suggests that bridge structures of the type $[H_2Al(NPh_2)_2AlH_4]^{=}$ may be reaction intermediates. The amide bridge has previously been postulated[7] in $(Me_2AlNMe_2)_2$

Reaction of Lithium Aluminum Hydride and Ethyl Bromide.—In an earlier study[8] the kinetics of the reactions of lithium aluminum hydride with *n*-butyl bromide and with *n*-amyl bromide in ether were investigated. In the present work the reaction of lithium aluminum hydride with ethyl bromide in ether was studied by following the rate of evolution of ethane. As in the cases of *n*-butyl and *n*-amyl bromides, the ethyl bromide-hydride system soon became heterogeneous. The evolution of gas became very slow after about one-fourth of the hydride had reacted. In order to test the effect upon this reaction of the catalysts for the hydride–hexyne reaction, some catalyst which had been prepared from pyridine N-oxide was added to the hydride-ethyl bromide system. No change in the rate or nature of the reaction was observed.

Experimental

1-Hexyne was prepared from sodium acetylide and freshly distilled *n*-butyl bromide in liquid ammonia. It was distilled twice and sealed in ampoules under dry nitrogen, b.p. 71°. **Ethyl bromide** (Dow Chemical Company) was dried over anhydrous magnesium sulfate and distilled. **Aniline**, *t*-**butylamine**, **diethylamine**, **N-methylaniline**, **piperidine** and **pyridine** were all dried over potassium hydroxide pellets and distilled. Samples of **γ-picoline** N-oxide, m.p. 180.5–181.2°, and **pyridine N-oxide**, which had been distilled at 80° and 1 mm. were obtained from Theodore Cohen, Department of Chemistry, University of Pittsburgh. The **diphenylamine** was Fisher Certified Reagent, m.p. 53.3–53.9°. The **triethylamine** was treated with lithium aluminum hydride in ether, distilled and sealed in ampoules under dry nitrogen.

The ether solution of lithium aluminum hydride was prepared by adding the pulverized solid hydride (Metal Hydrides, Inc.) to anhydrous ethyl ether and refluxing for eight hours. The resulting solution was filtered through a sintered glass filter under nitrogen pressure and standardized by measuring the hydrogen evolved upon the addition of excess alcohol. Also, a weighed sample of the solution was placed on a vacuum line and the ether was completely removed and measured. The weight of solids agreed with standardization results when the empirical formula was assumed to be $LiAlH_4$.

The apparatus and method for the rate measurements were essentially those which were used previously[9] for kinetic studies of some Grignard reactions. The reactions were followed by measuring the volume of a gaseous product. The solvent vapor was removed from the gaseous product and returned to the reacting mixture by a cold finger type Dry Ice–acetone condenser. The reacting mixture was maintained in a refluxing condition, and the reaction temperature was controlled by regulating the pressure. Duplicate runs gave results (volume *vs.* time) which agreed within 1% under the most favorable conditions. For rapid reactions, such as those with a half-life of less than ten minutes, the precision was not that good.[3]

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[7] N. Davidson and H. C. Brown, THIS JOURNAL, **64**, 316 (1942).

[8] D. J. Walter, John H. Wotiz and C. A. Hollingsworth, *ibid.*, **78**, 1311 (1956).

[9] John H. Wotiz, C. A. Hollingsworth and Raymond E. Dessy, *J. Org. Chem.*, **19**, 1545 (1955).

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

Alumina: Catalyst and Support. IV.[1] Aromatization and Dehydroisomerization of 1,1-Dimethylcyclohexane, 4,4-Dimethylcyclohexene and of Methylcycloheptane over Chromia-Alumina Catalysts[2]

BY HERMAN PINES AND CHAO-TUNG CHEN

RECEIVED DECEMBER 28, 1959

The aromatization of 1,1-dimethylcyclohexane (I), 4,4-dimethylcyclohexene (II) and of methylcycloheptane over chromia alone and chromia–alumina catalysts having different intrinsic acidities was studied. It was found that chromia alone is a dual function catalyst, it has both dehydrogenation and isomerization properties. In the presence of this catalyst compounds I and II on aromatization yield toluene and xylenes. Chromia–alumina catalyst prepared from alumina having intrinsic acidity aromatized compounds I and II to a mixture of hydrocarbons consisting of toluene, xylenes and ethylbenzene. When a catalyst prepared from alumina of low intrinsic acidity was used, only toluene was produced. The effect of the various catalysts upon the aromatization of methylcycloheptane has been studied. The dehydroisomerization reaction is interpreted as deriving from the acidic character of the catalyst.

