Aromatization of Heptane, Heptene and Hexene Isomers on Chromic Oxide

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Aliphatic alcohols containing six to eight carbon atoms have been found to be good sources of various aliphatic alkenes.[1] A convenient mechanism for the interpretation of the course of isomerization of these olefins on active non-dehydrogenating surfaces having been formulated, further work was undertaken on dehydrogenation. The present paper records a study of the effects of structure and rate of passage of hydrocarbons on the reactions involved in ring closure and aromatization.

Apparatus.—The apparatus and procedure were the same as described for the dehydrogenation of cyclooctene.[2] Samples of pure cyclohexene and 1,3-cyclohexadiene were kindly sent us from the Harvard Laboratories. Pure *n*-heptane, sulfur-free, was obtained from the California Chemical Company. All the other materials were prepared by dehydration of alcohols.

Analysis.—Because chromium oxide catalysts poison too quickly to give sufficient material for ready determination of composition by fractionation, a different method of analysis had to be used. Specific gravities and Hanus numbers were first determined for each sample. The spread of physical properties between aromatics and naphthenes, naphthenes and olefins, olefins and saturates, allowed the composition to be calculated fairly well from these determinations alone. The assumption is made that there are no substances present which do not belong to these classes. The compositions found were often checked both by calculation from off-gas volume and composition and from analysis of the liquids by means of dimethyl sulfate and bromination. There was never any disagreement between the various methods of checking. Fractionation of the liquid products from certain catalysts which do not poison over long periods of time gave still another check of the validity of the calculations used.

Experimental Results

Cyclohexene and Cyclohexadiene.—The results obtained are given in Table I.

Cyclohexene is observed to give a quantitative yield of hydrogen at 390° and the evolution of hydrogen ceases completely only below 300°. The cyclohexene continues to give benzene, however, to temperatures as low as 200° by a self reduction–oxidation on the surface. When temperatures below that causing evolution of hydrogen are used, raising the temperature of the catalyst does not cause evolution of hydrogen from fresh cyclohexene, but the value for conversion to

(1) Goldwasser and Taylor, THIS JOURNAL, **61**, 1751 (1939).
(2) Goldwasser and Taylor, *ibid.*, **61**, 1260 (1939).

benzene remains that of the lowest temperature used. After getting 0.9% benzene at 163°, a rise to 316° gave only 1% as compared with 20% at 305° after revivifying. Revivification by oxidation in the standard manner always restored full activity. It seems therefore that, at lower temperature, the cycloölefin, with a longer life on the surface than at higher temperatures, poisons the catalyst and remains on the surface, possibly as a hydrocarbon fragment desorbable only with difficulty.

TABLE I

Rate: 3.12 cc./hr./15 g. Cr₂O₃ catalyst

Olefin	T, °C.	Moles gas per mole olefin (100% H₂)	% benzene	% cyclo-hexane	% un-changed
Cyclohexene	395	2	100	0	0
Cyclohexene	337	0.5	50	50	0
Cyclohexene	276	0	10.4	20.8	68.8
Cyclohexene	211	0	8.17	16.3	75.5
Cyclohexene	163	0	0.90	1.8	97.2
Cyclohexene	239	0	0.80	1.7	97.2
Cyclohexene	316	0	1.0	1.7	97.3
Revivify for 24 hours					
Cyclohexene	305	0	20	40	39.7
Cyclohexene	175	0	2.3	4.7	93
Cyclohexene	246	0	2.1	4.9	93
Revivify for 24 hours					
Cyclohexene	510	2	100	0	0
Cyclohexadiene	193	0.9	97	3	0
Cyclohexadiene	137	0	43.6	21.8	34.6
Cyclohexadiene	146	0	44	22	35
Cyclohexadiene	95	0	33	17	50
Revivify for 24 hours					
Cyclohexadiene	137	0	48.6	21.3	35.6
Cyclohexadiene	95	0	33	17	50
Cyclohexadiene	193	0	34	18	48
Revivify for 24 hours					
Cyclohexadiene	95	0	33	17	50
Revivify for 24 hours					
Cyclohexadiene	500	1	100	0	0

