galactonic acid. After hydrolysis of 1.78 g. (0.01 mole) of D-galactono- γ -lactone by boiling with 100 ml. of 0.1N sodium hydroxide solution for 10 min., the solution was adjusted to pH 5 with hydrochloric acid and mixed with 100 ml. of 0.401N sodium hypochlorite solution (2 moles per mole of D-galactonate) at pH 5. The oxidation was completed in about 24 hr. at the pH range of 4.0–5.0 in the dark at 25°. Determination of D-lyxose by Willstätter-Schudel titration of the deionized sirup indicated that there was present 50.1% of the theoretical amount. The yield of crystalline α -D-lyxose, $[\alpha]_D^{25} -14^\circ \rightarrow +5.3^\circ$ (c, 1.0 in water) obtained from the final solution was 0.61 g. (40.7% of the theoretical amount); m.p. 103–106°, undepressed on admixture with authentic D-lyxose.

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LAFAYETTE, IND.

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(23) F. J. Bates, *Natl. Bur. Standards (U.S.) Circ. C440*, 210 (1942).

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY,
DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Alumina: Catalyst and Support. VI.¹ Aromatization of 1,1-Dimethylcyclohexane, Methylcycloheptane, and Related Hydrocarbons over Platinum-Alumina Catalysts^{2,2a}

HERMAN PINES AND THOMAS W. GREENLEE³

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The aromatization of 1,1-dimethylcyclohexane (I), 4,4-dimethylcyclohexene (II), methylcycloheptane (III), and 5,5-dimethylcyclohexadiene (IV) over platinum-alumina catalysts has been investigated. The catalysts were prepared by impregnating aluminas of various intrinsic acidities with a solution of dinitrodiammine platinum, $\text{Pt}(\text{NH}_3)_2\text{NO}_2$.

The relative acidities of the aluminas and the method of platinizing them were found to have a profound effect on the composition of the aromatized product. The aromatization of I and II was accompanied by isomerization and the extent of isomerization could be related to the intrinsic acidity of the alumina. The product of the isomerization was mainly *o*-xylene admixed with *m*- and *p*-xylene and in the presence of a catalyst having high intrinsic acidity, alkylcyclopentanes were also produced.

The aromatization of methylcycloheptane formed ethylbenzene and xylenes; the distribution of the various aromatic compounds depended upon the acidity of the alumina used.

Recent publications of this laboratory have stated that aluminas have intrinsic acidic proper-

ties and that the relative acidities of the aluminas depend upon the method of their preparation.⁴ It was demonstrated that alumina prepared from aluminum isopropoxide is more acidic than that prepared from potassium aluminate. The relative acidities of the aluminas were determined by the ease with which they brought about the isomerization of various olefins.^{4,5} Recently it has been shown

(1) For paper V of this series see: H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **82**, 2401 (1960).

(2) Paper III of the series of Aromatization of Hydrocarbons. For paper II see: H. Pines and C. T. Chen, *J. Am. Chem. Soc.*, **82**, 3562 (1960).

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(3) Postdoctoral Fellow, 1958–1959.

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that the catalytic behavior of molybdena-alumina⁶ and chromia-alumina^{2,7} is greatly influenced by the relative intrinsic acidities of the aluminas used in the preparation of these catalysts.

The use of platinum-alumina catalysts for the conversion of hydrocarbons has found wide application in industry.⁸ The UOP Platforming catalyst has been reported to be composed of platinum, alumina and halogen.⁹

It has been reported that 1,1,3-trimethylcyclohexane yielded *m*-xylene when passed over a platinum-alumina catalyst prepared from a commercial alumina; however, in the presence of added hydrogen chloride (arising from an alkyl chloride) the aromatization was accompanied by isomerization resulting in the formation of trimethylbenzenes.¹⁰

The purpose of the present study was to determine the effect of aluminas of various intrinsic acidities upon the behavior of the respective platinum-alumina catalysts toward the aromatization of 1,1-dimethylcyclohexane (I), 4,4-dimethylcyclohexene (II), methylcycloheptane (III) and 5,5-dimethyl-1,3-cyclohexadiene (IV). It was of particular interest to determine whether there is a correlation between the dehydroisomerization reaction of I and II and the intrinsic acidities of the aluminas used in the preparation of the catalysts.

