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Reactions between Hydrocarbons and Deuterium on Chromium Oxide Gel. IV. Addition of Deuterium to Olefins

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RECEIVED FEBRUARY 15, 1960

At −78 and 0° on a chromium oxide gel catalyst, the addition of deuterium to ethylene forms substantially pure ethane-1,2-d_2. At −11°, about 1% alkane-d_3 and -d_4 contaminates the alkane-1,2-d_2 resulting from deuterogenation of propylene and 1-butene. At 40°, cyclopentene gives about 2% and 1-hexene, about 5% d_3 and d_4. 2-Pentene leads to considerably more d_1 and d_3 and d_4 than 1-hexene. Increase in temperature of deuterogenation, particularly above 85°, results in wider isotopic distribution patterns and, at 150°, only about half of the products from 1-hexene, 2-pentene and cyclopentene is alkane-d_2. 1-Hexene in a stream of nitrogen is extensively isomerized on chromia at 200°. At 125 and at 200° with partially activated catalysts which give incomplete deuterogenation, the unreacted olefin is both isomerized and isotopically exchanged, but, at 50° and below, the unreacted olefin is negligibly isomerized or exchanged.

This paper reports the results of the addition of deuterium to ethylene, propylene, 1-butene, 2-pentene, cyclopentene, 1-hexene, 2-pentyne and 2-butyne. The temperature range of the experiments was −78 to 175°. In addition, certain related observations on double-bond migration are presented.

Experimental

Materials.—The chromium oxide gel catalyst has been described in paper II. Liquid olefins were fractionated before use (2-pentene and 1-hexene, Phillips Petroleum Company, Pure Grade; cyclopentene, Phillips Research Grade).

Experimental Procedure.—The molar deuterium to olefin ratio was 2.0. Mixtures of gaseous olefins and deuterium were prepared by the use of two capillary flowmeters. With liquid olefins, the deuterium stream was saturated with olefin at an appropriate temperature as described in paper II. The flow rates of deuterium and olefin were 0.024 and 0.012 mole per hour.

Contrary to the situation in the isotopic exchange experiments, the large heat of hydrogenation of an olefin caused problems of temperature control. To minimize this problem, a catalyst container of large area and small thickness was constructed by flattening a section of tubing so as to give a nearly rectangular cross-section of about 3 by 20 mm. About 2 g. of catalyst was employed. The reactor was placed in a thermostated liquid at temperatures below 100° further to facilitate temperature control. An air-bath was used above this temperature and, consequently, catalyst temperatures above 100° are less certain and temperature gradients may be worse.

Experimental Results

Activation of Catalyst.—The unactivated chromium oxide gel gives no detectable hydrogenation of an olefin at 200°. Hydrogenation activity develops with higher temperature treatment coincidentally with activity for isotopic exchange (see paper II). Since the hydrogenation of olefins is much faster than exchange of alkanes, even slightly activated catalysts exhibit some hydrogenation activity at 200°, whereas only well activated catalysts give exchange activity at 200°.

A. Ethylene and Propylene.—At −78°, a catalyst of maximum activity effected complete saturation of ethylene to nearly pure $C_2H_4D_2$ devoid of $C_2H_3D_3$. There was probably some C_2H_5D but not more than 4%. Similar results were obtained with this catalyst at 0° and also at 0° with a catalyst which had been used for over 50 runs and which was dying. On this inactive catalyst at −78°, the product was 25% $C_2H_4D_2$ and 75% C_2H_4 which contained negligible C_2H_3D.

At −11°, propylene gave a high yield of dideuteriopropane. There was also 1.5% trideuterio- and about 0.1% tetradeuteriopropane. The amount of monodeuterioalkane probably was similar to that obtained with ethylene.

B. 1-Butene, 2-Pentene, Cyclopentene and 1-Hexene.—Results with these olefins are presented in Table I. The values for D_0 and D_1 are of low accuracy when small particularly with the lower molecular weight hydrocarbons.

