

## Adsorption and Hydrogenation of Benzene-<sup>14</sup>C Vapor on Raney Nickel

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The adsorption and hydrogenation of <sup>14</sup>C labeled benzene on Raney nickel at room temperature was investigated in the gaseous phase. A fraction of benzene is adsorbed reversibly and for pressures less than 1 Torr, the isotherm is of a Freundlich type. This species does not play a role in hydrogenation. The other fraction of benzene is irreversibly adsorbed and for each molecule, 5.7 hydrogen molecules escape from the surface. The hydrogenation of this species is complete and gives chiefly cyclohexane and traces of benzene. There is much evidence that the ring is not destroyed and that its plane is parallel to the surface. A part of the irreversibly adsorbed <sup>14</sup>C labeled fraction is exchangeable by unlabeled benzene but the two irreversibly adsorbed species are hydrogenated with the same rate-limiting step. The unexchangeable fraction may be a partially dehydrogenated complex, thus presenting a more pronounced degree of linkage than the exchangeable portion which may be a "π-complex" or a "Balandin" type.

### 1. INTRODUCTION

Benzene hydrogenation has often been used to compare hydrogenation catalysts (1-3), though its well-studied mechanism has not been completely elucidated. The results of the kinetic studies show some discrepancies, for example, reaction orders with respect to hydrogen or benzene varying from 0 to 1 (4-9). For cyclohexane dehydrogenation, the hydrogen retarding effect observed by Ross and Valentine (10) and Viswanathan and Yeddanapalli (11), was not noticed by Andreev *et al.* (12). A similar effect, claimed by Herbo (13) for benzene, was not pointed out by Ross and Valentine (10). Most authors acknowledge that these reactions proceed by several sequences on the catalyst surface, but there is no agreement on their number and nature.

In the Balandin theory (14,15), the benzene ring on adsorption is presumed to be parallel to the surface with 6 C-Ni bonds. In this hypothesis, the 111 crystal planes would be more active for adsorption, dehydrogenation and hydrogenation of cyclic hydrocarbons (16).

This fact is partially verified by LEED (17). Using <sup>14</sup>C labeled molecules, Tetenyi and Babernics (18) showed that there is a maximum in the amount chemisorbed at 150°C for some nickel catalysts. Raney nickel exhibits a peculiar behavior since it adsorbs 10 times more benzene at a lower temperature (<100°C). In all the cases, a fraction of the adsorbate can be exchanged by nonlabeled benzene and it is removed by hydrogen to give cyclohexane and benzene. These facts are in agreement with an adsorption in which a fraction of the benzene adsorbs with breakage of the double bonds (19), the other fraction being bonded to the metal following breakage of the corresponding C-H bonds. A measure of the bond number has been made by magnetization experiments and has given a value ranging from 6 to 10 (20) with 8 being a more precise value recently obtained (21). The presence of hydrogen during the benzene adsorption (22), and the easy ex-

change of hydrogen atoms of this reactant with deuterium (23) may confirm a partial dehydrogenation mechanism. These last facts suggest two new possibilities for the adsorption process. The first consists of the formation of a bond between a carbon atom which has lost its hydrogen and the nickel, the ring being perpendicular to the surface (24). In the second, the ring is parallel to the surface (25).

In these published studies there has been such a diversity of methods and catalysts employed that it is difficult to compare the results. We must especially remark that the reversibly adsorbed benzene has not been taken into account and that the catalysts were poorly characterized.

This is not the case for the Raney nickel which has been the object of this study, which was well defined in respect of its texture and structure (26,27). Other authors have measured the activity for benzene hydrogenation in the liquid and the gaseous phase (1,28) and the activity for hydrogen-tritium atom exchange in the cyclohexane molecule (29). As the hydrogen adsorbed on the Raney nickel surface plays a prominent role, it is important to determine its influence on benzene adsorption.

