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Reactions between Hydrocarbons and Deuterium on Chromium Oxide Gel. II. Isotopic Exchange of Alkanes

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Chromium oxide gel develops significant catalytic activity for isotopic exchange between alkanes and deuterium only after it has been heated above 300°. A treatment temperature of about 470° results in maximum activity. Higher temperatures lead to declining activity. Exchange is readily measurable on an optimally activated catalyst at 200°. Two isotopic exchange processes occur simultaneously. The predominant one leads to the exchange of one hydrogen atom per period of adsorption; the minor one leads to extensively exchanged alkane. With hexane, the fraction of total exchange represented by the minor process increases throughout the temperature interval 200–350°. The general characteristics of isotopic exchange including activation energy are independent of the degree of activation of the catalyst. A primary hydrogen atom in propane exchanges at least six times as rapidly as a secondary one and primary hydrogen atoms in hexane exchange more readily than secondary ones. Correspondingly, neopentane exchanges somewhat faster than propane. The activation energies for exchange of propane and neopentane, 15 kcal., are essentially the same as that for hexane, 16 kcal.

This paper reports the results of isotopic exchange between deuterium and a series of alkanes on chromium oxide gel.

Experimental

Materials.—Chromium oxide gel was prepared by the hydrolysis of urea dissolved in a solution of chromium nitrate: A solution of 60 g. of chromium nitrate enneahydrate and 60 g. of urea in 4 liters of water is maintained at about 95°. After several hours, the gel precipitates abruptly. After a further ten minutes, the solution is allowed to cool and the gel is washed repeatedly by decantation, isolated by filtration, dried in air at 110° and, *in vacuo*, at 170° and finally crushed and sieved to 20–40 mesh.

Propane was Phillips Petroleum Company, research grade. Hexane was Phillips pure grade. The preparation of 3,3-dimethylpentane has been described.[35] Propane-1-*d*, propane-2-*d* and hexane-1-*d* were made from the corresponding alkyl bromides *via* the Grignard reagents and heavy water. *Neo*pentane was kindly provided by Professor Herman Pines.

Experimental Procedure.—Mixtures of deuterium (Stewart Oxygen Company) and hydrocarbon vapor were prepared by passing deuterium through a saturator containing the hydrocarbon. The saturator was maintained at an appropriate temperature. Mixtures of propane and deuterium were prepared by mixing the gases. Liquid hydrocarbons were deaerated *in situ* before the vapor stream was started over the catalyst. Unless otherwise stated, the deuterium–hydrocarbon ratio was 2.0 and the flow rate was 0.65 g. of hydrocarbon per hour per g. of catalyst.

After passage over the catalyst, the hydrocarbons were condensed in a cold trap and analyzed. The carbon–deuterium band at 4.6 microns was used to select samples of an appropriate degree of exchange for mass spectroscopy. With hydrocarbons which are gases at room temperature, it was also used for a quantitative measure of exchange. For this use, the infrared spectrometer (Baird Associates) was calibrated with propane-1-*d* and propane-2-*d*. Absorption at 4.6 microns was identical for the two hydrocarbons. Exchanged propanes were analysed by infrared using the 4.6 micron band for total deuterium, the 14.3 band for propane-1-*d* and the 15.0 band for propane-2-*d*. Mass spectrometric analyses were performed on a Westinghouse instrument in the Department of Chemical Engineering at this university.

Hexane was the most thoroughly investigated alkane. Its exchange with deuterium was used as the criterion of catalyst activity except in exchange studies involving hydrocarbons which are gases at room temperatures, in which case, propane exchange was employed.

Experimental Results

A. Higher Alkanes.—Chromium oxide gel after drying at 170° does not cause isotopic exchange between hexane and deuterium at 175°. If the catalyst is treated in a stream of nitrogen at successively higher temperatures and if the exchange activity is measured at each higher temperature, activity is first detected at 300°. Under such conditions, 11% of monodeuterated hexane was observed. Further increase in temperature raises the activity. Maximum activity is developed by treatment at about 470° under which conditions about 11% of monodeuterated hexane results from exchange at 200°. After pretreatment to 550°, a temperature of 225° is required for this degree of exchange.

Typical isotopic exchange patterns are shown in Table I. The first two runs are on a catalyst of low activity. Activity in the third run is higher and that in the fourth run, still higher.

TABLE I

ISOTOPIC EXCHANGE PATTERNS

	Hexane	Hexane	Hexane	Hexane	3-Methylhexane
Temp., °C.	360	318	301	248	345
% D_0	51.9	83.2	51.4	64.2	40.9
D_1	28.9	13.0	33.2	29.4	29.7
D_2	8.3	1.3	10.5	6.2	10.9
D_3	1.9	0.2	2.3	0.9	3.6
D_4	0.9	.2	0.4		2.2
D_5	.8	.2	.3		1.45
D_6	.9	.3	.3		1.45
D_7	1.0	.3	.3		1.45
D_8	1.1	.3	.3		1.45
D_9	1.1	.3	.3		1.45
D_{10}	1.0	.2	.5		1.45
D_{11}	1.0	.2			1.1
D_{12}	0.9	.2			1.1
D_{13}					0.7
D_{14}					.7
D_{15}					.4

The runs in Table I show that two types of exchange processes occur simultaneously. The major process involves the exchange of a few hydrogen atoms per molecule; the minor process involves the exchange of many. With greater sensitivity, small quantities of extensive multiple exchange can be detected in the run at 248° (paper III, Table IV). It is apparent that the relative amount of extensive multiple exchange of hexane increases with increasing temperature.