Non-catalytically at 500°, cyclohexane has been shown to give as products 25% benzene, 40% hydrogen and 22% ethane. In not one of the runs tabulated was there any decomposition. Even at 500°, although the catalyst had never been heated above 490°, the water vapor which must have come off had no effect on the cycloölefin, although it oxidized *n*-heptane and other aliphatic hydrocarbons. Here, with cyclohexene and a dehydrogenating catalyst, the production of ben-

Table II

Heptane on Chromic Oxide Gel

These runs were done in the order indicated and are the values found after twenty minutes. After an hour, poisoning has cut down the conversion from 40–50%. The catalyst was revivified between each run.

Catalyst	T, °C.	Liq. rate cc./hr./ 15 g.	Contact time, min. (gas)	Off-gas Mol./mol.	% H₂	% arom.	Liquid composition % satd.	% unsatd.
Cr₂O₃	468	3	9	3.75	95	100	0	0
Cr₂O₃	468	18	1½	3.03	92	92.3	5.9	1.8
Cr₂O₃	468	9	3	3.77	94	100	0	0
Cr₂O₃	468	3	9	3.75	95	100	0	0
Cr₂O₃	468	27	1	2.75	98	69	25	6
ThO₂	468	3	9	0.05	1	0	97.5	2.5
Al₂O₃	540	3	9	.05	4	0.5	99.1	.3
Al₂O₃ (act.)	540	3	9	.4	42	2	80	18

zene is so rapid that there is little chance for decomposition.

Cyclohexadiene is exactly similar to cyclohexene except that the lowest temperature at which hydrogen evolution occurs is 175° instead of 300°. Rise of temperature gives no hydrogen with new cyclohexadiene as with cyclohexene. At 95°, just a little above the boiling point of benzene, there is still 33% yield of benzene with 17% cyclohexadiene hydrogenated and 50% unchanged. This small yield is not the result of permanent poisoning as is shown by revivification and repetition at the low temperature without any intervening run.

n-Heptane.—The effect of rate on the conversion of *n*-heptane to toluene is shown in Table II.

The fastest rate at which complete conversion to toluene is found is 9 cc. per hour, with the vapor in contact with the catalyst for three minutes. At a rate three times this, conversion in one passage is still 69%.

The results with thoria and pure alumina show the normal amount of unsaturation which accompanies thermal decomposition. There is no aromatization. At 540°, small amounts of aromatic normally appear in thermal decompositions of hydrocarbons. The second alumina cited in the table has a small iron content and is sufficiently dehydrogenating to give some aromatization. The great difference between a dehydrogenating and an isomerizing catalyst is evident. The rate of poisoning or fall in the evolution of hydrogen with time decreases with increase of rate. Anything that decreases the life of an olefin on the active surface decreases the rate of poisoning.

Olefins.—The influence of structure of an olefin on aromatization is shown in Table III,

which presents some typical results found with various olefins. After each run there was a ten to twenty-four hour period of revivification, an eight to ten hour reduction period and a four to eight hour period for the flushing of hydrogen from the surface by the use of purified nitrogen as described in the procedure of the first paper in this series. The order of experiment is as listed.

The results obtained may be summarized as follows. (1) *Effect of Rate on Conversion of Olefin.*—Heptene-1 at 474° shows complete conversion at the slowest rate tried, but poisoning is more rapid than at high rates. In the experiments at the rapid rate, where poisoning takes place more slowly, a lower rate of aromatization than is the case for heptane is found. This indicates that the olefin is on the surface for a shorter time interval.

(2) *Effect of Temperature on Conversion.*—A rise in temperature of 50° doubles the percentage of heptene-1 converted to toluene and causes the time for half-way poisoning to be tripled. The heptene spends less time on the surface and is more readily dehydrogenated at the higher temperature. Aromatics do not poison the catalyst.

The effect of rise of temperature on the amount of conversion of the methylpentene is less marked, although the poisoning changes qualitatively in the same way. This smaller temperature effect reflects the fact that the necessary isomerization does not have as large a temperature coefficient as dehydrogenation, and that the slow process in the over-all reaction to benzene is the isomerization of the branched hexene to the straight chain hexene.

