Catalytic Dehydrogenation of Representative Hydrocarbons

By Alex G. Oblad, Robert F. Marschner and Llewellyn Heard

Recent investigations of catalytic dehydrogenation have extended to all classes of hydrocarbons. In consequence, the chemical behavior of almost any individual hydrocarbon, in the presence of some catalyst and under certain reaction conditions, can now be predicted with some accuracy. However, the different hydrocarbon classes have usually been studied under a wide variety of conditions of catalyst, temperature, rate, time and pressure. The classical work of Zelinski on cyclohexanes with the platinum group catalysts employed about 300° and very slow rates, under which conditions other naphthenes remained unaffected.[1] Demonstration of the paraffin–olefin equilibrium by Tausz and Putnoky,[2] required several hours reaction time at 300° with large amounts of platinum catalyst. Increasing the temperature to 350 or 400° and employing chromic oxide gel permitted equilibrium to be reached in a much shorter time.[3] With heavier paraffins at

Fig. 1.—Diagram of apparatus.

460–470° and about 0.4 volume of hydrocarbon per volume of catalyst per hour, the cyclodehydrogenation or aromatization reaction was encountered.[4] Five-minute runs at temperatures of 424 and 474° and at about half this rate were undertaken by Goldwasser and Taylor[5] to investigate the aromatization reaction of many olefins in the presence of this catalyst. Butene, which possesses too few carbon atoms to undergo aromatization, nevertheless dehydrogenates over chromic oxide to butadiene.[6,7] Grosse, Morrell and Mavity[8] have extended this reaction to other olefins, operating at 600°, 0.25 atmosphere and at short reaction times in order to reduce destructive dehydrogenation to carbon. The same workers dehydrogenated cyclopentane to cyclopentadiene at 500° and 0.25 atmosphere, using a chromium oxide-on-alumina catalyst. Various specially prepared chromic oxide catalysts have been employed[9] for the dehydrogenation of cyclohexane.

In the dehydrogenation of a mixture of hydrocarbons such as a petroleum naphtha, specific conditions obviously cannot be employed for each constituent; hence a knowledge of the relative behavior of the various hydrocarbon classes probably present, when subjected to a uniform set of conditions, seemed desirable. In the belief that our results are of general interest, such a comparative study is presented here.

Procedure, Apparatus and Materials

The apparatus employed (see Fig. 1) was conventional except for the feed mechanism, which was adopted after other methods had been found to give less constant slow rates over long periods of time. By means of a geared motor, a stainless steel piston was lowered into a cylindrical glass reservoir containing the hydrocarbon, the constant overflow of which drained into the reaction tube. Sealing of the piston was accomplished by a close-fitting stainless steel collar which was cemented into the open upper end of the reservoir. The annular space above the
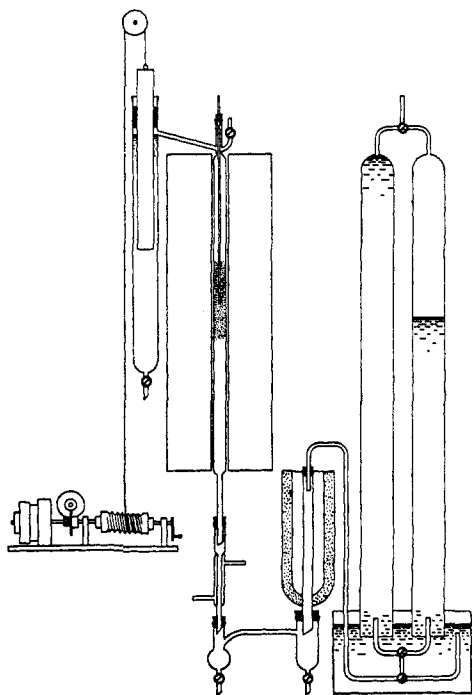
(1) Zelinski, J. Russ. Phys.-Chem. Soc., 43, 1220 (1911); C. A., 6, 598 (1912).

(2) Tausz and Putnoky, Ber., 52B, 1573 (1919).

(3) Frey and Huppke, Ind. Eng. Chem., 25, 54 (1933).

(4) Moldavski and Kamuscher, Compt. rend. acad. sci. U. R. S. S., 10, 355 (1936).

(5) Goldwasser and Taylor, This Journal, 61, 1766 (1939).

(6) Fedorov, Smirnova and Semenov, J. Applied Chem. (U. S. S. R.) 7, 1166 (1934); C. A., 29, 5808 (1935).

(7) Dementeva, Frost and Serebryakova, Compt. rend. acad. sci. U. R. S. S., 15, 141 (1937).

(8) Grosse, Morrell and Mavity, presented before the Petroleum Division of the American Chemical Society, Boston, September 11–15, 1939.