Introduction

The use of chromia–alumina as a catalyst for the dehydrogenation and aromatization of hydrocarbons has been studied extensively. In none of the published papers, however, is it suggested that alumina may exert an effect upon the catalytic properties of the mixed catalyst and that the products resulting from such aromatization reaction may depend to a great extent upon the type of alumina.

Recent studies in our Laboratory have revealed that alumina has intrinsic acidic properties and that the strength of the acid sites depends upon the method used for the preparation of the aluminas.[4] It also has been shown recently that the change in the C^{14} distribution pattern during the aromatization reaction of *n*-heptane-1-C^{14} and *n*-octane-1-C^{14} depends upon the type of alumina used in the preparation of the chromia–alumina catalysts.[5] It was also observed that the differing types of alumina influence the catalytic behavior of molybdena–alumina catalysts.[6]

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[1] For paper III of this series see W. O. Haag and H. Pines, THIS JOURNAL, **82**, 2488 (1960). Paper II of the series "Aromatization of Hydrocarbons." For paper I see ref. 5.

[2] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said Fund.

[3] (a) For a review of the literature see: A. H. Steiner, in "Catalysis," Vol. IV, edited by P. H. Emmett, Reinhold Publishing Corporation, New York, N. Y., 1956, pp. 529–560. (b) G. F. Ciapetta, R. M. Dobres and R. W. Baker, *ibid.*, pp. 492–692.

[4] H. Pines and W. O. Haag, THIS JOURNAL, **82**, 2471 (1960).

[5] C. T. Chen, W. O. Haag and H. Pines, *Chem. & Ind.* (*London*), 1379 (1959).

[6] H. Pines and G. Benoy, THIS JOURNAL, **82**, 2483 (1960).

The present study was undertaken in order to determine the effect of different chromia–alumina catalysts upon the aromatization of geminal dimethylcyclohexane (I), 4,4-dimethylcyclohexene (II) and of methylcycloheptane (IV). Compounds I and II were selected since it has been observed[7] that in the case of platinum–alumina catalyst, depending on the intrinsic acidity of the alumina used, the product of aromatization may consist of either toluene or of a mixture of toluene and xylenes.

Experimental

1. **Catalysts. Catalyst 1. Chromia.**—The chromia alone was prepared according to the method of Burwell and Taylor.[8] A solution of 60 g. of chromic nitrate monohydrate and 60 g. of urea in 4 l. of water was heated to boiling and simmered gently until precipitation was completed (two or three hours). The precipitate was washed, filtered and dried at 120° for 48 hr. It then was heated slowly and maintained at 300° in a stream of hydrogen for one hour and then heated to 500° in nitrogen.

Catalyst 2. Chromia–Alumina A.—The alumina was prepared by hydrolysis of aluminum isopropoxide, filtered, dried at 120° for two days and then calcined at 645–680° for four hours in a stream of nitrogen. The alumina was screened to collect particles of 60–100 mesh, mixed with 4% of 60–100 mesh stearic acid and made into $^1/_8 \times {}^1/_{16}$ inch pills. The pills were heated at 500° for four hours in a stream of air.

To 6.3 g. of chromic acid in 26 ml. of water was added 30 g. of the alumina pills. The wet catalyst now was dried at 120° for one hour and then the catalyst was placed in a glass tube through which a stream of purified air was passed. The catalyst next was heated at 500° for 30 minutes.

Catalyst 3. Chromia–Alumina B.—The alumina was prepared from potassium aluminate, according to the method of Selwood.[9] Aluminum shavings, 54 g., which were prepared from a 99.99% pure aluminum bar,[10] were dissolved in 336 g. of potassium hydroxide and 3 l. of water. The filtrate was acidified with 180 ml. of iron-free 70% nitric acid until precipitate only slowly redissolved. Precipitation was completed by bubbling carbon dioxide through the solution at room temperature until *p*H 8–10 (Rainbow indicator) was attained. The precipitate was washed by decantation ten times until washings were neutral to litmus. The material was dried at 110° for 16 hr. and then calcined at 350–360° for 18 hr. This was made into pills and impregnated with chromic acid as described for Catalyst 2.