## 2. APPARATUS AND MATERIALS

### 1. The Radiomanometer

In order to work in the presence of both benzene and hydrogen, it is necessary to employ a partial pressure detector. It is very easy to use the  $^{14}\text{C}$  labeled benzene molecule to detect the pressure of this reactant. The total pressure is measured by a commercial quartz spiral gauge. We have also another restraint due to the very high reactivity of Raney nickel when it has been degassed *in vacuo*. Care has been taken to avoid any hydrocarbon vapor coming from greases or rubber joints. In our case, the benzene pressure is proportional to the disintegration rate of  $^{14}\text{C}$

atoms. These are detected by a europium-activated  $\text{CaF}_2$  crystal which has such physicochemical properties that it can be put directly in contact with the gas phase without degassing and dissolving any benzene. This detector also has a good behavior in high vacuum and can measure pressures up to 2 Torr (1 Torr =  $133.3 \text{ N m}^{-2}$ ) with 1% error, as we described earlier (30).

### 2. The Microbalance

The amount adsorbed is measured in a Sartorius balance and weight variations are automatically registered on a chart recorder. For the reasons indicated above, the parts of the apparatus in direct contact with the gas phase are exclusively made of Pyrex glass and metal. The balance enclosure is linked to the radiomanometer and to a quartz spiral pressure gauge. The leak tightness of the assembly is ensured by the means of gold joints and glass-to-metal seals.

Introduction of gases is made by means of stainless steel valves and the mixture is homogenized by a glass circulating pump. Two mercury diffusion pumps are mounted in series and are able to extract and compress the gas into a 6 liter tank where the pressure increase is proportional to the volume removed (26). The mercury vapor is trapped by liquid nitrogen followed by a gold foil trap. A zeolite trap prevents backstreaming of the rotary pump oil.

For all the experiments the temperature was maintained constant in the range of 20–29°C, being stabilized by a thermostated bath.

### 3. The Catalyst

The Raney nickel used is free of alumina and contains 4.7% aluminum metal. Its surface area, measured by the BET method, was  $87 \text{ m}^2 \text{ g}^{-1}$  after treatment *in vacuo* at ambient temperature. In the same conditions, the loop in the nitrogen adsorp-

tion isotherm corresponds to an open porosity where the pores have a mean diameter of 45 Å. The total quantity of hydrogen desorbed under vacuum is 1.65 mmol g<sup>-1</sup> after treatment at 390°C. For all experiments, the samples are first degassed *in vacuo* at ambient temperature until their mass is stabilized. This treatment releases 0.36 mmol g<sup>-1</sup> of hydrogen.

Raney nickel being pyrophoric it is absolutely necessary to keep it from any contact with air. To this end, we introduced the damp sample into the balance after weighing it in a pycnometer. When the vacuum is established in the balance, water is evacuated and causes a fall in temperature which freezes the catalyst slurry. This the pyrophoric metal is protected against oxygen until the vacuum is sufficiently low (10<sup>-6</sup> Torr). The first traces of hydrogen desorbed in these conditions are moistened by water which is trapped at liquid nitrogen temperature. We have verified by mass spectrometry that only hydrogen was pumped into the rough vacuum tank. The same process is used to measure the hydrogen removed by irreversible adsorption of benzene.

For all hydrogenations we used very pure hydrogen, containing less than 20 ppm of O<sub>2</sub>. The labeled benzene was synthesized from BaCO<sub>3</sub> (31). Its purity was checked with a gass chromatograph.

### 3. RESULTS

#### 1. Preliminary Data

The adsorption on Raney nickel under 0.4 Torr of benzene and at a temperature of 24°C is very rapid. It is not completely reversible and, following desorption under high vacuum, 0.077 mmol g<sup>-1</sup> remain adsorbed on the catalyst surface. We observe also that we cannot completely condense the gas in equilibrium with the adsorbate. The noncondensable fraction is not radioactive and the mass spectrograph shows that it is hydrogen, coming either from

benzene decomposition or from the catalyst surface. Thus hydrogen evolved is to be taken into account for the calculation of the amount of benzene adsorbed. The analysis of the condensate by gas chromatography shows that it is composed of 99% benzene and traces of cyclohexane when some hydrogen evolved is present. We have only benzene when there is no hydrogen in the gas phase. So the hydrogen adsorbed on the surface is not able to hydrogenate the benzene at 24°C.