(9) Balandin and Brusov, Z. physik. Chem., 34B, 96 (1936).

TABLE I

DEHYDROGENATION OF VARIOUS HYDROCARBONS OVER CHROMIC OXIDE

Temperature, 480°; space velocity, 0.5; duration, 3.0 hours

| Hydrocarbon | Product | Gas evolved Vol./vol. hydrocarbon | | | Mean mol. wt. | Liquid product Vol. % conversion[d] | | | Olefins, wt. % | Residue on catalyst, wt. % of feed |
		1st hr.	2nd hr.	3rd hr.		1st hr.	2nd hr.	3rd hr.		
Cyclohexane	Benzene	510	740	530	5.5	62	72	54	..	0
n-Heptane	Toluene	310	270	200	5.3	33	22	..	15.0	4
2,2,4-Trimethylpentane	Aromatics[b]	170	120	50	22.0	4	0	0	12.1	1
Ethylbenzene	Styrene	30	20	[c]	12.5	6	10	[c]	..	3
50% Cyclohexane[a] + 50% Ethylbenzene	Benzene	390	200	140	..	32	11	7	..	1

[a] Run at 1.0 space velocity.   [b] Assuming refractive index of $n^{20}D$ 1.5000.   [c] Run duration 2.0 hours only.   [d] To product listed in second column.

collar and between the reservoir and the piston was sealed with mercury. The 24-mm. vertical Pyrex reaction tube was electrically heated over a 60 cm. length and about 50 cc. of catalyst occupied the middle 15 cm. A thermocouple extended in a Pyrex well to the center of the catalyst bed. Liquid by-products were condensed with tap water and dry-ice and the gas evolved was collected alternately in two calibrated 2-liter gas burets.

Eastman Kodak Co. cyclohexane, methylcyclohexane, ethylbenzene, toluene and caprylene (about 3:1 ratio of octene-2:octene-1) were used without purification. The n-heptane and 2,2,4-trimethylpentane were certified octane number standards. Methylcyclopentane was prepared from cyclohexane by refluxing with 15 weight per cent. aluminum chloride for fifteen hours under a helix-packed, 10-plate fractionating column, the methylcyclopentane being removed as formed. The distillate contained about 20% cyclohexane.

Two chromic oxide catalysts were employed. One was prepared by reduction of chromic acid with ethanol to give a hydrated chromic oxide mud which was filtered, dried at 150°, and screened to 8–16 mesh before use. The results obtained are shown in Table I. The other catalyst, which was needed in larger amounts, was prepared by the somewhat simpler method of thoroughly soaking 9 parts by weight of granular alumina with sufficient aqueous chromic acid to give, after reduction by heating to 650°, 1 part by weight of chromic oxide. Alternatively, the alumina was powdered before soaking, and granulated after reduction by forming a paste with water, drying, breaking, and screening. Table II contains results obtained with this catalyst.

After starting the feed mechanism, the run was initiated from the time that evolution of gas occurred. Thereafter, the gas and liquid volumes and the refractive index of the liquid were measured half-hourly. The molecular weight of the gas and the olefin content of the liquid were determined by the effusiometer and Francis methods, respectively. After the desired period of time, the run was ended by discontinuing the flow of hydrocarbon and sweeping the remaining vapor from the system with nitrogen. The residual material upon the catalyst was burned off with a slow stream (less than 100 volumes/volume catalyst/hour) of dry, carbon dioxide-free air. The water and carbon dioxide formed were collected in calcium chloride and ascarite.

For simplicity, rates are expressed as the space velocity,

or the volume of liquid hydrocarbon passed over each volume of catalyst each hour. The conversion obtained in the various runs was determined through the refractive index, the proper corrections for olefin content and other factors being applied.

Results

Table I presents data obtained with a single sample of the gel catalyst, any loss in activity being restored by burning with excess air after each run. The rapid conversion of cyclohexane to benzene is contrasted with the difficult reaction of the other hydrocarbons. The extent of reaction in the case of the two paraffins decreases rapidly with time, whereas with cyclohexane this effect is not pronounced. The hydrogen produced from cyclohexane was contaminated largely with feed and product, whereas with the less volatile n-heptane, the impurities appeared to be gaseous hydrocarbons. The 2,2,4-trimethylpentane underwent considerable cracking, as shown by the heavy gas, about 20% of which consisted of C_3 and C_4 hydrocarbons. A small amount of aromatics was produced during the first hour, in spite of the fact that the longest linear chain in 2,2,4-trimethylpentane contains less than six carbon atoms. Taylor and Turkevich[10] found similar cases among the olefins. The small amount of gas obtained from ethylbenzene was contaminated with nitrogen.

