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The Reactions of Hydrocarbons on Transition Metal Catalysts in the Presence of Tritium

I. The Labeling of Cyclohexane by Exchange with Tritium Gas on Raney Nickel

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The reaction of liquid phase cyclohexane at 60° with low-pressure tritium adsorbed on Raney nickel yielded labeled cyclohexane, benzene, and a trace of cyclohexene, the latter two being present at very low mass concentrations. The proportion of tritium incorporated (18% to 98%), the rate of incorporation of tritium, and the final distribution of activity between cyclohexane (50% to 99%) and benzene (50% to less than 0.1%) varied with the batch of catalyst. This variation is explained in terms of the distribution of the tritium between accessible and inaccessible catalyst sites.

Cyclohexane of high radiochemical purity can be consistently produced by the use of high tritium to catalyst weight ratios (1800 millicuries / gram of catalyst dry weight) and long exchange times (100 hr). The results are not affected by low concentrations of benzene impurities (less than 0.1%) nor is the radiochemical purity of the product appreciably affected by the storage of the catalyst under ethanol for several months.

INTRODUCTION

Following our preliminary report of labeling of cyclohexane by exchange with tritium gas on a Raney nickel catalyst (*1*) we now report a more detailed study of this system under varying conditions carried out for the purpose of developing an efficient method of labeling cyclohexane.

EXPERIMENTAL

Materials. The cyclohexane (Riedel de Haen) was purified by gas-liquid chromatography on a column packed with 40% benzyldiphenyl on Celite , when it revealed no impurities on analysis with columns packed with silicone oil (May and Baker) and benzyldiphenyl (May and Baker) on Embacel, the limit of detection of an impurity such as benzene being of the order of 0.002%.

The tritium gas was obtained from Oak Ridge National Laboratory (purity 99%) and contained approximately 5% helium-3 from tritium decay.

Preparation of catalyst. A Raney nickel catalyst was prepared from a 50:50 nickel-aluminum alloy (B.D.H.) according to the method of Dominguez *et al.* (*2*). The catalyst was stored under ethanol usually at -15°C. The catalyst slurry was pumped dry and heated to 300°C for 3 hr under vacuum to remove adsorbed materials.

Reaction procedure. The degassed catalyst sample (0.30 ± 0.04 g dry weight at the end of the reaction, unless otherwise stated) was exposed to 63 mc (unless otherwise stated) of tritium gas initially at a pressure of approximately 0.1 mm. Rapid adsorption of more than 95% of the tritium gas occurred as observed by the pressure drop in the system, the final tritium pressure being about 0.001 mm to 0.005 mm. (Accurate estimates of this pressure were unobtainable in the presence of the helium-3.) The catalyst was then dropped into cyclohexane (1.0 ml) previously degassed by repeated freezing and pumping. The sealed reaction tube was warmed to the reaction temperature of 60°C.

Samples were withdrawn from the reaction mixture by decantation into a constricted side limb which was sealed off from the reaction mixture while both sample and reaction mixture were held at liquid air temperature.

Analysis of products. Samples (2 μl) were analyzed immediately after opening to the atmosphere by injection of liquid aliquots into a Pye gas-liquid chromatograph using argon as carrier gas. A 4 ft column packed with 10% benzyldiphenyl on Embacel was used at 25°C as the standard column but the analyses were confirmed with similar columns packed with silicone oil and di(2-cyanoethyl) ether on Embacel. On the standard column, cyclohexane, cyclohexene, and benzene peaks were completely resolved.

Four percent of the effluent from the column was passed through a Lovelock detector and the remainder through a 10 ml ionization chamber connected to a vibrating reed electrometer coupled with a pen recorder. Mass and radioactivity chromatograms were thus obtained simultaneously.

RESULTS

The dependence of the product distribution on the following were considered: (1.) variations between batches of catalyst; (2.) ratio of amount of tritium to catalyst weight; (3.) presence of benzene impurity; (4.) storage age of catalyst.

No major byproducts were detected with the Lovelock detector, but traces of benzene the only by-product detected, were occasionally observed at a concentration of about 0.004%, the concentration being always less than 0.01%.

The products observed with the activity detector were cyclohexane and benzene and in some cases a small amount (always less than 1% of the incorporated activity) of cyclohexene.

Variations in Batches of Catalyst

Although the same method of preparation was used in each case a considerable variation between batches of catalyst was observed, as shown in Table 1. From the results catalysts were graded into three functional classes (some catalysts being intermediate between classes) as follows:

Class A Catalysts. About 20% of the total tritium on the catalyst was incorporated mainly into cyclohexane and benzene in under 1 hr and no further reaction was observed over a period of several hundred hours.