The aluminas used were of known composition and could be prepared reproducibly.⁴ The aluminas were platinized by impregnation with hot aqueous solutions of dinitrodiammine platinum. Care was exercised to avoid the introduction of halide ions as it is known that hydrogen halide increases the catalytic acidic properties of aluminas¹¹ and sodium chloride reduces such acidity.⁴ Two commercial platinum-alumina reforming catalysts were compared with our platinum-alumina.

EXPERIMENTAL

Preparation of catalysts (a) Alumina *ex* isopropoxide was prepared by hydrolysis of aluminum isopropoxide. The alumina was filtered and dried at 120° for 2 days. The alumina was screened to collect particles of 60–100 mesh, mixed with 4% of 60–100 mesh stearic acid and made into 1/8 × 1/8 inch pills. The pills were heated at 500° for 4 hr.

(5) W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 2488 (1960).

(6) H. Pines and G. Benoy, *J. Am. Chem. Soc.*, **82**, 2483 (1960).

(7) C. T. Chen, W. O. Haag, and H. Pines, *Chem. & Ind.*, 1379 (1959).

(8) For a review of the literature see: G. F. Ciapetta, R. M. Dobres and R. W. Baker, "Catalytic Reforming of Pure Hydrocarbons and Petroleum Naphthas," in *Catalysis*, ed. P. H. Emmett, Reinhold, New York, 1958, Vol. VI, pp. 492–692.

(9) G. R. Donaldson, L. F. Pasik, and V. Haensel, *Ind. Eng. Chem.*, **47**, 731 (1955).

(10) H. Pines, E. F. Jenkins, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **75**, 6226 (1953).

(11) H. Pines, R. C. Olberg and V. N. Ipatieff, *J. Am. Chem. Soc.*, **74**, 4872 (1952).

in a stream of air and finally calcined at 700° for 4 hr. in a stream of air.

(b) Alumina *ex* potassium aluminate was prepared according to the detailed description given previously.³ The precipitated alumina was washed five times by decantation and centrifugation.

(c) Platinum-alumina catalysts. The platinum complex dinitrodiammine platinum was prepared as described in the literature.¹² Calcined alumina pellets (10 cc., 7.1 g.) were treated with a hot aqueous solution containing dinitrodiammine platinum to give the desired platinum content. The minimum amount of water was used to dissolve the dinitrodiammine platinum. The pellets were dried under a heat lamp and heated to 500° in an air stream to decompose the complex.

A list of the various platinum-alumina catalysts which were prepared, and their designations are given in Table I.

TABLE I

PLATINUM-ALUMINA CATALYSTS			
Designation	Source of Aluminas	% Pt	Remarks ^a
A	Al(OC ₃ H ₇) ₃	1	—
B	KAlO ₂	1	Washed five times, 0.09% K (estimated) ⁴
C	KAlO ₂	1	Washed seven times, 0.06% K (estimated) ⁴
AA	Al(OC ₃ H ₇) ₃	1	Al ₂ O ₃ equilibrated with Pt(NH ₃ .NO ₂) ₂ solution 24 hr. at 100°
D	Al(OC ₃ H ₇) ₃	5	—
E	Al(OC ₃ H ₇) ₃	1	Al ₂ O ₃ equilibrated with water at 100° for 24 hr. before platinizing
Harshaw	Commercial	1	Commercial alumina platinized in this laboratory
X	Commercial	0.6	"Reforming Catalyst"
Y	Commercial	?	"Platinum reforming catalyst/gamma alumina/precipitated from acid medium with NH ₄ OH"

^a Details of catalyst preparation are found in the Experimental section.

Catalyst A was prepared by impregnating alumina *ex* aluminum isopropoxide with 1% platinum.

Catalyst B was prepared by impregnating alumina *ex* potassium aluminate with 1% platinum.

Catalyst C differs from *Catalyst B* only in that its alumina had been washed seven times instead of five.

Catalyst D was prepared from the same alumina as that used for *Catalyst A* and was impregnated with 5% platinum.

Catalyst E was prepared by keeping the calcined but unplatinized alumina used for *Catalyst A* in contact with water at 100° for 24 hr. The alumina was then dried and platinized with 1% platinum.