The amount of residue upon the catalyst varies widely with the several hydrocarbons. Cyclohexane gave none, whereas the paraffins gave appreciable amounts, indicating that such coating of the catalyst surface is the cause of the declining activity. Ethylbenzene gave a large amount of residue, and the relatively small amount of hydrogen produced suggests the presence of condensed or polymerized hydrocarbons rather than carbon

(10) Taylor and Turkevich, presented before the Petroleum Division of the American Chemical Society, Baltimore, April 3–7, 1939.

TABLE II

DEHYDROGENATION OF VARIOUS HYDROCARBONS OVER SUPPORTED CHROMIC OXIDE

Temperature, 482°; space velocity, 1.0; duration, 5.0 hours.

Hydrocarbon	Product	Gas produced — Vol./vol. liquid					Mean mol. wt.	Wt. % yld.	Liquid product — Vol. % conversion[a]					Wt. % olefins	Vol. % yld.	Residue — Anal., % C	H	Wt. % yield
		1st hr.	2nd hr.	3rd hr.	4th hr.	5th hr.			1st hr.	2nd hr.	3rd hr.	4th hr.	5th hr.					
Cyclohexane	Benzene	166	196	173	204	216	3.3	3.3	15	19	19	20	21	..	94.9	85.5	14.5	0.069
Methylcyclohexane	Toluene	116	141	141	136	144	2.9	2.1	14	18	17	17	17	..	95.7	84.6	15.4	.082
n-Heptane	Toluene	81	77	67	62	57	4.9	2.0	7	6	5	4	4	9.5	95.7	93.4	6.6	.287
n-Heptane	Toluene	82	74	63	61	54	[b]	1.7	6	5	4	4	3	9.5	96.0	94.7	5.3	.313
50% Cyclohexane + 50% n-heptane	Benzene	76	91	92	85	84	4.2	2.0	14	18	17	16	15	5.0[c]	94.2	92.6	7.4	.243
75% n-Heptane + 25% toluene	Toluene	71	64	55	52	46	[b]	1.6	7	7	4	4	4	7.5[c]	97.0	99.4	0.6	.209
2,2,4-Trimethylpentane	Olefins	25	40	43	46	46	10.7	2.5	5	9	8	7	7	9.0	97.5	91.8	8.2	.178
Ethylbenzene	Styrene	39	38	33	35	32	3.3	0.5	16	17	16	16	14	3.0	94.7	94.0	6.0	.426
Octenes-1 and -2	Xylene	147	82	67	65	64	5.5	2.6	22	11	8	8	7	87.0	86.6	99.7	0.3	1.266
Methylcyclopentane	Cyclic Olefins	62	59	53	47	[d]	6.7	2.0	13	12	14	14	[d]	6.8	96.6	99.7	0.3	1.556

[a] To product listed in second column. Calculated from refractive index and corrected for diluents and for olefins produced.   [b] Assumed molecular weight of 5.0.   [c] Based upon total liquid product; 10% based upon n-heptane content only.   [d] Duration of run only 4.0 hours.

upon the catalyst. Attempts to dehydrogenate cyclohexane in one-hour runs over an ethylbenzene-treated catalyst gave far smaller conversions than over untreated catalyst:

Hours of treatment with ethylbenzene	0	1	2
Volumes gas/volume cyclohexane	513	216	112
Conversion to benzene, %	62	32	16

Thus the residual material left by ethylbenzene during one hour halved the conversion of cyclohexane, and a similar two-hour treatment reduced it to one-quarter of the original value. Passage of air over the catalyst burned off the residue, and the activity was restored completely. The final run of Table I shows the cumulative poisoning effect of ethylbenzene upon the conversion of cyclohexane. The behavior of the mixture was not unlike that of n-heptane.

The broader series of runs which are summarized in Table II was then made with particular attention being paid to the amount and composition of the residues deposited on the catalyst. Each run employed unused catalyst to eliminate any possible effects of catalyst regeneration. The results substantiate and extend those of Table I. Methylcyclohexane was somewhat more difficult to convert than cyclohexane, contrary to the results of Balandin and Schuikin.[11] The duplicate runs with n-heptane are in very good agreement. The gas production of the mixture of cyclohexane and n-heptane was two-thirds of the average of the runs upon the individual components, showing that n-heptane has less effect upon the catalyst than had ethylbenzene. Although the toluene produced from n-heptane

(11) Balandin and Schuikin, C. A., 32, 2515 (1938).