Class B Catalyst. Some 10% to 20% of the

TABLE 1

ACTIVITIES OF PRODUCTS FROM CYCLOHEXANE WITH THREE CLASSES OF RANEY NICKEL

Catalyst class	Exposure time (hr)	Total activities of products: Cyclohexane (mc)	Benzene (mc)	Cyclohexene (mc)	Percentage of starting tritium incorporated into organic products (%)
A	0.25	2.4	1.8	0.02	7
	1	7.9	3.3	0.04	18
	18	7.7	3.4	0.04	18
	95	8.2	3.5	0.04	18
	360	7.9	3.4	0.02	18
B	0.25	0.50	1.4	—[a]	3.0
	1	0.76	3.0	—	6.0
	3.5	2.4	6.9	—	15
	18	5.0	9.1	—	22
	67	45	3.9	—	77
	528	61	0.1	—	96
C	0.25	58	0.40	0.02	93
	1	61	0.49	0.02	98
	18	60	0.42	0.02	97

[a] Indicates activity less than 0.01 mc.

TABLE 2
PRODUCT VARIATION WITH RATIO OF TRITIUM TO CATALYST[a]

W[b] (mc/g)	Percentage distribution of incorporated activity: Cyclohexane (%)	Benzene (%)	Total activity incorporated (mc)	Percentage of starting activity incorporated in organic products (%)
200	24	76	4.1	17
400	45	55	7.7	16
800	48	52	18	19
1000	60	40	24	20
1200	72	28	37	25
1400	82	18	44	26
1600	85	15	61	32
1800	91	9	88	41

[a] Weight of catalyst 0.12 (±0.02) g. Products analyzed after exposure time 20 hr.

[b] W, total tritium (mc) adsorbed on catalyst/gram of catalyst.

total tritium on the catalyst was incorporated into cyclohexane and benzene during the first few hours of reaction and this was followed by a redistribution of the activity into cyclohexane over about 100 hr, together with an increase in total activity of products corresponding to incorporation of most of the remainder of the tritium on the catalyst.

Class C Catalysts. All the tritium on the catalyst was incorporated into mainly cyclohexane in under 1 hr.

We have not been able to correlate these catalyst types with variables in the conditions of preparation.

Ratio (W) of Amount of Tritium to Catalyst Weight

The variation of product distribution with W (mc of tritium/g catalyst) has been studied for catalysts of Class A (Table 2) and class B (Fig. 1), using constant weights of catalyst and cyclohexane.

With both catalyst types the proportion of incorporated activity appearing in cyclohexane increased with increasing W. With Class B catalysts the rate of redistribution of incorporated activity and the rate of incorporation of the more slowly incorporated part of the tritium was approximately independent of W.

Presence of Benzene Impurity

In order to ascertain whether the activity results were dependent on undetectable concentrations of benzene present in the starting material (less than 0.002%) the effect of small amounts of added benzene were checked with the three types of catalyst. Results for catalyst Classes A and C

TABLE 3
ACTIVITIES OF PRODUCTS FROM CYCLOHEXANE CONTAMINATED WITH BENZENE[a]

Catalyst class	Starting benzene concentration (%)	Activities of products: Cyclohexane (mc)	Benzene (mc)	Percentage of starting tritium incorporated in organic products (%)
A	<0.002	8.9	9.0	28
A	0.1	10.0	10.0	31
C	<0.002	61	0.5	97
C	0.01	59	0.4	94
C	0.1	58	2.9	97
C	0.3	42	17	94
C	1.0	16	43	95

[a] Products analyzed after exposure time of 20 hr.