Catalyst AA was made by keeping calcined but unplatinized alumina in contact with platinizing solution (1% platinum) at 100° for 24 hr. The resulting material was decomposed as described above.

Harshaw catalyst was prepared by impregnating the commercial alumina with the platinum complex (1% platinum). The intrinsic acidity of this alumina was less than that of the alumina which was used for the preparation of *Catalyst B*. The evaluation of the acidic properties of the *Harshaw* alumina has been described previously.⁴

(12) L. A. Chugaev and S. S. Kiltinovich, *J. Chem. Soc.*, **109**, 1286 (1916); M. Vezes, *Bul. soc. chim.*, [3] **21**, 481 (1899).

Platinum-alumina reforming Catalysts X and Y were obtained from commercial sources. The details of their preparation were not revealed; they contained 0.6 to 1% platinum.

Synthesis of hydrocarbons. 1,1-Dimethylcyclohexane (I), 4,4-dimethylcyclohexene (II) and methylcycloheptane (III) were obtained by methods previously reported.¹

5,5-Dimethylcyclohexadiene (IV) was synthesized from II as previously described.^{1a}

Experimental procedure. Samples of the platinum-alumina catalysts (5 or 10 cc.) were placed in Pyrex reaction tubes (1 cm. diameter). The space above the catalyst was filled with glass beads to act as a preheater. The tubes so prepared were heated overnight in a vertical furnace at 350° in an air stream. Before each reaction the catalyst was purged with nitrogen and reduced at 350° for 30-60 min. in a stream of hydrogen.

The delivery pump and product recovery apparatus have been described previously.² Liquid products were condensed at 0° and noncondensable gasses were collected over saturated aqueous sodium chloride solution.

During the experiments listed in Table II consecutive 1- and 2- ml. samples were collected and analyzed separately. The averages of such determinations are reported. Usually the first sample collected would show an anomalously high degree of isomerization and was, therefore, ignored in computing the average. From three to eight samples were collected during experiments lasting from 45 min. to 3 hr.

To obtain samples from the experiments listed in Table IV, the first milliliter collected at each space velocity was discarded and the next retained for analysis. The delivery rate of the pump was then changed and the process repeated. These experiments were always performed in order of increasing space velocity, *i.e.*, of decreasing contact time.

Identification and estimation of products made use of a gas-liquid partition chromatographic column of dipropyl tetrachlorophthalate.³ The identities of products were established by comparing their retention times with those of authentic specimens. Infrared spectroscopy confirmed the presence of major constituents. Ultraviolet spectroscopy was used to detect and estimate the conjugated cyclic dienes produced.

The relative retention times for the various hydrocarbons using dipropyl tetrachlorophthalate at 102° were: Compound (relative time); unknown (3.9): 1,1-Dimethylcyclohexane (I) [8.0]; 4,4-Dimethylcyclohexene (II) [8.8]; Toluene and methylcycloheptane [11.0]; 5,5-Dimethyl-1,3-cyclohexadiene (IV) [12.5]; ethylbenzene (17.3); *m*- and *p*-Xylene (19.5); *o*-xylene (24.3).

Silicone column was used to determine the fractions containing toluene, methylcycloheptane and 1,1-dimethylcyclohexane. The relative retentions were: methylcycloheptane and 1,1-dimethylcyclohexane 20.5, and toluene 31.5.

DISCUSSION OF RESULTS

Experiments 1, 2 and 6 (Table II) show that in the aromatization of 1,1-dimethylcyclohexane (I), the yield of the *o*-xylene, product of skeletal isomerization, increases in the order of Harshaw < B < A. The same order of increasing acidity has been noted in cyclohexene isomerization over the corresponding aluminas.⁴ Catalyst A, which was prepared from the most acidic alumina, catalyzed the formation of isopropylcyclopentane and of some isomeric cyclopentanes, while progressively smaller amounts of these compounds were produced with the less acidic catalyst. It is interesting

to note that *m*- and *p*-xylene, amounting to 6-7% of the total aromatics, were produced even in the presence of the less acidic catalyst; in addition, about 1% of ethylbenzene was also present in the aromatic product.