The adsorbed quantities versus equilibrium pressure for a fresh catalyst are shown in Fig. 1. If a first adsorption under a pressure *P* leads us to the point A of Fig. 1 and then if high vacuum is applied, some irreversibly adsorbed benzene remains (point B) while some hydrogen is simultaneously desorbed by pumping. We will place a point B' which has the same ordinate as B, on the same vertical as A to facilitate the demonstration. The adsorption can be repeated for the same equilibrium pressure and leads us to the point C; after pumping, we reach point D (D') and

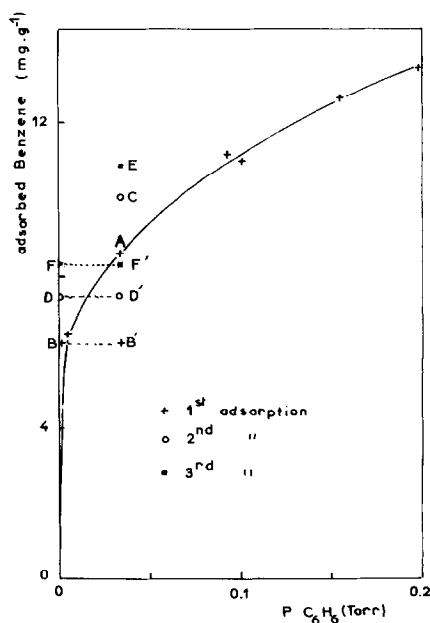


FIG. 1. Benzene adsorption isotherm on Raney nickel at 24°C.

a new quantity of hydrogen is pumped off. We can repeat the adsorption again and reach points E and F (F'). It is sufficient to remove hydrogen by pumping to irreversibly adsorb a new amount of benzene at a given equilibrium pressure. Thus we can increase the irreversibly adsorbed quantity by steps, but their heights are uncontrollable.

### 2. Reversibly Adsorbed Benzene

If we consider Fig. 1, the reversibly adsorbed amounts are represented by the length of the segments AB', CD', EF'. These are equal and consequently the reversibly adsorbed quantity is constant for a fixed pressure.

We have established the isotherm at 24°C. It can be described by the Freundlich equation as a linear plot of  $\log m$  against  $\log P$ , where  $m$  is the weight of reversibly adsorbed benzene and  $P$  the benzene pressure (Fig. 2). These results are in agreement with those obtained by Babernics and Tetenyi (32) for higher temperatures.

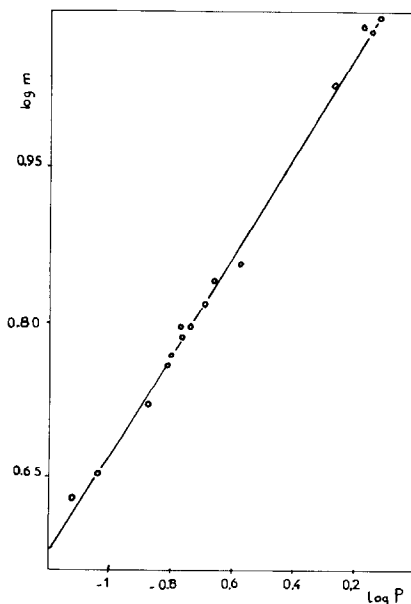


FIG. 2. Benzene reversible adsorption isotherm on Raney nickel at 24°C.

### 3. Irreversibly Adsorbed Benzene

Every time that the balance is evacuated, some hydrogen is evolved from the catalyst and the irreversibly adsorbed quantity of benzene increases during the next adsorption (points B, D, F of Fig. 1). Above a pressure of 0.05 Torr, the extent of the irreversibly adsorbed benzene depends only on the volume of hydrogen removed. Thus it is not possible to have an isotherm. For the first point the determination of the quantity of evolved hydrogen during evacuation of the sample is imprecise. Therefore, we plot in Fig. 3 the differences between the first and the following quantity of evolved hydrogen against the quantity of the corresponding irreversibly adsorbed benzene. The slope of the straight line obtained indicates that one molecule of benzene can be irreversibly adsorbed when 5.7 molecules of hydrogen are removed. As shown below in Sect. 5, the hydrogen removed does not come from the cracking of the benzene molecule, because further hydrogenation changes 90% of the adsorbed benzene into cyclohexane.