Table III of paper III will show that both exchange processes also occur with cycloalkanes. However, our runs with 3,3-dimethylpentane (Table II) disclosed no evidence for any extensive multiple exchange.

TABLE II

ISOTOPIC EXCHANGE PATTERNS OF HEXANE AND 3,3-DIMETHYLPENTANE

Temp., °C.	% D_0 Exp.	% D_0 Calcd.	% D_1 Exp.	% D_1 Calcd.	% D_2 Exp.	% D_2 Calcd.	% D_3 Exp.	% D_3 Calcd.	% D_4 Exp.	% D_4 Calcd.
					Hexane					
248	60.3	60.7	31.5	30.9	7.3	7.3	1.0	0.8	...	0.1
238	81.8	81.9	16.6	16.5	1.6	1.5	...	0.1		
224	88.6	88.7	10.8	10.7	0.6	0.6	...	....		
198	92.6	92.5	7.0	7.2	0.4	0.3	...	....		
199	95.6	95.5	4.2	4.4	0.2	0.1	...	....		
					3,3-Dimethylpentane					
330[a]	11.1	9.9	24.2	24.6	27.5	28.7	20.3	20.8	10.5	10.6
260[b]	63.6	61.7	28.4	30.3	6.3	6.9	1.1	1.0	0.4	0.1
230[c]	85.6	85.8	13.1	13.2	1.07	0.94	0.19	0.041	0.08	0.001

[a] % D_5, exp. 4.2, calcd. 3.9; % D_6, exp. 1.5, calcd. 1.1; % D_7, exp. 0.5, calcd. 0.25; % D_8, exp. 0.0, calcd. 0.04. [b] % D_5, exp. 0.2, calcd. 0.0; % D_6, exp. 0.1. [c] % D_5, exp. 0.03, calcd. 0.000; % D_6 0.03.

TABLE III

ENERGIES OF ACTIVATION FOR ISOTOPIC EXCHANGE OF HEXANE

Pretreatment temp., °C.	E_a, kcal./mole	Relative activity
350	15 ± 1	5.5
480	16	48
500	17	46
550	16	32

Results on hexane at lower conversions (Table II) suggest that the major process involves exchange of but one hydrogen atom per adsorption step. If such is the case, the isotopic distribution would follow the random patterns given by the equation[21]

$$P_\alpha = \frac{n!(\%D/\%H)^\alpha}{(1 + \%D/\%H)^n\alpha!(n - \alpha)!}$$

where P_α is the probability of a molecule which contains α deuterium atoms, n is the total number of exchangeable hydrogen atoms and %D/%H is the average ratio of deuterium atoms to hydrogen atoms in the exchanged hydrocarbon. This equation is tested in Table II. Agreement is excellent. We assume here that all fourteen hydrogen atoms in hexane and all sixteen in 3,3-dimethylpentane are equivalent but, at these levels of exchange, the results would be very similar if one were to confine exchange to the primary hydrogen atoms.

As judged by gas chromatography, the products of the isotopic exchange of 3,3-dimethylpentane at 330° (Table II) and of a hexane run at 350° were unisomerized.

As shown in Table III, we examined the effect of catalyst pretreatment upon the activation energy of isotopic exchange between hexane and deuterium. After each pretreatment, rate constants for the monodeuteration process were determined at four temperatures in the range 199–247°. For the least active catalyst, the range was 270–350°. Good Arrhenius plots resulted. The relative activities in Table III are those obtained by extrapolation to 261°.

B. Exchange of Lighter Hydrocarbons.—The sample of chromium oxide employed for these experiments weighed 30 g. in contrast to the 2–4 g. samples employed in the experiments previously described. One sample was used for 244 runs. It was reactivated periodically for a total of 37 times by passing nitrogen over the catalyst at 475°, cooling to 300° with nitrogen flow and exposing to hydrogen or deuterium flow at 300° for 20 minutes. The catalyst was then evacuated and cooled to room temperature. The catalyst was about as active at the end of this study as at the beginning.

Initial activity after reactivation varied unpredictably from the average activity by a factor of about two. Usually one observed a drop in activity of about 20% between the first and second runs, following which the drop in activity was slower or negligible. The relative initial drop in activity seemed to be augmented in those instances where initial activity was unusually high. Any exposure to air results in a large decline in activity. We are not sure whether the slow decline in activity usually associated with isotopic exchange runs is inherent or the result of small amounts of poisons.