Experiments 1, 3, and 4 illustrate vividly the effect of platinizing procedure on catalyst acidity. The three catalysts (A, AA, and E) contain the same amount of platinum and were prepared from alumina of the same batch. Catalyst A, prepared by rapid absorption of the platinizing solution, exhibits high acidity as shown by its high *o*-xylene and low toluene yields. Catalyst AA was prepared by keeping the alumina in prolonged contact with the platinizing solution. Maatman and Prater¹⁴ have found that when *alpha* alumina pellets (3 mm.) are placed in contact with chloroplatinic acid solution, equilibration of platinum content throughout the pellets requires some 23 hours. Experiment 3 shows Catalyst AA to be considerably less acidic than Catalyst A. The acidity decrease is probably due to an extensive neutralization of acid sites by preferential absorption of the platinum complex. However, the possibility remains that the acidity decrease is due to partial hydration of the aluminas. To distinguish between these alternatives a sample from the same batch of alumina was kept in contact with hot water for 24 hours and then was platinized by rapid absorption of the complex. Experiment 4 shows the catalyst so prepared to be less acidic than Catalyst A but more acidic than Catalyst AA. This might indicate that the diffusion of the dinitrodiammine platinum on a partially hydrated alumina is more rapid and that the platinum was able to penetrate to the center of the alumina pill and, hence, to neutralize more uniformly the stronger acid sites.

The present results indicate that platinum-alumina catalysts having acidic properties and capable of causing skeletal isomerization during aromatization of saturated hydrocarbons may be prepared even in the absence of halogen acids as previously indicated.¹⁰

The olefinic *gem*-dimethylcyclohexenes are known to be more susceptible to skeletal isomerization during the aromatization than the corresponding saturated hydrocarbons.¹⁰ This was also confirmed by the present study (Exp. 9 and 10). Even the weakly acidic Catalyst B caused extensive isomerization (Exp. 2 *vs.* 9). Catalyst C (Exp. 10) differed from Catalyst B only in having been more thoroughly washed and hence slightly more acidic.⁴ The data (Exp. 9 *vs.* 10) seem to bear out this observation so far as the formation of *o*-xylene is concerned. However, the difference is small and may not be significant.

In this connection it is important to indicate that

(13) H. Pines and R. H. Kozlowski, *J. Am. Chem. Soc.*, **78**, 3776 (1956).

(14) R. W. Maatman and C. D. Prater, *Ind. Eng. Chem.*, **49**, 253 (1957).

TABLE II
 AROMATIZATION OF 1,1-DIMETHYLCYCLOHEXANE(I) AND OF 4,4-DIMETHYLCYCLOHEXENE(II)

Exp.	Substrate	Cat.	% Conv. ^b	Reaction Products, %					
				C ₆ H ₈ CH ₃	C ₆ H ₈ C ₂ H ₅	<i>o</i> -Xylene	<i>m</i> - + <i>p</i> -Xylene ^c	IPCP ^d	Other ^e
1	I	A	65	18	1	60	7	6	9
2	I	B	49	54	1	32	6	Trace	7
3	I	AA	67	60	1	29	6	Trace	4
4	I	E	63	39	1	48	6	Trace	5
5	I	D	76	69	1	19	6	Trace	6
6	I	Harshaw	62	80	1	13	6	Trace	Traces
7	I	X	80	33	1	54	10	2	0
8	I	Y	73	18	1	70	4	3	4
9	II'	B	62	7	1	82	1	5	6
10	II'	C	67	5	1	79	5	6	6
11	<i>cis</i> -1,2-DMCH ^h	A	98	—	0.1	97.5	0.2	—	2 ⁱ

The experiments were made at 350° and at HLSV^a = 0.5.

^a Vol. liquid passed per hour per vol. catalyst used. ^b Moles reaction products per total moles in isomerate. ^c Infrared spectroscopy showed *meta/para* ratio = 2.2–3.5. ^d Isopropylcyclopentane. ^e Complex mixture of low-boiling compounds including 1,1,3-trimethylcyclopentane. ^f In these reactions I in the isomerate is calculated as starting material. ^g A mixture of some 16 low-boiling compounds. ^h Dimethylcyclohexane. ⁱ Various dimethylcyclohexanes.

cis-1,2-dimethylcyclohexane yielded 97.5% *o*-xylene when passed over the most acidic catalyst. The extent of skeletal isomerization was less than 3% (Exp. 11). Thus, it might be concluded that 1,2-dimethylcyclohexyl species once formed does not undergo skeletal rearrangement.