(3) *Effect of Structure on Conversion.*—(a) 7-Carbon olefin: the position of the double bond in the straight chain heptene does not cause any

TABLE III

OLEFINS ON CHROMIC OXIDE GEL

Rate: 3.1 cc./hr./15 g.

The data given are for the first five minutes of the run. The last run carried out was a heptane run in order to make sure that the catalyst had not changed activity during many runs. Several of the above were repeated on fresh catalysts with no change in results. The heptene runs were done in the order tabulated to test reproducibility of results.

Olefin	T, °C.	Moles gas per mole reagent	Liquid sp. gr.	Liquid compn. % arom.	% sat.	% unsat.	% H₂	Gas compn. % sat.	% unsat.	Time ½ poisoned, min.
5-Methylhexene-2	424	2	0.78	50	12	38	31	57	12	10
Heptene-3	350	0	.70	0	5	95				
Heptene-3	420	1.5	.78	48	12	40				10
Heptane (check)	460	2.9	.860	100	0	0	98	1	1	
Heptene-1	424	1	.775	45	13	42	92.3	7	0	10
Heptene-1	398	0.3	.750	36	32	32	15	85	0	Rapid
Heptene-1	474	2.2	.84	90	2	8	89.5	4	6	40
Heptene-1	424	1	.770	44	15	41	91.5	8	0	10
Heptene-1	474	2.1	.839	90	2	8	89	3	8	40
2-Methylpentene-2	474	1.0	.755	32.5	7	60	56	34	10	30
3-Methylpentene-2-t	474	1.0	.760	32	5	62	55	38	7	30
2-Ethylbutene-1	474	1.0	.759	32	6	62	57	35	8	30
Octene-1	474	2.57	.849	84	1	15	94	3	3	
Heptene-1 18 cc./hr.	474	1.5	.78	48	1	51	93	5	2	70
Heptene-1 0.5 cc./hr.	474	2.9	.860	98	0	2	99	0	1	10
3-Methylpentene-2-t	424	0.6	.780	21	18	61	95	4	1	10
2-Methylpentene-2	424	.83	.735	27	24	49	92	6	2	10
2-Ethylbutene-1	424	.59	.720	20	20	60	93	6	1	10
Heptane (check)	460	3.9	.860	100	0	0	98	0	2	

marked difference in the rate of conversion to an aromatic. The rate is also that of 5-methylhexene. As was seen in the work on isomerization, the branched chain olefin is formed with great rapidity from the straight chain. 5-Methylhexene-2 is readily cyclicized and dehydrogenated. (b) 6-Carbon olefin: unless methylcyclopentane is first formed and then ring enlargement to cyclohexane occurs, any branched chain 6-carbon olefin must isomerize to the straight chain olefin before ring closure takes place. At 474°, the three isomers tried showed identical properties over chromium oxide. There is 32% conversion and the same amount of decomposition and poisoning for each. At 424°, 2-methylpentene-2 shows somewhat the higher rate of conversion to benzene, gas evolution is higher but it is of the same composition. 2-Ethylbutene-1 and 3-methylpentene-2-t are equal in conversion and poisoning rates, but are slower than the 2-methylpentene.

(4) *Effect of Structure on Poisoning.*—The slower the conversion to aromatics, the faster the poisoning becomes. Branched chain olefins are found to poison the catalyst more rapidly than straight chain. Again it is seen that increase of life of an olefin on the surface of a catalyst increases the rate of poisoning.

Discussion.—The conclusions to be drawn from the cycloölefin experiments are several. Once a 6-membered ring is formed on chromic oxide catalyst, the ring is not broken again at these temperatures. If the temperature is high enough to dehydrogenate an olefin, or cyclohexane or its homologs, the temperature is already too high to allow the presence of more than minute amounts of cyclohexene and even less cyclohexadiene. When cyclohexene is dehydrogenated, no cyclohexadiene intermediate can be expected to be isolated since, as has been shown, cyclohexadiene yields its hydrogen quantitatively at a temperature 100° below the lowest temperature at which cyclohexene evolves the gas. Indeed, the temperature is 25° below the temperature at which cyclohexene poisons the catalyst so that there is even no disproportionation. Although only a small amount of cyclohexene may be formed in a given reaction, the subsequent reactions to cyclohexadiene and to benzene are so rapid and complete at the higher temperatures, that the total reaction is far displaced and in some cases even 100% conversion is found.