We must note that all the hydrogen is

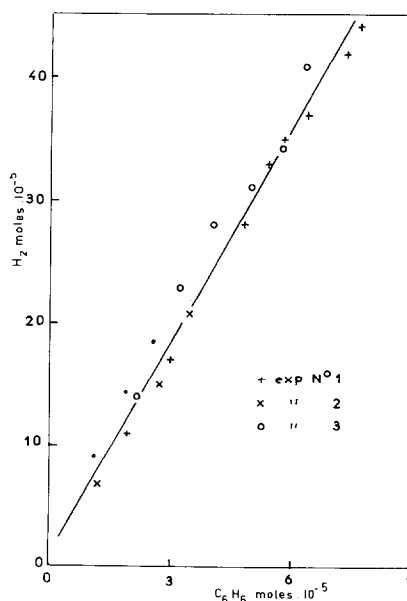


FIG. 3. Quantity of hydrogen removed as a function of irreversibly adsorbed benzene.

not present in the gas phase during the adsorption. A fraction of the evolution of this gas occurs during the pumping operation.

#### 4. *Isotopic Exchange of the Irreversibly Adsorbed Benzene*

We have established that benzene was adsorbed under a reversible and an irreversible form. Tetenyi and Babernics (18) showed that  $^{14}\text{C}$  labeled chemisorbed benzene was exchanged with inactive benzene at  $150^\circ\text{C}$ . We repeated these experiments with greater precision at ambient temperature. When we introduce nonlabeled benzene over the catalyst covered with irreversibly adsorbed benzene, some radioactive gas appears in the gas phase and gas chromatography shows that it is benzene. Only a part of the irreversibly adsorbed reactant is concerned because after repeated and prolonged contacts, the action of hydrogen on the adsorbate gives cyclohexane, a part of which is radioactive. Further, the hydrogen completely removes the benzene from the catalyst surface and a count of radioactivity by liquid scintillation gives a fraction of 27% of labeled product not exchanged.

For confirmation we have studied the equilibrium of labeled and unlabeled adsorbate. The balance measures the initial mass  $M_0$  of labeled benzene irreversibly adsorbed and the total mass  $M$  adsorbed. The reversibly adsorbed amount  $M_2$  is the difference between  $M$  and  $M_0$ . A spiral quartz gauge indicates the total pressure  $P$  and the radiomanometer gives the partial pressure  $p$  of labeled benzene. Since the

volume is known, we can calculate the total mass  $M_3$  of gaseous benzene in the balance and  $k = p/P$ , the percentage of labeled molecules. We shall reasonably suppose that  $k$  has the same value for the reversible adsorbate and exchangeable irreversibly adsorbed benzene  $M_1$  as for gaseous mixture. We can establish the following equation for successive equilibrium pressures if we neglect the very weak isotopic effect:

$$\frac{1-k}{k} = \frac{1}{M_1} (M_2 + M_3). \quad (\text{A})$$

If the value obtained gives a straight line, passing through the origin, we are sure to have a true equilibrium for the removal of radioactive benzene and the slope gives the true value for the amount not exchangeable. For  $M_0 = 1.50$  mg the data collected during four experiments are given in Table 1. As shown in Fig. 4, we have a straight line the slope of which gives the quantity not removed as 30%. This value is in good agreement with the previous estimate. Thus we have three species of radioactive benzene on the surface, namely, reversibly adsorbed, irreversibly adsorbed and not exchangeable, irreversibly adsorbed and exchangeable.

#### 5. *Hydrogenation of Adsorbed Benzene*

The attempt to determine the role of the differently adsorbed species in catalytic hydrogenation was interesting. We observe two facts in hydrogenation of the adsorbate: cyclohexane constitutes more than

TABLE 1  
ISOTOPIC EXCHANGE OF THE IRREVERSIBLY ADSORBED BENZENE

Expt no.	$P$ (Torr)	$p$ (Torr)	$k$	$(1-k)/k$	$M_3$	$M$	$M_2 + M_3$
1	0.11	0.31	0.280	2.2	0.90	3.23	2.63
2	0.31	0.073	0.143	6.1	4.20	3.51	6.21
3	0.80	0.082	0.102	8.8	6.50	4.03	9.03
4	1.46	0.100	0.069	14.5	12.0	4.73	15.23