Catalyst 4. Impregnated Chromia–Alumina.—Catalyst 2, 33 g., was added to a solution of 0.76 g. of potassium nitrate and 0.60 g. cerium nitrate in 25 ml. of water, according to the method of Archibald and Greensfelder.[11] The catalyst was dried at 120° for one hour and then calcined at 500° for 30 minutes in a stream of air.

2. **Hydrocarbons. 4,4-Dimethylcyclohexene (II)** was prepared according to the method described previously.[12]

1,1-Dimethylcyclohexane (I), b.p. 117–119°, n^{20}_{D} 1.4290, was formed in over 80% yield when II, 114 g., was hydrogenated in *n*-pentane, 100 cc., over nickel–Kieselguhr catalyst, 10 g., at hydrogen pressure of 125 atm. and at 110–125°.

Methylcycloheptane (IV).—(a) **Methylcycloheptanol** was prepared by the conventional Grignard reaction of methyl iodide with cycloheptanone in 80% yield. It distilled at 88° at 23 mm., n^{22}_{D} 1.4570–1.4571 (lit.,[13] b.p. 183–185°, n^{22}_{D} 1.4677).

b. **Methylcycloheptene** was obtained by heating the alcohol with a small amount of iodine. The yield was 80% and the crude olefin distilled at 135–139°, n^{22}_{D} 1.4575 (lit.,[13] b.p. 137.5–138.5°, $n^{19.5}_{\mathrm{D}}$ 1.4581).

c. **Methylcycloheptane (IV).**—The olefin was dissolved in equal volume of *n*-pentane and hydrogenated at 120° under 100 atm. of hydrogen and in the presence of 10% by weight of nickel–Kieselguhr catalyst. The methylcycloheptane, yield over 77%, distilled at 136–138°, n^{23}_{D} 1.4409 (lit.,[14] b.p. 133–135°, n_{D} 1.4410).

The methylcycloheptane on redistillation gave a pure compound, according to gas chromatographic analysis.

3. **Apparatus and Procedure.**—The apparatus consisted of a Pyrex tube having a zone of 2.0 cm. outside diameter heated by a thermostatically controlled furnace. The lower end of the reaction tube was attached to a liquid receiver, which in turn was attached through a Dry Ice–acetone cooled trap to a gas measuring bottle containing saturated sodium chloride solution.

Catalyst was placed in the reaction zone and heated to 500°. The tube was flushed with nitrogen, and a stream of hydrogen was passed for one hour. Hydrocarbons were introduced by means of a motor driven syringe. Liquid product was withdrawn from time to time from the receiver and analyzed. After each experiment the catalyst was held at 500° overnight while air was passed to burn off carbonaceous materials which were deposited on the catalyst.

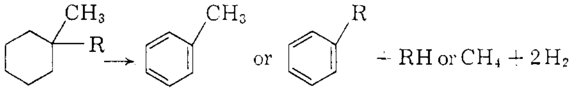
In the experiments using chromia alone, the furnace with the reaction tube was heated to 300° in a stream of hydrogen and held at 300° for one hour. Nitrogen then was passed while heating to 450°. Finally, hydrogen was passed while the catalyst was heated to 500° and held at this temperature for one hour before hydrocarbons were introduced.

The amount of catalyst used was as follows: catalyst 1, 20 ml. (24.2 g.); catalyst 2, 20 ml. (17.0 g.); catalyst 3, 14 ml. (10.3 g.); catalyst 4, 20 ml. (17.3 g.).

The product obtained from reaction was analyzed by infrared spectroscopy and by gas chromatography using a 35 ft. copper column packed with 85 g. of 20–40 mesh fire-brick impregnated with 7% by weight of dipropyl tetrachlorophthalate (b.p. 208–214° at 7 mm., n^{31}_{D} 1.5342; lit.,[15] b.p. 170–175° at 1 mm., n^{25}_{D} 1.5348).

Discussion of Results

1. **1,1-Dimethylcyclohexane (I) and 4,4-Dimethylcyclohexene (II). a. Chromia Alone.**—The aromatization of geminal dialkylcyclohexanes over chromia–alumina promoted by potassium and cerium (Catalyst 4) was reported previously.[16,17] In each case the aromatization was accompanied by a removal of alkyl group and the formation of alkylbenzene.