TABLE I

ADDITION OF DEUTERIUM TO 1-BUTENE, 2-PENTENE, CYCLOPENTENE AND 1-HEXENE

Run	Temp., °C.	D_0, %	D_1, %	D_2, %	D_3, %	D_4, %	D_5, %	D_6, %	D_7, %	Av. atoms D/molec.
				1-Butene						
A	−11	^{a}	4.2	95.2	0.4	0.2				
B	26	1.3	4.6	92.5	2.2	0.5	0.16	0.04		1.99
				2-Pentene						
C	27	2.8	8.8	78.1	9.2	1.0	0.1			1.97
D	61	2.7	8.9	77.3	8.8	1.2	.1			1.97
E	99	3.1	15.2	63.4	14.9	2.8	.4	0.1		2.01
F	133	3.4	15.0	60.5	16.4	3.7	.7	.2		2.05
G	165	3.9	16.7	50.2	19.8	6.7	1.9	.6	0.3	2.19
				Cyclopentene						
H	43	0.0	2.1	96.1	1.6	0.2	0.02			2.00
I	70	.0	1.7	95.3	2.7	.3	.03	0.02		2.02
J	98	.0	3.2	91.5	4.8	.5	.05	.02		2.03
K^b	130	.1	9.0	76.6	10.5	2.1	.7	.4	0.3	2.13
L^c	170	.6	13.9	55.2	20.1	6.3	2.1	1.0	0.5	2.32
				1-Hexene						
M	42	0.3	5.2	89.5	4.4	0.5				2.00
N	62	.1	5.2	87.8	6.4	.5				2.02
O	83	.3	6.6	84.9	7.2	.8	0.1			2.02
P	103	.3	9.0	78.3	10.2	1.8	0.4			2.05
Q	150	1.6	15.5	53.8	19.8	5.8	1.7	0.8	0.5	2.23
R	150	3.7	17.2	37.6	26.3	11.1	3.0	0.7	.3	2.37
S	175	3.3	13.7	28.3	27.0	17.2	7.4	2.5	.8	2.79

[a] Saturation but 60% complete. D_0 was not unequivocably computable and, therefore, was ignored. It was probably about 1%. [b] D_8, 0.2; D_9, 0.1; D_{10}, 0.04. [c] D_8, 0.2; D_9, 0.1; D_{10}, 0.02.

Dew point considerations prevented us from carrying the runs with cyclopentene and 1-hexene to temperatures below 40°. However, a comparison of the results with 1-butene and 1-hexene indicates that the addition of deuterium to these two hydrocarbons proceeds in a nearly identical fashion. At the lowest temperatures, the product appears to be principally 1,2-dideuteroalkane. The mass spectra fragmentation patterns of runs such as B and M are consistent with this assumption. Further evidence is the fact that the mass spectra of two runs at different low temperatures

(A and B, or M and N) are very similar. If alkane-d_2 was a mixture, it is unlikely that the components of the mixture would be formed at similar rates at different temperatures. Further, run A on a less active catalyst at −11° contained 40% unreacted butene. This was almost entirely unchanged 1-butene. From the mass spectrum, 1.4% or less of this butene was butene-*d*.

We have a large number of results of deuterogenation of 1-hexene of which certain typical ones are presented in Table I. The isotopic distribution patterns at 70° and below were readily duplicated. At 125° and at 150°, however, there was considerable variation from run to run. Runs Q and R typify the extremes of such variation

The absolute rates of deuterogenation at the higher temperatures must be very large, all of the deuterogenation must occur in a very small layer of catalyst and some measure of diffusional control might be involved in determining the shapes of the distribution patterns.

