Reactions between Hydrocarbons and Deuterium on Chromium Oxide Gel. III. Isotopic Exchange between Deuterium and Cycloalkanes

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This paper reports investigation of isotopic exchange on a chromia catalyst between deuterium and these various hydrocarbons: the cycloalkanes, cyclopropane to cyclooctane, methane, ethane, hexane and 2,3-dimethylbutane. At 200°, the rates of exchange relative to cyclohexane are: cyclopropane, 50; ethylcyclobutane and cyclooctane, 5; ethane, 0.13. The others fall in the range, 1 to 3, except for methane which is about twice ethane. The activation energies of exchange of cyclopropane and of ethane are 7 and 22 kcal. Cyclopropane exchange can be detected even at 25°, and, at 100°, ring opening with an activation energy of 12 kcal. becomes detectable. The exchange patterns of ethane, 3,3-dimethylpentane and cyclopropane very closely follow the random distribution characteristic of a process which introduces but one deuterium atom per adsorption step. For the others, at about 200°, 95 to 99% of the exchanged molecules follow such a pattern. A few % follow a pattern involving extensive multiple exchange, and with cycloalkanes, a few % appear as excess cycloalkane-d_2 and -d_3.

This paper reports studies of reaction between deuterium and cyclopropane on chromium oxide gel; of relative rates of exchange between deuterium and several alkanes and the cycloalkanes, cyclopropane to cyclooctane; and of the relation of extensive multiple exchange to simple exchange at about 200°.

Experimental

Materials.—Ethylcyclobutane[40] contained about 0.5% hexanes, mainly *n*-hexane. Methylcyclohexane, methane and ethane were Phillips Petroleum Co., research grade; cyclopropane, Ohio Chemical Co. Other hydrocarbons have been described.[35]

Techniques.—We employed the same procedures for cyclopropane as for propane (paper II, section A) including infrared absorption analysis for isotopic exchange. Comparative rates of exchange (sections B, C and D) were measured on more suitable apparatus. Deuterium and gaseous hydrocarbons were purified by passage through liquid sodium–potassium alloy except for methane which was passed over charcoal at −190°. Deuterium was bubbled through the liquid hydrocarbons *via* a porous disk, and the resulting vapor stream was passed through a helix maintained at that temperature which led to the desired deuterium/hydrocarbon ratio. The temperature of the bubbler was kept about 10° above that of the helix.

Comparative rates were measured by inserting a run with a hydrocarbon between two with cyclohexane. Results were accepted only if the cyclohexane runs were essentially identical. All runs in this paper employed the sample of catalyst used for the experiments in sections B and C of paper II (30 g.). The catalyst was occasionally reactivated. Mere treatment with a stream of hydrogen or deuterium at 300° usually led to adequate reactivation.

At the conclusion of the runs on this catalyst, a run like the cyclohexane standardizing runs in section D was performed in which a cyclohexane–thiophene mixture was placed in the saturator. The flow rates of deuterium and hydrocarbon were 24 and 12 millimoles per hour and the thiophene/cyclohexane ratio was about 0.02. Even after 8 hr., no thiophene had appeared in the exit stream. Clearly thiophene is very strongly retained by the catalyst. The degree of exchange of cyclohexane dropped slowly during the run and was about 0.3 of the initial at the termination of the run. The general characteristics of the isotopic exchange patterns were unchanged.

An aliquot of the catalyst was examined by X-ray fluorescence analysis. It contained about 40 parts per million of iron, 5 of nickel, less that 5 of cobalt and about 2000 parts of sulfur. The catalyst was still black. However, upon grinding, it changed to olive green. Both the ground and unground catalyst gave identical X-ray diffraction patterns characteristic of microcrystalline *α*-chromia of a particle size of roughly 200 Å.[50]

Mass spectrographic analyses were obtained on the Consolidated instrument at the Institute of Gas Technology,

(50) The authors are indebted to the Whiting Research Laboratories of the Standard Oil Company (Indiana) for these X-ray determinations.

