

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Isomerizing Action of Cyclizing Catalysts*

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The process of aromatization of heptane and other saturated hydrocarbons has been reported by Moldavski¹ and his co-workers, Taylor and Turkevich,² Grosse, Morrell and Mattox,³ and Hoog, Verheus and Zuiderweg.⁴

Most of the work has been done on normal hydrocarbons and on oxides of chromium, vanadium and molybdenum. The question arises whether these catalysts have any isomerizing properties, *i. e.*, whether on the one hand there is any isomerization of the charged heptane which is not dehydrogenated to olefins and aromatics; and on the other hand whether there is any aromatization of branched chain hydrocarbons not having a string of at least six carbon atoms. Though both processes involve isomerization, the detection of the first possibility involves great analytical difficulty. Consequently, the yield of aromatics from 2,2,4-trimethylpentane was used as a criterion of isomerization properties of the catalysts in the temperature range in which aromatization takes place. Absence of aromatics from this substance would serve as indication that the isomerizing properties were low, for even on cracking of the molecule, one cannot get a string of six carbon atoms, to form a six-membered aromatic ring. The 2,2,4-trimethylpentane must rearrange to give a benzene derivative.

Apparatus and Procedure

The experiments were all carried out at 475° with a feed rate of 4.2 cc. per hour for six hours. The apparatus was essentially that of Hoog.⁴ Detailed description is to be given in a forthcoming paper by Turkevich, Fehrer and Taylor. The liquid was analyzed for aromatics and olefins by the method of Kattwinkel,⁵ while the olefins were determined by the Hanus⁶ method. The aromatics were determined by difference.

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(1) B. L. Moldavski and G. D. Kamuscher, *Compt. rend. Acad. Sci., U. S. S. R.*, **1**, 355 (1936); B. L. Moldavski, G. D. Kamuscher and M. V. Kobylskaya, *J. Gen. Chem., U. S. S. R.*, **7**, 169 (1937); *op. cit.*, 1835; B. L. Moldavski, F. Bezprozvanneya, G. D. Kamuscher and M. V. Kobylskaya, *ibid.*, 1840.

(2) H. S. Taylor and J. Turkevich, *Trans. Faraday Soc.*, **XXXV**, 921 (1939).

(3) A. V. Grosse, J. C. Morrell and W. J. Mattox, *Ind. Eng. Chem.*, **32**, 528 (1940).

(4) H. Hoog, J. Verheus and F. J. Zuiderweg, *Trans. Faraday Soc.*, **XXXV**, 993 (1939).

(5) R. Kattwinkel, *Brennstoff Chem.*, **8**, 353 (1927); *C. A.* **22**, 3039 (1928).

(6) H. C. Sherman, "Methods of Organic Analysis," The Macmillan Company, New York, N. Y., 1929, p. 153.

The procedure consisted in making two runs with *n*-heptane, two with 2,2,4-trimethylpentane, and one with *n*-heptane. In between runs the catalyst was flushed successively with nitrogen, air, nitrogen, and hydrogen. The consistency of the heptane runs was used as criterion of the constancy of catalyst activity.

Materials.—Normal heptane was obtained from the California Chemical Company and purified by careful distillation. 2,2,4-Trimethylpentane (b. p. 99.4°, *d*²⁰, 0.6922, *n*²⁰_D 1.3915) was obtained from Röhm and Haas.

The catalysts were prepared as follows, after which they were dried and calcined: no. 1 by reduction of chromic acid (Baker c. P.) by alcohol (details are given in the forthcoming paper of Turkevich, Fehrer and Taylor); no. 2 by soaking no. 1, previously dried overnight at 110°, with a solution of aluminum nitrate (Merck Reagent) sufficient to be just absorbed by the chromic oxide and to give the desired amount of alumina; nos. 3, 4 and 5, by treating activated alumina (Alorco) with solutions, respectively, of ammonium dichromate (General Chemical Reagent), ammonium molybdate (Baker and Adams), and ammonium metavanadate (Eimer and Amend c. P.), sufficient to be just absorbed by the alumina and to give, respectively, 10% of Cr₂O₃, Mo₂O₃, and V₂O₃, on alumina.

Discussion

The table shows that at 475°, Cr₂O₃ alone, Cr₂O₃ on alumina, alumina on Cr₂O₃, and vanadium oxide on alumina do not give any aromatics from 2,2,4-trimethylpentane, whereas a considerable amount of aromatics is formed from *n*-heptane. Our results differ from those of Hoog,⁴ who finds 3% aromatics from 2,2,4-trimethylpentane on chromium oxide. However, his method of olefin analysis involves the use of thioglycolic acid. The latter does not remove completely branched chain olefins.⁷ The small negative values for aromatic content presumably are due to some substitution taking place in the Hanus method for determining olefins. The olefin content of the products is higher from the 2,2,4-trimethylpentane than from the *n*-heptane. Marked stability of catalytic action, as determined by gas evolution, is conferred by depositing Cr₂O₃ on alumina. No stabilization of catalyst is ob-

(7) H. Hoog and E. Bichwald, *Rec. trav. chim.*, **58**, 487 (1939).