A similar reaction occurred when 1,1,3-trimethyl-*x*-cyclohexene was aromatized; *m*-xylene and methane were formed. The aromatization reaction was not accompanied by isomerization.

It was presently found that skeletal isomerization can accompany the aromatization of geminal dimethylcyclohexane and dimethylcyclohexene depending upon the intrinsic acidity of the alumina used as support. It was also observed that chromia as such has dual function properties and acts as a dehydrogenation and as an isomerization catalyst (Table I).

Thus, over chromia alone 1,1-dimethylcyclohexane underwent not only the expected loss of methane but also isomerization giving xylenes, *o*-

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[7] H. Pines and T. W. Greenlee, unpublished work.

[8] R. L. Burwell, Jr., and H. S. Taylor, THIS JOURNAL, **58**, 697 (1936).

[9] P. W. Selwood, "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951, p. 41.

[10] Obtained from the Aluminum Company of America.

[11] R. C. Archibald and B. S. Greensfelder, *Ind. Eng. Chem.*, **37**, 356 (1945).

[12] H. Pines, F. J. Pavlik and V. N. Ipatieff, THIS JOURNAL, **73**, 5738 (1951).

[13] O. Wallach, *Ann.*, **345**, 140 (1906).

[14] L. R. Ruzicka and C. F. Seidel, *Helv. Chim. Acta*, **19**, 424 (1936).

[15] B. W. Nordlander and W. E. Cass, THIS JOURNAL, **69**, 2679 (1947).

[16] H. Pines, E. F. Jenkins and V. N. Ipatieff, *ibid.*, **75**, 3719 (1953).

[17] H. Pines and J. Marechal, *ibid.*, **77**, 2819 (1955).

TABLE I

AROMATIZATION OF 1,1-DIMETHYLCYCLOHEXANE (I) AND OF 4,4-DIMETHYLCYCLOHEXENE (II) AT 500° AND H.L.S.V.,[a] 0.9

Exp. no.	Catalyst	Starting material[b]	Fraction[c]	Conversion, %	Product formed: Aromatics wt. %	Product formed: Non-aromatics *d*	Product formed: Non-aromatics I	Composition of aromatics, wt. %: Toluene	*o*-Xylene	*m* + *p* Xylene	Ethylbenzene
1	1	1,1-DCH	1	99	100	..	..	95	4	1	..
		(I)	3	75	100	..	..	87	10	3	..
			5	29	100	..	..	62	34	4	..
2	1	4,4-DCH	1	100	99	1		73	24	3	..
		(II)	3	81	83	6	11	38	56	6	..
			5	87	74	14	12	36	59	5	..
3	2	1,1-DCH	1	63	100			41	46	10	2
		(I)	3	38	100			32	55	13	..
			5	33	100			36	52	12	..
4	2	4,4-DCH	1	~99	94	6		19	41	35	5
		(II)	3	~99	76	24		21	38	36[f]	5
			5	~99	62	38		21	39	36	3
5	2	1,2-DCH	1	58	100			~1	90	10	
		(III)	3	33	100			~1	88	12[g]	
			5	20	100			~1	99	~1	
6	2	*o*-Xylene	1	1	100			1	99	0	
7	3	1,1-DCH	1	96	100			>99			
		(II)	3	94	100			>99			
8	3	4,4-DCH	1	98	100			>98		<2	
		(I1)									
9	4	1.1-DCH	1	78	100			>99			
		(1)	3	70	100			>99			
			5	68	100			>99			
10	4	4,4-DCH	1	100	99		1	99		1	
		(11)	3	100	74		26	>98		<2	
			5	100	65		35	>98		<2	

[a] Hourly liquid space velocity or volume of liquid passed per volume of catalyst per hour. [b] 1,1-DCH (I)–1,1-dimethylcyclohexane; 4,4-DCH (II)–4,4-dimethylcyclohexene; 1,2-DCH (III)–a mixture of *cis*- and *trans*-1,2-dimethylcyclohexane. [c] A total of 10 ml. was passed in each experiment and five 2 ml. fractions were taken. [d] Assumed to be alkylcyclopentanes. [e] Ratio of *m*-xylene/*p*-xylene = 1.7. [f] Ratio of *m*-xylene/*p*-xylene = 1.9. [g] Ratio of *m*-xylene/*p*-xylene = 2.0.

xylene being the chief isomerization product. The catalytic activity related to toluene formation decreased rapidly with time, leading to formation of relatively higher amounts of xylenes. These facts indicate that chromia catalyst may contain two kinds of active sites, one being active mainly for methane splitting and the other for isomerization, which is associated with the acidity of the catalyst. The former appears to be poisoned more rapidly than the latter.