Table IV exhibits successive isotopic exchange runs on propane under two conditions of catalyst activation, the first three runs at slightly above average activity, the second three at low activity. In computing relative rate constants for the determination of activation energies, we have used first order kinetics with the assumption that only the primary hydrogen atoms exchange. The assumption that all hydrogen atoms are exchangeable would change the values but little. In these experiments, the deuterium/propane ratio was 4.7 and the propane flow rate, 115 cc. per hour, much less than in the previously described experiments.

TABLE IV

ISOTOPIC EXCHANGE OF PROPANE

Temp., °C.	Deuteration[a] %	Activ. energy, kcal./mole
200	12.0	
225	25.4	15.1
200	11.0	
200	3.2	
250	13.9	14.7
200	3.1	

[a] From infrared and expressed as % C_3H_7D with the assumption that all deuterium occurs in this species.

Thus, the activation energy for propane exchange is about 15 kcal. and differs little, if at all, from that of hexane. The actual isotopic distribution patterns determined mass spectrographically were of the random pattern described for hexane.

Table V exhibits the results of a series of successive runs with neopentane and propane. From runs D, E and F, neopentane reacts about 1.7 times as fast as propane, but this figure is only approximate since deuteropropane calibrations were used for neopentane in our infrared analysis. Run C and the average of runs B and D lead to an activation energy of 14.7 kcal./mole. Although this value is not very good because of the rather large difference between runs B and D, it does indicate that the activation energy of neopentane is close to that of propane.

TABLE V

ISOTOPIC EXCHANGE OF PROPANE AND NEOPENTANE

Run	Hydrocarbon	Temp., °C.	Deuteration, %
A	Propane	200	10.6
B	Neopentane	200	13.7
C	Neopentane	225	26.4
D	Neopentane	200	10.7
E	Propane	200	6.0
F	Neopentane	200	9.7

C. Relative Rates of Exchange of Primary and Secondary Hydrogen Atoms.—A number of isotopic exchange runs on propane were analysed by infrared absorption for propane-1-*d*, propane-2-*d* and total deuterium. Results are presented in Table VI. The catalyst was reactivated before runs I, K (at 250°, not shown because of too extensive exchange) and M. In no case could any propane-2-*d* be detected. We added 1.05% propane-2-*d* to one reaction product and determined, following this, 1.3% of propane-2-*d*. We believe that no more than 0.8% of propane-2-*d* could have been present in any reaction product. The difference between the % propane-1-*d* and % deuteration should represent deuterium present in di- and trideuterospecies. As a check upon this, we computed the total deuteration which should accompany each amount of propane-1-*d* assuming random distribution among the six primary hydrogen atoms. As will be seen, the agreement is reasonably good. It is difficult to estimate possible interference of multiply deuterated species in the infrared analysis. However, it seems reasonable to conclude that a primary hydrogen atom in propane exchanges at least six times as fast as the secondary one.

Experiments involving the competitive dedeuteration of propane-1-*d* and propane-2-*d* with hydrogen gave results consistent with this, but we were able to achieve higher sensitivities with the runs involving deuteration of propane.

TABLE VI

PRIMARY AND SECONDARY HYDROGEN ATOM EXCHANGE IN PROPANE

Run	Temp., °C.	Propane-1-*d*	Deuteration	Deuteration (calcd.)
G	250	11.9	13.5	13.3
H	250	7.7	8.3	8.3
I	250	25.9	33.6	35.0
J	200	5.5	6.5	5.9
L	225	21.8	26.2	27.5
M	200	17.0	20.8	20.0
N	200	11.8	13.6	13.2
O	200	11.0	12.0	12.2
P	225	20.3	25.5	25.1
Q	200	9.5	11.0	10.4
R	250	27.2	36.1	37.6

One sample of exchanged propane (D_1, 12.3%; D_2, 1.1%) along with the monodeutero standards was examined mass spectrographically by Mr. S. Meyerson of the Whiting Research Laboratories of the Standard Oil Company (Indiana). It was not possible to set definite figures on the relative exchange at the primary and secondary positions, but the ratio of peaks at masses 31 and 46 for the dideutero species and at 30 and 45 for the monodeutero indicated that the deuterium atoms distinctly predominated in primary positions.

Our examination of the mass spectrographic cracking patterns of exchanged hexanes containing about 10% D_1 led to a similar result. If the amyl carbonium ion results from expulsion of a terminal methyl radical, then hexane-1-*d* should give, with equal probability, a light carbonium ion and a monodeutero one if one assumes no isotope effect upon the rupture. The amyl carbonium ion derived from hexane-2-*d* should always contain one deuterium atom. Similar consideration applies to the butyl carbonium ion and hexane-3-*d*. Analysis on this basis indicated a slight preference for exchange at the primary position. However, analysis of hexane-1-*d* by this process gave 30% of hexane-2-*d* plus hexane-3-*d*. If we correct our analysis for this isotope effect, it appears that a primary hydrogen atom in hexane exchanges about five times as fast as a secondary one. Possible error in this figure is large but it does confirm the results for propane.