C. Attempted Deuterogenation of Acetylenes.—An attempt to add deuterium to 2-pentyne at 27° with a ratio of deuterium to pentyne of 2 and at 40° with a ratio of 4 led to the rapid poisoning of the catalyst. The catalyst was dead for hexane exchange after these runs. We also attempted the deuterogenation of 2-butyne at 100° with a ratio of 3.7. Some product of the addition of deuterium was collected at the beginning of the run but within an hour the catalyst was dead. The initial product of deuterogenation was about 25% *cis*-2-butene, 10% *trans*-2-butene and 65% butane. We did not attempt an isotopic analysis of this material.

D. Double-bond Migration.—If one passes a mixture of 1-hexene and hydrogen or deuterium over an unactivated chromium oxide catalyst at 125°, no reaction of any nature is observed. At 225°, one observes extensive double-bond migration but no hydrogenation. As one increasingly activates the catalyst by the method of paper II, isomerization activity increases, but activity for hydrogenation (and simultaneously for isotopic exchange with hexane) increases much more rapidly. Thus, even on the incompletely activated catalyst of run A (Table I, 1-butene at −11°), the rate of deuterogenation is at least 100 times that of double-bond migration.

1-Hexene in a stream of nitrogen was rapidly isomerized at 200° on catalysts which gave 50 to 100% hydrogenation at that temperature. All runs gave almost identical products: 1-hexene, 6%; *trans*-2-hexene, 72%; *cis*-2-hexene, 22%. This may represent equilibrium in this system since the following values have been computed[52] for 227°: 8%, 61% and 31%. Gas chromatography gave no indication of the presence of other hexenes. Since our purposes required analysis for 1-hexene only, this matter was not critically examined and must be left open. We did not establish by test with authentic 3-hexenes that the 3-hexenes might not have coincided with 2-hexenes. One may compute that the 3-hexenes would amount to about 30% of an equilibrium mixture of 1-, 2- and 3-hexenes.[52]

Table II presents results of the incomplete deuterogenation of 1-hexene. Runs T and Y were on catalysts which had been partially activated by treatment below 400°. Runs Z were on a catalyst which was dying and were run successively in the inverse order of listing.

TABLE II

PARTIAL DEUTEROGENATION OF 1-HEXENE

Run	Temp., °C.	Composition of product stream -ane, %	1-ene, %	*trans*-2-ene, %	*cis*-2-ene, %
T	200	2	18	40	40
U	200	62.5	2.5	27	8
V	200	93	nil	5.5	1.5
W	125	48	22	16	14
X	72	65	32.5	1.5	1.0
Y	55	49	49	0.5	0.5
Z3	100	10.5	62.5	7.5	19.5
Z2	74	15	68	5	12
Z1	50	70	22	5	3

The degree of isotopic exchange of the unhydrogenated olefins of the runs of Table II was roughly calculable from the mass spectra of the products. However, accuracy is not high since mass 85, hexene-d_1, is not free from interference by the parent less 1 and parent less 2 peaks of hexane and hexane-d_1. In run U, the ratio of hexene-d_0 to hexene-d_1 was about 1. In run V, the ratio was about $^2/_3$. In runs U and V, the amount of hexene-d_0 almost surely exceeded that of 1-hexene. In run W at 125°, the ratio of hexene-d_0 to hexene-d_1 was about 4.5. In runs X and Y at lower temperatures, no exchanged hexenes could be surely detected. The concentration of hexene-d_1, if any, could not have exceeded that of the sum of the 2-hexenes. Thus, at lower temperatures as with 1-butene at −11° (run A, Table I), unreacted hexenes are substantially unexchanged and but very slightly isomerized. Furthermore, the isotopic distribution patterns of the alkane product of runs W, X and Y were almost identical with equivalent runs on 1-hexene on the most active catalysts. Thus, the partly activated catalysts seem to differ from the most active catalysts only in total activity.

On the dying catalyst at 50° (run Z1), behavior was somewhat different. The amounts of 2-hexenes are larger and isotopic exchange of olefin is detectable. In this run, 2-ene/1-ene = 0.35 and ene-d_1/ene-d_0 = 0.2.

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(52) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).