TABLE I
 EXPERIMENTAL RESULTS

Compound	Catalyst No. 1 Cr ₂ O ₃ on CrO ₃ , 15 g.			Catalyst No. 2 Al ₂ O ₃ on Cr ₂ O ₃ , 12 g.			Catalyst No. 3 Cr ₂ O ₃ on Al ₂ O ₃ , 30 g.			Catalyst No. 4 Mo ₂ O ₃ on Al ₂ O ₃ , 30 g.			Catalyst No. 5 V ₂ O ₅ on Al ₂ O ₃ , 30 g.		
	Vol. % Olef.	Gas Arom.	0-6 hr. cc./min.	Vol. % Olef.	Gas Arom.	0-6 hr. cc./min.	Vol. % Olef.	Gas Arom.	0-6 hr. cc./min.	Vol. % Olef.	Gas Arom.	0-6 hr. cc./min.	Vol. % Olef.	Gas Arom.	0-6 hr. cc./min.
<i>n</i> -Heptane	14	18	28 to 11	10	13	15 to 8	16	11	14 (constant)	9	20	48 to 20	10	1	2 to 6
<i>n</i> -Heptane	15	16	19 to 9	10	11	14 to 7	15	17	14	9	24	41 to 20	10	1	3 to 5
<i>n</i> -Heptane	14	16	24 to 7	10	11	15 to 8	15	13	13	10	23	36 to 27	11	9	4 to 10
2,2,4-Trimethyl- pentane	19	- 3	6 to 2	14	- 2	5 to 2	18	- 1	4	9	3	19 to 10	15	- 3	2 to 3
2,2,4-Trimethyl- pentane	19	- 1	6 to 2	16	- 2	4 to 3	18	- 1	4	11	1	15 to 8	18	- 6	2 to 5

tained by depositing alumina on chromium oxide.

The behavior of molybdenum oxide on alumina is different. Aromatics are definitely formed from 2,2,4-trimethylpentane, while the olefin content is the same from both *n*-heptane and 2,2,4-trimethylpentane.

Further work is in progress on the determination of isomerization properties of aromatizing catalysts at higher temperatures.

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Conclusions

1. Chromium oxide unsupported, chromium

oxide on alumina, alumina on chromium oxide, vanadium oxide on alumina do not aromatize 2,2,4-trimethylpentane at 475°.

2. Molybdenum oxide on alumina at 475° gives small but definite amounts of aromatics from 2,2,4-trimethylpentane, indicating isomerizing properties of this cyclizing catalyst.

3. Olefin production from *n*-heptane and 2,2,4-trimethylpentane on aromatizing isomerizing catalyst is the same, while on aromatizing non-isomerizing catalyst, 2,2,4-trimethylpentane yields more olefins than *n*-heptane.

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The Reduction of Cystine at the Dropping Mercury Electrode¹

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In a previous paper² the anodic current-voltage curves obtained with cysteine at the dropping mercury electrode have been presented and discussed. The most important conclusion arrived at was that cysteine is not oxidized to cystine at the dropping electrode but that it depolarizes the electrode with the formation of mercurous cysteinate, HgSR. In the present paper the reduction waves obtained with cystine (denoted in the following as RSSR) at the dropping electrode are presented and discussed. The reduction of cystine at the dropping mercury electrode has received little attention from workers in the field of polarography. Brdicka³ found that when cystine was electrolyzed in a buffer solution of 0.1 *N* ammonium chloride and 0.1 *N* ammonia he

obtained a polarographic wave, the height of which was proportional to the concentration of cystine, and he inferred that the reduction involved two electrons. Brdicka further found the "reduction potential" (depolarization potential) of 0.005 *M* cystine in 1 *N* hydrochloric acid to be -0.37 volt (*vs.* N. C. E.) and in 1 *N* sodium hydroxide to be -1.15 volts. From the difference of 0.78 volt Brdicka concluded that the dependence of the reduction potential upon the *pH* of the solution was in accord with the thermodynamically reversible reduction of cystine to cysteine. Considering that cystine has both weakly acid and basic functions this relation would not be expected to be fulfilled over such a wide range of *pH* values as from 0 to 14. Brdicka's results do not indicate that the reduction of cystine at the dropping electrode is reversible in a thermodynamic sense. A somewhat more detailed study was made by Roncato.⁴ He studied

(1) From a thesis submitted to the Graduate School of the University of Minnesota by Cyrus Barnum in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1940.

(2) I. M. Kolthoff and Cyrus Barnum, *THIS JOURNAL*, **62**, 3061 (1940).

(3) R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **5**, 238 (1933).

(4) A. Roncato, *Arch. sci. biol.*, **20**, 146 (1934).