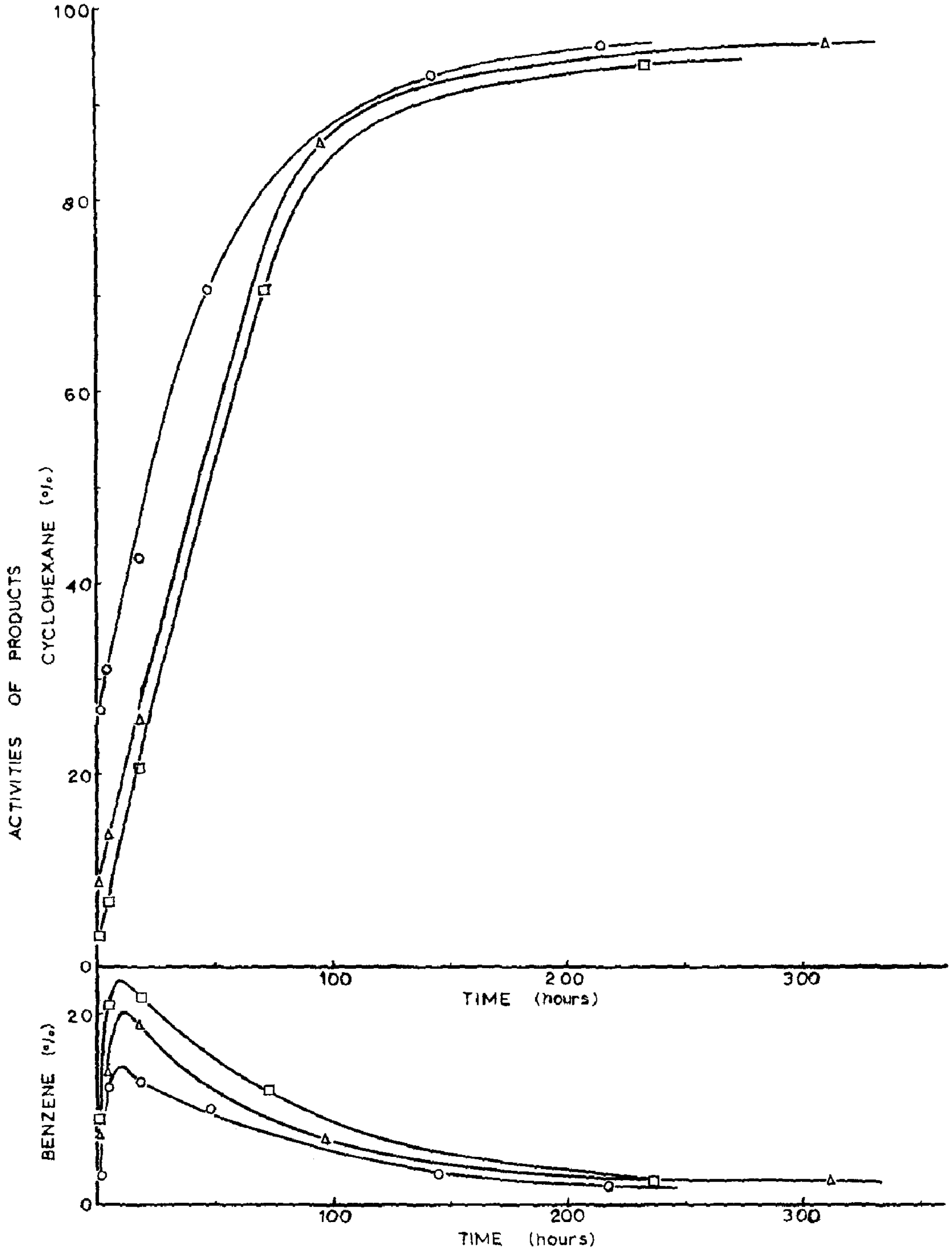

Fig. 1. Product distribution against exposure time for various tritium to catalyst weight ratios on catalyst of Class B. The activities of products are expressed as percentage of total tritium on catalyst at start: □, $W = 200$; △, $W = 800$; ○, $W = 1600$.

TABLE 4
PRODUCT VARIATION WITH STORAGE AGE OF CATALYST[a]

Catalyst stored at −15°C				Catalyst stored at room temperature			
	Activities of products				Activities of products		
Storage time (days)	Cyclohexane (mc)	Benzene (mc)	Cyclohexene (mc)	time (days)	Cyclohexane (mc)	Benzene (mc)	Cyclohexene (mc)
0	28	0.6	.01	0	28	0.6	.01
7	25	1.5	.02	1	19	1.4	.01
13	22	1.6	.02	6	18	1.6	.01
21	23	1.5	.02	20	18	1.1	.01
48	20	1.6	.03	49	15	1.5	.02
119	16	1.8	.02	120	15	1.7	.01
183	15	1.7	.03	184	16	1.8	.02

[a] Products analyzed after exposure time of 20 hr.

are presented in Table 3. On a Class B catalyst a run with 0.1% benzene in the starting material showed insignificant changes in product distribution with time.

On all catalysts benzene concentrations below 0.1% have insignificant effect on product distribution.