Chicago. High pressures and high ionizing currents were used to obtain maximum sensitivity.[2]

A. Cyclopropane.—Results are presented in Table I. Cyclopropane flow rates were about 8 millimoles per hour (for 30 g. of catalyst) and the deuterium/hydrocarbon ratio was about 2.6. Propane was determined by gas chromatography using a column of tricresyl phosphate on fire brick. The runs were made in the sequence given. The run preceding A was a standardizing run with propane at 200° following reactivation of the catalyst. The catalyst was at about the same activity level as that obtaining in paper II, Table V.

TABLE I

REACTIONS OF CYCLOPROPANE

Run	Temp., °C.	Deuteration[a], %	Propane, %
A	100	37	1.2
B	75	17.6	0.4
C	50	7.8	0.0
D	100	34	1.6
E	25	3.2	0.0
F[b]	200	..	41.6
G	175	..	18.8
H	150	..	7.4
I	100	..	1.5

[a] Expressed as % C_3H_5D assuming all deuterium appears in this species, analysis by infrared at 4.4 μ. [b] This and subsequent runs employed hydrogen.

Cyclopropane undergoes isotopic exchange many times more rapidly than any other hydrocarbon which we have examined. The runs A-E lead to an activation energy of about 7 kcal., a value much below that of propane, 15 kcal. (paper II, section B). At 100° and above, hydrogenolysis to propane becomes significant. Runs F–I lead to an activation energy of 12 kcal. for the hydrogenolysis.

Hydrogenolysis must lead to some of the measured introduction of deuterium in runs A, B and D. In activation energy computations, we corrected observed deuteration by assuming that hydrogenolysis with deuterium leads to $C_3H_6D_2$. We do not know whether or not this is correct but an error in this assumption would not affect the computed activation energy very seriously.

The value for cyclopropane in Table I of paper I depends upon a run at 77.5° in which the product contained 87.8% of unexchanged cyclopropane by mass spectrographic analysis. The isotopic

TABLE II

ISOTOPIC EXCHANGE OF ETHANE

Run	Hydrocarbon	Temp., °C.	Deuterium flow, mmole/hr.	Rate	Alkane d_0, %	Alkane d_1, %
J	Cyclohexane	200	24.5	See Table III		
K	Ethane	234.5	21.4	0.00470	97.25	2.68
L	Ethane	261	21.2	.0138	92.25	7.39
M	Ethane	302.5	86.3	.0602	91.36	8.15

exchange was, in fact, present. The pattern resembled that of the hexane run at 235° given in Table IV of the present paper except that the ratio of multiple to simple exchange was about twice as great in the 238° run as in the 235° one. If one corrects for the multiply exchanged species, agreement between runs on the two mass spectrometers is excellent.

Analysis with the Consolidated mass spectrometer at high inlet pressures and large ionizing

TABLE III

ISOTOPIC EXCHANGE PATTERNS OF CYCLOALKANES[a]

Hydrocarbon	Cyclopentane		Cyclohexane			Cycloheptane	Cyclooctane
Temp., °C.	202	235	150	200	235	201	199
D_0[b]	93.1 (93.03)	79.2	95.6	95.7 (95.62)	79.6	86.8 (86.75)	74.7 (74.33)
D_1	6.30 (6.37)	17.5	3.79	4.04 (4.174)	16.3	11.5 (11.78)	19.3 (20.23)
D_2	0.242 (0.197)	2.00	0.258	0.143 (0.083)	2.79	0.922 (0.743)	2.89 (2.58)
D_3	.024 (0.004)	0.205	.067	.013 (0.001)	0.549	.061 (0.029)	0.379 (0.196)
D_4	.023	.067	.025	.006	.097	.014 (0.001)	.055 (0.011)
D_5	.022	.066	.019	.006	.031	.012	.022 (0.001)
D_6	.027	.083	.019	.006	.028	.013	.021
D_7	.033	.112	.019	.010	.029	.015	.024
D_8	.045	.183	.020	.008	.038	.018	.027
D_9	.086	.291	.025	.007	.047	.023	.031
D_{10}	.138	.285	.034	.012	.079	.024	.037
D_{11}			.049	.017	.161	.032	.039
D_{12}			.058	.039	.220	.048	.039
D_{13}						.124	.086
D_{14}						.361	.203
D_{15}							.636
D_{16}							1.461
Multiple exchange, %	.40	1.2	.27	.12	.66	.69	2.7

[a] Numbers in parentheses are the random distributions computed with exclusion of extensive multiple exchange. Flow rates about 24 and 12 millimoles of D_2 and hydrocarbon per hour except 5 and 2.5 for cyclohexane at 150°. [b] D_0–D_{16} expressed as per cent. values.

distribution followed the random pattern reasonably well. No extensive multiple exchange could be detected.