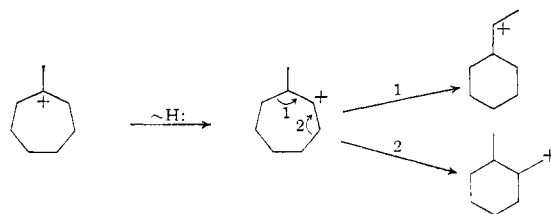
The sensitivity of *o*-xylene formation to catalyst acidity suggests that it arises chiefly *via* 1,2-methyl migration of the 2,2-dimethylcyclohexyl carbonium ion, followed by dehydrogenation. Formation of such an ion from II *via* protonation of a carbon-carbon double bond would be expected to occur more readily than its formation from I, a process requiring either hydride ion abstraction or previous dehydrogenation to an olefin. Experiments 9 and 10 show that indeed II is more readily isomerized.

It was shown that compound I forms predominantly toluene and compound II forms *o*-xylene when passed over Catalyst B (Table II). It could therefore be concluded that during aromatization the olefinic hydrocarbons II and IV which presumably precede the formation of the aromatic compounds are not desorbed from the dehydrogenation sites of the catalyst prior to demethanation. In the presence of the more acidic Catalyst A, however, the protonation of the adsorbed species II and IV can probably occur, leading to an isomerization reaction.

The increase in platinum concentration from 1% to 5% decreases the isomerization properties of the catalyst (Exp. 5 *vs.* 1). This can be explained by a more thorough neutralization of the stronger acid sites on the alumina used in the preparation of the catalyst. It is, however, not excluded that the relative rate of protonation of the adsorbed species decreases with the increase of platinum concentration.

The presence of *m*- and *p*-xylene and of small amounts of ethylbenzene is difficult to explain by means of a carbonium ion mechanism. The presence of the *m*-xylene could be explained by the thermal decomposition of 5,5-dimethylcyclohexadiene (IV)¹³; this, however, would not explain the formation of *p*-xylene or ethylbenzene.

The formation of *m*- and *p*-xylene and ethylbenzene could best be explained by a ring expansion of I or II to form a seven-membered ring intermediate. It was found that methylcycloheptane (IV) on aromatization forms toluene, xylenes, ethylbenzene and 1,1-dimethylcyclohexane (Table III). The yield of ethylbenzene increased and the yield of I decreased with the acidity of alumina. This increase in ethylbenzene formation can be explained by an ionic mechanism by which the formation of methylcycloheptyl carbonium ion can be assumed to be one of the intermediate steps. Ring contraction of this carbonium ion would lead to the formation of *sec*-cyclohexylethyl carbonium ion rather than to methylcyclohexylmethyl carbonium ion inasmuch as the formation of the former would involve the participation of secondary and tertiary carbonium ions without the formation of the less stable primary carbonium ions.







The aromatization of methylcycloheptane seems to proceed preferentially through an intermediate

TABLE III
 AROMATIZATION OF METHYLCYCLOHEPTANE (III) AND OF 5,5-DIMETHYLCYCLOHEXADIENE (IV). T = 350°

Exp.	Substrate	Cat.	HLSV ^a	% Conv. ^b	Products, %							
					C ₆ H ₅ CH ₃	C ₆ H ₅ C ₂ H ₅	<i>o</i> -Xylene	<i>m</i> - + <i>p</i> -Xylene	I	"?" ^c	IPCP ^d	Other ^e
12	IV	A	0.6	87 ^g	3	—	84	10 ^f	0	—	—	3
13	IV	A	2.0	86 ^g	7	—	82	5 ^f	0	6	—	1
14	IV	B	0.6	60 ^g	15	—	74	2 ^f	0	9	—	Trace
15	III	A	0.5	95	11	22	32	29	7	—	Trace	Trace
16	III	A	4.0	26	8	18	26	24	9	—	8	7
17	III	AA	0.5	89	21	11	24	29	15	—	Trace	—
18	III	B	0.5	36	32	8	18	27	15	—	—	—
19	III	D	0.5	97	29	6	22	27	16	—	—	—

^a See Table II, footnote ^a. ^b See Table II, footnote ^b. ^c Probably cycloheptane or cycloheptadiene. ^d Isopropylcyclopentane. ^e See Table II, footnote ^e. ^f Infrared examination showed *meta* >> *para*. ^g Only traces of IV found in isomerate. I and II calculated as starting material.