The isomerization may be interpreted in terms of carbonium ion mechanisms involving the acidic sites of chromia.[18] The saturated hydrocarbon could form 2,2-dimethylcyclohexyl carbonium ion either by partial dehydrogenation to the corresponding geminal dimethylcyclohexene followed by protonation, or by a direct hydride removal from the saturated compound. The carbonium ion thus formed would give, through a methide migration, 1,2-dimethylcyclohexyl carbonium ion, which then would aromatize rapidly to *o*-xylene.

The formation of small amounts of *m*- and *p*-xylene require stronger acid sites than are required for *o*-xylene inasmuch as this reaction would probably involve the formation of primary carbonium ions.[6]

4,4-Dimethylcyclohexene (II) over chromia alone (Exp. 2) gave more isomerization than did the saturated analog. This is not surprising since compound II, owing to the presence of a double bond can readily undergo protonation. The aromatization reaction was accompanied by disproportionation resulting in the formation of 1,1-dimethylcyclohexane. Some of the non-aromatic hydrocarbons obtained in this reaction were not identified but were presumed to be composed of alkylcyclopentanes.

The acidic character of chromia could probably be ascribed to a thermal dissociation of the oxide to form a Lewis acid site and a Lewis base site, similar to the type of dissociation which was suggested for alumina.[19] The Lewis acid site is probably associated with the metal and the base with the oxygen of the chromium oxide.

The loss of catalytic activity of the chromia with time manifests itself more pronouncedly in the case of compound I than with compound II. The demethanation reaction probably is preceded by the formation of 5,5-dimethylcyclohexadiene,[20] the latter either through a Diels–Alder or an ionic polymerization would form higher boiling com-

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(18) The thermal isomerization of the possible 5,5-dimethylcyclohexadiene which could be formed as an intermediate would produce only *m*-xylene. See H. Pines and R. H. Kozlowski, THIS JOURNAL, 78, 3776 (1956).

(19) S. G. Hindin and S. W. Weller, *J. Phys. Chem.*, 60, 1501 (1956).

(20) H. Pines and T. Greenlee have found that at short contact time in the presence of platinum–alumina 5,5-dimethylcyclohexadiene is the main product of dehydrogenation of compound I.

TABLE II

AROMATIZATION OF METHYLCYCLOHEPTANE (IV) AT 500° AND H.L.S.V., 0.65

Exp. no.	Cata- lyst	Frac- tion[a]	Composition of product, wt. %[b]					
			IV + others[e]	Toluene[c]	*o*-Xylene	*m* + *p*[c] Xylene	Ethylbenzene	Ratio *m*-/*p*-xylene
11	1	1	4.2	14	32.9(40)	45.5(56)	3.4(4)	1.0
		3	23.0		29.2(38)	44.0(57)	3.8(5)	
		5	77.6	1.8	7.3(35)	10.5(51)	2.8(13)	1.2
12	2	1	8.9	1.2	39.4(44)	38.7(43)	11.8(13)	1.2
		2	23.9		32.0(42)	32.2(42)	11.9(16)	
		3	31.1		28.1(41)	29.3(43)	11.5(17)	
		5	46.6		21.4(40)	22.5(42)	9.5(18)	
		7	52.1	1.1	18.6(40)	19.8(42)	8.4(18)	1.4
13	3[d]	1	29.2	5.4	25.3(39)	34.7(53)	5.2(9.0)	1.5
		2	41.6		20.0(34)	32.6(56)	5.8(10)	
		3	43.5		19.1(34)	31.7(56)	5.7(10)	
		5	48.9		17.5(34)	28.4(56)	5.2(10)	
		7	52.8		16.9(35)	25.8(55)	4.5(10)	
		9	60.6	5.4	11.9(34)	19.6(56)	3.5(10)	2.3