B. Exchange of Ethane.—Table II presents the results of the exchange of ethane at a deuterium/ethane ratio of 2.0. The runs were preceded and followed by agreeing control runs with cyclohexane. Rates are computed by the conventional procedure for isotopic exchange reactions using the equation appropriate to a flow reactor,

$$- \text{rate} = LX^{eq} \ln (1 - X/X^{eq}) \qquad (1)$$

where L is the space velocity, X the fraction of the hydrogen atoms in the alkane which have exchanged, and X^{eq}, the fraction at equilibrium, here 0.4. Since we are concerned only with relative values, L is arbitrarily set equal to unity in runs K and L.

The conventional plot gives an activation energy of 21.7 kcal. No sign of extensive multiple exchange could be detected in any ethane run. Ethane-d_4, -d_5 and -d_6 were each less than 0.01%.

C. Exchange of Alkanes and Cycloalkanes.—Tables III and IV present isotopic distribution patterns of the products of runs with several cycloalkanes and alkanes at 150–235°. In the analysis of similar runs on the Westinghouse mass spectrometer (paper II), no extensive multiply exchanged species could be detected since that instrument has a limit of sensitivity of about 0.1%. Reexamination of the hexane run at 238° of Table II in Paper II showed that extensive multiple

TABLE IV

ISOTOPIC EXCHANGE PATTERNS OF ALKANES[a]

Hydrocarbon	n-Hexane		2,3-Dimethyl-butane
Temp., °C.	200	234	235
D_0[d]	88.7 (88.65)[b]	68.2 (68.11)[b]	78.7 (78.60)[c]
D_1	10.5 (10.50)	26.2 (26.17)	18.3 (18.53)
D_2	0.574 (0.559)	4.51 (4.524)	2.08 (2.003)
D_3	.029 (.018)	0.527 (0.464)	0.182 (0.131)
D_4	.012 (.0004)	.062 (.031)	.029 (0.006)
D_5	.029	.047 (.001)	.062
D_6	.019	.038	.074
D_7	.021	.038	.070
D_8	.022	.039	.078
D_9	.028	.053	.051
D_{10}	.028	.065	.047
D_{11}	.030	.070	.047
D_{12}	.047	.075	.076
D_{13}	.019	.064	.092
D_{14}	.016	.036	.086
% Multiple exchange	.28	.71	.73

[a] Numbers in parentheses are the random distributions computed with exclusion of extensive multiple exchange. [b] 10 exchangeable hydrogen atoms assumed. [c] 12 exchangeable hydrogen atoms assumed. [d] D_0 –D_{14} expressed as per cent. values.

currents always showed the presence of small amounts of multiply exchanged species except with methane, ethane, 3,3-dimethylpentane and cyclopropane.

The accumulation of data for section D required a number of runs on cyclohexane at 200°, all on the same catalyst. There was considerable variation in the relative amount of extensive multiple ex-

change. The cyclohexane run at 200° in Table III represents the least degree of multiple exchange. Other runs gave up to 2.5 times as much multiple exchange relative to simple exchange.

With hexane, the relative degree of multiple exchange definitely increases with temperature (paper II, Table I). To within the uncertainty caused by the variability in multiple exchange, the ratio of multiple exchange to simple exchange is independent of temperature in the range 150–235° for cyclohexane, cyclopentane (Table III) and methylcyclohexane.

As shown in Tables III and IV, multiple exchange amounts to but a few % of total exchange. Most of the exchange follows rather well the random pattern characteristic of simple exchange (see paper II).

However, more detailed examination shows that D_2 and D_3 are often too large. With alkanes the excess is so small that we cannot be sure that it is real (see Table IV). With cycloalkanes (Table III), D_2(obsd.) − D_2(comp.) which we shall call ΔD_2, amounts to a few % of total exchange.