Storage Age of Catalyst

A batch of catalyst of Class A was divided into two parts and stored under 1 inch of ethanol, one part at room temperature and the other at −15°C. The results of runs with with cyclohexane at various storage times are presented in Table 4.

The activity incorporated into cyclohexane decreased to approximately half its original value over a period of storage of some 100 days. At room temperature the decrease was initially faster than the decrease at −15°C, an equilibrium catalyst activity being reached after about 30 days at room temperature and of the order of 100 days at −15°C. A slight increase in the benzene activity was also apparent.

DISCUSSION

Variations in Batches of Catalyst

The reason for the variation between batches of catalyst is not clear, as the same method was adopted for their preparation in all cases although slight variations in temperature and stirring rates during preparation were inevitable owing to the large amount of heat and gas liberated in the preparation reaction.

Classes A and B catalysts clearly demand that some (~20%) of the tritium is adsorbed on catalyst sites readily accessible to exchange, and the remainder on sites inaccessible on Class A catalysts and accessible with difficulty on Class B catalysts. Class C catalyst behavior demands that all the tritium is on accessible sites.

The reactions which occurred may be considered in three parts.

(1) An initial rapid uptake of tritium into cyclohexane and benzene.

(2) A subsequent slow uptake of the initially inaccessible tritium on the catalyst either by diffusion of that tritium to catalyst sites where rapid reaction with cyclohexane occurred, or by slow reaction of cyclohexane on the less accessible sites.

(3) A slow redistribution of activity between organic products towards isotopic equilibration when effectively all the incorporated activity appeared in cyclohexane.

Reaction (3) presumably occurs as a result of readsorption of the labeled molecules on the catalyst surface. Because of the low concentrations of labeled species this reaction will necessarily be slower than reaction (3).

The major differences between batches of catalyst may be considered to have resulted from two effects.

(1) A difference in distribution of adsorbed tritium between readily accessible and inaccessible catalyst sites.

(2) A variation in the rates of Reactions (2) and (3). Thus with Class A catalysts

the time for reactions (2) and (3) to occur to a significant extent was greater than 500 hr while for Class B the time was of the order of 10-100 hr. It is noteworthy that, although the rates of reactions (2) and (3) were not equal, on any particular catalyst an increase in the rate of one reaction was always accompanied by an increase in the rate of the other. This suggests that the same catalyst sites were responsible for the two reactions.

Ratio of Tritium to Catalyst Weight (W)

On both Class A and B catalysts a greater concentration of tritium on the surface favored the formation of labeled cyclohexane rather than benzene. This result is to be expected since the probability of a molecule desorbing as cyclohexane rather than as benzene would increase with the concentration of hydrogen on the surface.

The increase in the percentage of total tritium incorporated with increasing surface coverage indicates that the distribution of tritium between readily accessible and inaccessible sites varied with coverage, the proportion of tritium adsorbed on accessible sites clearly increasing with coverage.

Presence of Benzene Impurity

Since benzene concentrations below 0.1% had insignificant effects on the benzene activity in the product it is clear that the benzene activity produced in the runs with pure cyclohexane did not result from exchange of undetectable amounts of benzene in the starting material. Thus benzene molecules became labeled during the same residence on the catalyst as that in which they were produced by dehydrogenation of cyclohexane. From this it can be concluded that the hydrogen retained in the adsorbed species during its dehydrogenation to benzene must be labile in the time of residence of that species on the catalyst.

Storage Age of Catalyst

Over a period of 5 months about a 50% change in the ability of the catalyst to induce exchange was observed. Most of the drop in activity occurred within the first day. Mars, Mond, and Scholten (*3*) reported that greater than 95% of the activity of Raney nickel stored under ethanol at room temperature was retained at 4 months as measured by the ability to promote hydrogenation of phenol. These authors may not have observed the initial drop in activity if their first analysis was performed more than 1 day after preparation or, alternatively, the catalyst may not show this effect in the presence of phenol.

CONCLUSIONS

Although it is not possible to prepare reproducible batches of Raney nickel by the method described it is possible to choose conditions which yield labeled cyclohexane of high purity on all batches of catalyst. These conditions are (a) high tritium to catalyst ratios—of the order of 1800 mc/g, (b) long exposure times—of the order of 100 hr.

The results are not affected by low concentrations of benzene impurities in the starting material, nor is the proportion of the incorporated tritium appearing in cyclohexane (90-98%) appreciably affected by the storage of the catalyst over a period of some months.

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