[a] Fractions collected at 2, 2, 2, 8, 2, 8, 2, 8, 2 ml. of feeding. [b] Determined by vapor phase chromatography using a dipropyl tetrachlorophthalate column. Values in parentheses are calculated percentages on the basis of total C_8-aromatics. [c] Determined by infrared spectroscopy. [d] 15 ml., 11.0 g. [e] The product consisted of about 90–95% of compound IV and of lower boiling hydrocarbons which were not identified.

pounds which could be adsorbed on the catalyst surface. In the case however of the 4,4-dimethylcyclohexene, due to the unsaturation the methyl migration is relatively rapid and takes preference over the dehydrogenation of I to the geminal dimethylcyclohexadiene, thus avoiding the condensation reaction.

The deactivation of the catalyst might also be associated with isomerization of a six-carbon ring to a five-carbon ring. The alkylcyclopentadienes which would result from such reaction then would undergo polymerization and thus deposit on the catalyst.

b. Chromia-Alumina Catalysts.—The catalytic properties of chromia-alumina depend upon the alumina used in their preparation. Experiments 3 and 4 show that deep-seated skeletal isomerization accompanied the aromatization of 1,1-dimethylcyclohexane and of 4,4-dimethylcyclohexene. The catalyst used in these experiments contained alumina having high intrinsic catalytic acidity. The aromatic hydrocarbons were composed mainly of xylenes and of smaller amounts of ethylbenzene. In the case of 4,4-dimethylcyclohexene the aromatic fraction contained large amounts of *m*- and *p*-xylene while the saturated fraction contained a substantial amount of hydrocarbons corresponding to alkylcyclopentanes.

Experiment 4 shows that the rate of toluene formation decreases and that of skeletal isomerization, including alkylcyclopentane formation, increases with time. This is in agreement with the experiment made with chromia alone.

The formation of the various hydrocarbons is associated with strong acids and could be explained by a carbonium ion mechanism similar to the one described previously.[6,21]

o-Xylene did not undergo isomerization (Exp. 6) nor did 1,2-dimethylcyclohexane undergo dehydroisomerization (Exp. 5) under conditions used for experiments 3 and 4. It may then be concluded that *m*- and *p*-xylene were not derived directly from *o*-xylene but could have been derived from 1,2-dimethylcyclohexane or from an adsorbed species of the latter.

The formation of *m*- and *p*-xylene and that of ethylbenzene could be explained by repeated ring contraction and expansion, as described previously.[6,20] However, it is not excluded that ring expansion leading to a seven-membered ring could also take place followed by ring contraction and dehydrogenation leading to the formation of xylenes and of ethylbenzene. The experiments with methylcycloheptane described below justify such conclusion.

In contrast to chromia alone and catalyst 2, impregnated catalyst 2 (catalyst 4) and catalyst 3 did not cause dehydroisomerization reaction (Exps. 7–10). It follows that the alumina prepared from potassium aluminate had not only very weak intrinsic acidic properties but also neutralized the original acidity of the chromia. In catalyst 4 the acidity of catalyst 2 was destroyed through impregnation with cerium and potassium nitrate.

2. Methylcycloheptane.—Table II shows that methylcycloheptane over catalyst 3 yielded ethylbenzene, *o*-xylene and *m*- and *p*-xylene in a constant proportion of 10:34:56 throughout the aromatization experiment. The product distribution and the inability of catalyst 3 to cause isomerization as shown in Table II point out that the aromatization of methylcycloheptane over catalyst 3 does not involve a carbonium ion mechanism at all. If the aromatization proceeded by a carbonium ion mechanism, ethylbenzene would have been formed in the largest amount since its formation would involve a secondary to secondary carbonium ion transformation whereas the formation of xylenes would involve a secondary to primary carbonium ion transformation which is energetically an uphill process. Ethylbenzene, however, was formed in the least amount of all. The aromatization, therefore, may be depicted as follows:

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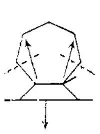
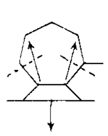
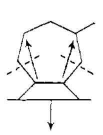
(21) H. Pines and A. W. Shaw, THIS JOURNAL, 79, 1474 (1957).