It is evident that, for aromatization of an aliphatic hydrocarbon, dehydrogenating conditions are required which improve the chance that cyclohexene or its homologs may be formed. That there is a small but definite chance of this

happening without any special catalyst is shown by the fact that the same reaction occurs to a small extent in a Pyrex vessel and, as shown, on alumina and thoria. The reaction goes to a larger extent when dehydrogenating conditions are present. Save for the cracking reactions, the conversion of heptane to toluene is quantitative on chromic oxide gel with sufficient contact time.[3]

The data on the aromatization of the olefins agree with the results from isomerization experiments. The 6-carbon branched chain olefins, while giving only 32% aromatics as compared with 90% for the straight chain compound under the same conditions, are all quite similar. It has been shown that isomerization from one branched olefin to another is rapid at this temperature with the methyl group tending to centralize. The reason for the comparatively low yield must be the necessary isomerization to and low concentration-of the straight chain olefin. This is further borne out at the lower temperature where isomerization is slower, and the differences of structure of the starting materials have more influence. The 2-methylpentene-2 isomer gives a better conversion to benzene than does either 2-ethylbutene-1 or 3-methylpentene-2-*t*, two isomers which have

(3) Moldavski and Kamusher, *Bull. Soc. Acad. Sci.*, *U. S. S. R.* (*N. S.*), 1936, have shown that *n*-heptane, *n*-octane, and *n*-hexane cyclicize on chromic oxide gel but not on thoria, alumina, uranium oxide, zinc oxide, nickel chromate and floridin. Subsequent work by the present writers will show that cyclization actually does occur on special preparations of uranium oxide which have marked dehydrogenation properties.

been shown to be about equal in rate of reaction on an active surface. The reason seems to be that there is one step less to the straight chain from the 2-methyl than from the 3-methyl isomer.

The other properties of the olefins can be summarized similarly. Both liquid and gaseous products show the occurrence of disproportionation at the lower temperatures. As the evolution of hydrogen decreases with decreasing temperature, hydrogenation to saturates begins and poisoning increases. The olefin content of the off-gas at lower temperatures is small and the liquid products have a higher concentration of saturates.

Summary

1. The dehydrogenation of cyclohexene and 1,3-cyclohexadiene on chromic oxide gel surfaces has been investigated.

2. The influence of character of catalyst on aromatization has been shown. For the conversion of aliphatic hydrocarbons to aromatic hydrocarbons, a dehydrogenating catalyst must be used.

3. The influence of structure of olefin on poisoning, aromatization and disproportionation has been demonstrated.

4. Conclusions concerning isomerization drawn from these experiments agree with those found on other catalysts.

The Electron Diffraction Investigation of the Structure of Benzene, Pyridine, Pyrazine, Butadiene-1,3, Cyclopentadiene, Furan, Pyrrole, and Thiophene

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The determination of values of interatomic distances in molecules has been found to provide much information regarding electronic structure, especially in the case of substances which resonate among two or more valence–bond structures. The interpretation of interatomic distances in terms of the types of bonds involved is made with use of an empirical function formulated originally for single bond–double bond resonance of the carbon–carbon bond.[1] There are given in this

(1) L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935); L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937).

paper the results of the determination of the configurations of two molecules involving Kekulé resonance, pyridine and pyrazine, of two molecules with conjugated double bonds, butadiene and cyclopentadiene, and of three five-membered heterocyclic molecules, furan, pyrrole, and thiophene, together with the conclusions regarding their electronic structures reached by application of the bond type–interatomic distance function. In addition, because of the improvement in electron diffraction technique since the study of benzene in these Laboratories four years