The run for cyclohexane at 200° in Table III represents about the average ratio of ΔD_2 to total exchange in a series of cyclohexane runs. In one, ΔD_2 and ΔD_3 were zero. In certain others they were larger than shown in Table III. Variability in ΔD_2 did not seem to correlate with variability in relative degree of extensive multiple exchange. We do not understand the origin of these variabilities.

Methylcyclohexane gave patterns similar to those of cyclohexane in Table III. With both, there is some suggestion that the relative values of ΔD_2 and ΔD_3 decline as temperatures are raised in the range 150–234°. However, variability in relative ΔD_2 is too large for us to be sure of this.

Thus, at temperatures of about 200° we observe a major process leading to simple exchange, a minor process leading to small excess amounts of D_2 and D_3 and a minor process leading to extensive multiple exchange. For cyclopentanes and higher cycloalkanes, the activation energies of both minor processes must lie within a few kilocalories of the value for the major process, about 16 kcal.

Neither minor process is likely to involve *desorbed* benzene as an intermediate in the case of cyclohexanes since the activation energy for any such process must at least equal the heat of hydrogenation of benzene, about 39 kcal., provided that the rate of hydrogenation of benzene does not decrease with increasing temperature. Further, neither benzene nor toluene could be detected by gas chromatography in the cyclohexane and methylcyclohexane runs.

At 200° and at 235°, ethylcyclobutane gives an isotopic exchange pattern of the type: characteristic declining concentrations of species d_1 to d_4 (following the random pattern); low concentrations of species d_4 to d_{12}; somewhat lower concentrations of species one to four mass units greater than C_6D_{12}. These last species must result from a

small amount of ring opening, and we cannot exclude the possibility that all species d_4 to d_{12} are associated with ring opening.

The 235° run was also analyzed using the peaks resulting from loss of a methyl radical. The results are consistent with the assumption that the $\overline{\text{CH}_3}$-group and the $\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_3}$-group were exchanged to about the same extent.

D. Relative Rates of Exchange of Hydrocarbons.—Table I of paper I presents rates of exchange of a series of alkanes and cycloalkanes relative to cyclohexane. Because of the variation in the amount of cyclohexane-d_2, cyclohexane was not the best possible choice of reference compound. However, most of the data involved in the table had been accumulated before this variation became evident. In most cases, we estimate that the relative values suffer intrinsic errors in measurement of about ± 15%.

The value for cyclopropane involved an extrapolation from 77.5° assuming an activation energy of 7 kcal. Ethane involved an extrapolation from 234.5° using an activation energy of 21.7 kcal. Some of the other values required small corrections for slight changes in catalyst activity during a series, for slight differences in flow rates or for slight departures of temperatures from 200 or 235°. Their relatively low vapor pressures would not permit cycloheptane and cyclooctane to be run at the usual deuterium/hydrocarbon ratio of 2.0 because a water-bath was used about the saturator which established the ratio. They and their standard cyclohexane runs were run at a ratio of 14.

Relative rates were determined by

$$\text{relative rate} = \log X_6/\log X_6^0$$

X_6 is the fraction of alkane-d_0; X_6^0 is the fraction of cyclohexane-d_0. This relation ignores the effect of isotopic dilution but correction for this would involve no significant changes in the relative rates.

The relation given above gives relative rates of exchange of *molecules*. One might wish to correct for the fact that cyclooctane contains four times as many hydrogen atoms per molecule as methane. This can readily be done for most of the listed hydrocarbons by multiplying by the ratio, 12/(number of hydrogen atoms per molecule). However, ethylcyclobutane, hexane, 2,3-dimethylbutane and methylcyclohexane have more than one kind of hydrogen atom and it is not clear just how this correction should be performed. The values in parentheses give the values corrected for the number of hydrogen atoms. Rather arbitrarily, ethylcyclobutane and hexane are assumed to have nine equivalent exchangeable hydrogen atoms and dimethylbutane, twelve.[51] Listed differences in relative rate between 200 and 235° are smaller than possible errors in measurement except for ethane for which a larger than average activation energy of exchange was definitely established.

(51) The theory of such corrections is treated by S. W. Benson, THIS JOURNAL, 80, 5151 (1958).