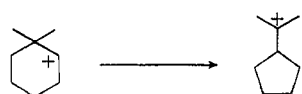
 TABLE IV
 EFFECT OF CONTACT TIME ON THE AROMATIZATION OF 1,1-DIMETHYLCYCLOHEXANE

Exp.	HLSV-1 ^a	Cat.	% Conv. ^b	Reaction Products								
							Toluene	<i>o</i> -Xylene	<i>m</i> - + <i>p</i> -Xylene	Ethylbenzene		Others ^f
20	2.0	A	65	—	—	—	8	80	5	1	1	5
21	1.0	A	41	—	—	Trace	5	82	6	1	2	5
22	0.5	A	18	—	—	1	2	78	8	1	1	10
23	0.25	A	3	—	—	11	5	64	12	—	Trace	9
24	2.0	B	33	—	7	—	52	34	6	1	—	—
25	1.0	B	15	1	12	Trace	38	46	3	1	—	—
26	0.5	B	9	1	20	6	29	40	4	—	—	—
27	0.25	B	4	1	48	7	21	23	—	—	—	—

^a See Table II, footnote ^a. ^b See Table II, footnote ^b. ^c Identified by ultraviolet spectroscopy, $\lambda_{\max} = 234\text{--}235\text{ m}\mu$ and gas chromatography. ^d 3,3- and/or 4,4-Dimethylcyclohexene. ^e Identified by $\lambda_{\max} = 257\text{ m}\mu$. ^f Table II, footnote ^e.

formation of 1,1-dimethylcyclohexyl species. This is indicated by the high yield of toluene and of compound I formed when a catalyst of lower acidity is used (Table III).

The formation of isopropylcyclopentane from compound I in the presence of the more acidic catalyst (Table III) can be explained by a ring contraction of 2,2-dimethylcyclohexyl carbonium ion.



The amount of *o*-xylene formed is higher in the case of Catalyst A than B, 32% vs. 18% (Exps. 15 and 18). This is not too surprising because in the presence of the more acidic catalyst 1,1-dimethylcyclohexane aromatizes preferentially to *o*-xylene rather than to toluene.

The effect of contact time upon the aromatization of I over Catalyst A (having an alumina of high intrinsic acidity) was studied (Table IV). The composition of the aromatic fraction was almost constant with the conversion changing from about 65% to 18% (Exps. 20–22). When the contact time was reduced still further, so as to obtain only 3% conversion, 11% of 5,5-dimethyl-1,3-

cyclohexadiene (IV) was present in the reaction product.

Compound IV when passed over Catalyst A yielded mainly xylenes. (Table III) and only 3–7% of toluene (Exps. 12 and 13). In the presence of the less acidic Catalyst B, the yield of toluene was 15% (Exp. 14). Since the reaction product contained also compounds I and II it can not be excluded that toluene might have been produced preferentially from compound I.

The effect of contact time upon the aromatization of 1,1-dimethylcyclohexane over the less acidic Catalyst B has been studied also (Table IV) and the composition of the product examined by a combination of gas chromatography and ultraviolet spectroscopy. It was observed that at the longest contact time, the main products of reaction were toluene, *o*-xylene, and smaller amounts of *gem*-dimethylcyclohexene. As the contact time decreases, the concentration of the *gem*-dimethylcyclohexene and that of *gem*-dimethylcyclohexadiene increases, while the amount of *o*-xylene decreases. The concentration of toluene decreases with decrease in contact time. It is interesting to note that according to the ultraviolet spectroscopy about 1% of product corresponding to conjugated methylenecyclohexene or to 3-methylene-4-methyl-

cyclohexene were also present; the first compound may be the precursor of toluene. The absorptivity value used for this calculation was reported previously.¹³

The experimental results summarized in Table IV suggest that the aromatization of 1,1-dimethylcyclohexane to *o*-xylene proceeds stepwise, via the formation of *gem*-dimethylcyclohexene and cyclohexadiene and that the latter then undergoes a dehydroisomerization reaction as indicated in Table IV.