might be analogous to ethylbenzene, the next run, in which n-heptane was diluted with toluene, gave 85% as much gas as pure n-heptane, approximately as expected considering the 25% smaller concentration of n-heptane present. The 2,2,4-trimethylpentane underwent less cracking than under the more drastic conditions shown in Table I, but ethylbenzene surprisingly gave higher conversions than before. The conversion to styrene (16%), as calculated from the increase of the refractive index, does not agree with the actual olefin analysis (3%). The discrepancy is explained by polymerization of the expected product, styrene; this results in an unanticipated higher refractive index as well as in the low olefin content. The octenes gave large amounts of aromatics during the first hour, but this decreased very rapidly during subsequent hours. Evidently the product of a side reaction adversely affects the catalyst. Finally, methylcyclopentane underwent considerable dehydrogenation, presumably mostly to cyclic diolefins.[8]

The residue analyses are very interesting. Cyclohexane and its methyl homolog not only left less than 0.1% residue upon the catalyst, but, because of the 15% hydrogen content, this may have been simply adsorbed or otherwise withheld reagents, which contain 14.3% hydrogen. The paraffins deposit 0.2–0.3% of residue containing 5–8% hydrogen. If it is assumed that as much paraffin as cyclohexanes is retained by the catalyst, the remaining burned residue must have consisted almost entirely of carbon. The residue from ethylbenzene, as in the case of paraffins, was poorer in hydrogen than the feed; however,

assuming again the presence of a constant amount of withheld reagent, the major portion of the residue shows a hydrogen content of 5%. This points to the presence of heavy styrene polymers on the catalyst in agreement with the previous evidence that lighter polymers were present in the liquid product. Despite the evidence of Goldwasser and Taylor[12] that under certain conditions styrene does not lower catalyst activity, we find it difficult to avoid the conclusion that styrene polymers destroy the activity of the catalyst for the straightforward dehydrogenation of cyclohexane to benzene. Entirely different is the behavior of octenes and of methylcyclopentane; the amount of residue is nearly twenty times that from the cyclohexanes. The assumption previously made that a constant small amount of feed is retained in the reaction tube would predict the low hydrogen content observed here. Most of the residue is, like that from paraffins, carbon rather than tar-like hydrocarbons.

It appears likely that the carbon is produced by side reactions involving extensive dehydro-condensation of linear and cyclic diene polymers. One can then explain by a common mechanism the catalyst poisoning of such apparently unrelated hydrocarbons as ethylbenzene, octenes, cyclopentanes and ethylene.[10] The more or less refractory nature of styrene polymers leads to little actual carbonization but instead leaves appreciable amounts of strongly adsorbed aromatic hydrocarbon as such in the residue. When diluted with cyclohexane, n-heptane gave almost as much residue as alone. Added toluene had the exceptional effect of decreasing the hydrogen content of the residue. These results with mixed reagents are not readily explained by the generalizations derived from the pure hydrocarbons. Further work on mixtures and kinetic treatment of the data are necessary.

Conclusions

1. Representative hydrocarbons of all classes have been dehydrogenated over chromic oxide catalysts under identical high-rate, high-temperature conditions.

2. Cyclohexanes are converted to aromatics for extended periods and practically no residual products are formed.

3. Paraffins are much less rapidly converted than cyclohexanes, the activity of the catalyst steadily decreases, and elementary carbon is deposited. Olefins are more readily converted than paraffins, but the activity decline and carbon deposition are far more pronounced.

4. Cyclopentanes are slowly dehydrogenated, but closely resemble olefins in depositing large amounts of carbon.

5. Simple methylated aromatic hydrocarbons are unaffected, but alkyl aromatics with longer side-chains, such as ethylbenzene, are slowly dehydrogenated to products which strongly poison the catalyst. The residue probably responsible consists of tar rather than elementary carbon.

(12) Goldwasser and Taylor, THIS JOURNAL, **61**, 1260 (1939).

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The Hydration of Unsaturated Compounds. VIII. The Rate of Hydration of β,β-Dimethylacrylic Acid; the Rates of Dehydration and Decarboxylation of β-Hydroxyisovaleric Acid

BY DAVID PRESSMAN AND H. J. LUCAS

Introduction

In order to determine the effect of various substituents upon the heat of hydration of the ethylenic double bond, a number of compounds must be studied. It is reasonable to believe that the influence of the substituent may be exerted through two principal effects. One, which is the inductive effect, is shown by all substituents. The other, which affects the double bond character through resonance, is exhibited by only certain substituents. In addition there is bound to be a certain interaction between these two effects.

It is the purpose of the present hydration studies to evaluate the two principal effects and their interactions. The heats of hydration are determined from equilibria or kinetic data as in previous work.[1,2,3] A study is being made also of the kinetics and mechanism of the hydration and

(1) W. F. Eberz and H. J. Lucas, THIS JOURNAL, **56**, 1230 (1934).
(2) S. Winstein and H. J. Lucas, ibid., **59**, 1461 (1937).
(3) D. Pressman and H. J. Lucas, ibid., **61**, 2271 (1939).