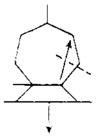
o-Xylene
m-Xylene



Ethylbenzene
p-Xylene



m-Xylene
Toluene



o-Xylene

Over catalyst 2, methylcycloheptane gave the corresponding product distribution of 18:40:42. By the same reasoning as before, the aromatization proceeded essentially according to the non-ionic mechanism; however, a contribution of a carbonium ion mechanism in this case is not excluded inasmuch as catalyst 2 was able to dehydroisomerize 1,1-dimethylcyclohexane to *o*-xylene. The relatively higher yield proportion of ethylbenzene and of *o*-xylene than that obtained with catalyst 3 also suggests participation to a small extent of a carbonium ion mechanism.

The behavior of chromia alone toward the aromatization of methylcycloheptane is similar to that experienced with compounds I and II (Exps. 1 and 2). At first the chromia acted as an aromatization catalyst without showing acid catalytic tendencies. However, with time the dehydrogenation sites of the catalyst were deactivated while acid sites increased. This is indicated by the relatively greater amount of ethylbenzene formed.

Conclusion

The experimental results discussed above show: (1) that chromia is a dual action catalyst having dehydrogenation and isomerization properties; the latter are associated with the intrinsic acidity of the chromia and (2) that alumina of different intrinsic acidities influences the catalytic properties of chromia-alumina catalysts in aromatization reactions with respect to involvement of carbonium ion mechanism therein.

[CONTRIBUTION FROM THE BIOLOGY DEPARTMENT, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

Studies on the Formation of Helical Deoxycholate Complexes[1,2]

BY D. M. BLOW AND ALEXANDER RICH

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It was previously found that under appropriate conditions sodium deoxycholate aggregates in solution to form a gelatinous complex of macromolecular dimensions; X-ray diffraction studies of fibers of this complex showed that the molecules had assumed an elongated helical configuration 36Å. in diameter. Viscometric measurements have been used for the study of the conditions favoring formation of the complex and for observing thixotropic behavior. Complexing is favored by lower *p*H (down to the point where the insoluble acid is precipitated) and by raising the ionic strength; at sufficiently high ionic strength solutions of sodium deoxycholate will gel without added acid. The results suggest that the formation of the complex is highly specific since closely related compounds do not exhibit this effect. Solutions of deoxycholate show noticeable rises of *p*H during formation of the complex; it has been shown that this absorption of hydrogen ions is correlated with the extent to which the gel is broken up by stirring. The mechanism of the thixotropic behavior and the implications of these observations with respect to the molecular structure of the complex are discussed.

Introduction

In an earlier paper, we described the various changes which occur upon the slight acidification of solutions of sodium deoxycholate.[3] When the *p*H is lowered, the solution gradually becomes viscous and ultimately gels if allowed to stand in a beaker. These effects also have been observed by Sobotka and Czeczowiczka.[4] When in the form of this viscous "complex," deoxycholate behaves in many ways like a polymer of high molecular weight. The solutions are slightly turbid, and in the ultracentrifuge show a rapidly migrating peak. The solutions can be drawn into fibers which dry into glassy, birefringent rods.

X-Ray diffraction photographs of these fibers showed a remarkably detailed pattern which is characteristic of a helical aggregate.[3] The elongated units are organized in the fiber in hexagonal packing with a distance of 36.2 Å. between the centers. This diameter increases if other molecules, such as amino acids or peptides, are in the solution during the formation of the complex. The diffraction pattern suggests that the other complexing species is attached to the outside of the helical steroid core.

In order to reach a clearer understanding of this polymer-like complex, we have studied its formation under a variety of conditions. Viscosity measurements have been used chiefly to trace the formation of the complex; a *p*H change also has been observed during its formation, indicating that hydrogen ions are being removed from the solution. The effect has been found to be rather specific for deoxycholate and most other bile salts show no sign of similar behavior.

There is evidence that the phenomenon is related to micelle-forming properties of deoxycholate but that these are greatly enhanced by lowering the *p*H. We believe that under these conditions a specific system of hydrogen bonding becomes possible within the micelle, leading to formation of huge micelles with a regular or "crystalline" internal structure.

Materials and Methods

For most experiments commercial preparations of sodium deoxycholate were used (Fisher Scientific Co. and Nutritional Biochemical Corp.). The solutions were filtered before

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(3) A. Rich and D. M. Blow, *Nature*, **182**, 423 (1958).

(4) H. Sobotka and N. Czeczowiczka, *J. Colloid Sci.*, **13**, 188 (1958).