SUMMARY

(1) The effect of aluminas in the platinum-alumina catalysts have been investigated in regard to the aromatization of 1,1-dimethylcyclohexane (I) and 4,4-dimethylcyclohexene (II).

(2) The aromatization of I and II can be used as a measuring stick for the determination of acidic properties of platinum-alumina catalysts; for catalysts with weak acidic properties, compound II is recommended.

(3) High activity dehydroisomerization catalysts

were prepared, even in the absence of halogen acids, when aluminas of high intrinsic acidity were used.

(4) Platinum seems to neutralize the acidic sites of aluminas.

(5) The dehydroisomerization reaction can be explained by a carbonium ion mechanism.

(6) The demethanation reaction to form toluene seems to proceed through a stepwise dehydrogenation to II and IV. The dehydrogenated species are not desorbed from the catalyst prior to demethanation. In the presence of catalyst having acidic properties the adsorbed species are probably protonated before they are aromatized.

(7) The aromatization of I and II seems to proceed in part through a ring expansion, followed by a ring contraction. This would explain the presence of *m*- and *p*-xylene and of ethylbenzene in the reaction product. The aromatization of methylcycloheptane gives data in accordance with this hypothesis.

EVANSTON, ILL.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY,
DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Alumina: Catalyst and Support. VII.¹ Aromatization of *n*-Heptane-1-C¹⁴ Over Chromia-Alumina Catalysts^{2,3}

HERMAN PINES AND CHAO-TUNG CHEN

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The aromatization of *n*-heptane-1-C¹⁴ over chromia alone and chromia-alumina catalysts having different intrinsic acidities was studied. The catalysts exhibited specific activity decrease patterns and the C¹⁴ distribution in the product toluene was found to depend on the nature of the catalysts and change with time. The results were interpreted by mechanisms involving five-, six-, and seven-membered ring intermediates of which the relative contributions depend on the nature of the catalyst and change of time. Cycloheptane was aromatized over chromia-alumina catalysts in good yields. Ethylcyclopentane was aromatized over chromia-alumina catalyst having high intrinsic acidity but not over chromia-alumina catalyst in which the alumina had low intrinsic acidity.

The mechanism of catalytic aromatization of alkanes has been the subject of considerable interest for the last twenty-five years.^{4a-c} Chromia-

alumina was found to be one of the best catalysts for this reaction. The mechanisms of Twigg,⁵ Herington and Rideal,⁶ Pitkethly and Steiner,⁷ and Wheatcroft⁸ would all predict 50% methyl labeled toluene from *n*-heptane-1-C¹⁴. Recently Mitchell⁹ has reported values of 27-29% in disagreement with the prediction and postulated three mechanisms to account for the low value of methyl label. These include an intermediate formation of a transannular bridge,⁶ rapid five- to six-membered

(1) For Paper VI of this series see: H. Pines and T. W. Greenlee, *J. Org. Chem.*, **26**, 1052 (1961).

(2) Paper IV of the series of aromatization of hydrocarbons. For Paper III see Ref. 1.

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(4) (a) For a review of the literature see: A. H. Steiner, "Catalytic Cyclization and Aromatization of Hydrocarbons," in *Catalysis*, Vol. IV, pp. 529-560, edited by P. H. Emmett, Reinhold, New York, 1956. (b) G. F. Ciapetta, R. M. Dobres, and R. W. Baker, "Catalytic Reforming of Pure Hydrocarbons and Petroleum Naphthas," in *Catalysis*, Vol. VI, pp. 492-692, edited by P. H. Emmett, Reinhold, New York, 1958. (c) C. Hansch, *Chem. Revs.*, **353** (1953).

(5) G. H. Twigg, *Trans. Far. Soc.*, **34**, 1006 (1939).

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(7) R. C. Pitkethly and A. H. Steiner, *Trans. Far. Soc.*, **35**, 979 (1939).

(8) R. W. Wheatcroft, dissertation, University of California, August 1, 1949.

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