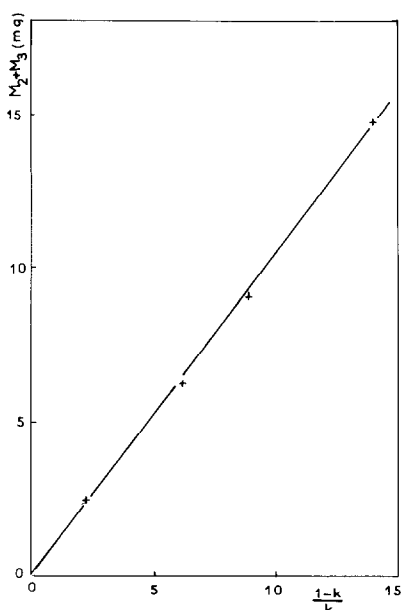


FIG. 4. Check of Eq. (A) (see text).

90% of the product and benzene, 5 or 6%. Cyclohexane is only completely removed from the surface by trapping at liquid nitrogen temperature. For irreversibly adsorbed benzene, kinetics of weight variations, of gas phase radioactivity and of total pressure decrease are shown in Fig. 5. After a 4 hr reaction and trapping in liquid nitrogen (point A), the amount adsorbed is negligible as also is the partial pressure of organic compounds. It is difficult to see if, at point A, we have new consumption of  $H_2$ . But it should be very weak in any case, because the partial pressure of  $H_2$  is not appreciably lowered. Thus the hydrogenation is complete at point A, a part of the formed cyclohexane remaining reversibly adsorbed on the catalyst.

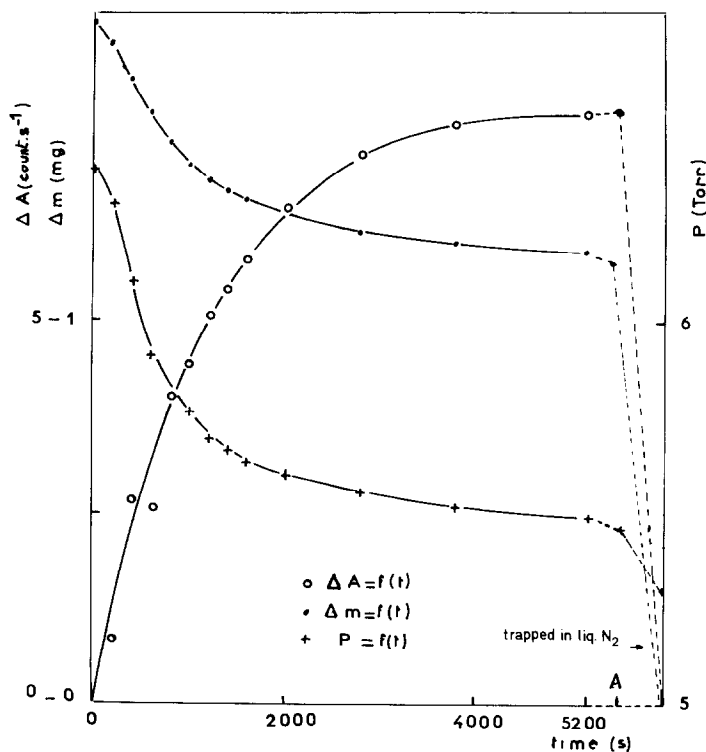


FIG. 5. Kinetics of weight variation, of gas phase radioactivity and of total pressure decrease during benzene hydrogenation on 0.312 g of Raney nickel.

TABLE 2  
 DISTRIBUTION OF LABELED BENZENE IN THE ADSORBATE BEFORE HYDROGENATION

Reaction conditions for adsorbate	Case			
	I	II	III	IV
Irreversibly adsorbed (non-exchangeable)	$^{14}\text{C}$	$^{14}\text{C}$	$^{14}\text{C}$	$^{12}\text{C}$
Irreversibly adsorbed (exchangeable)	$^{14}\text{C}$	$^{12}\text{C}$	$^{12}\text{C}$	$^{14}\text{C}$
Reversibly adsorbed	0	$^{12}\text{C}$	0	0
Ratio $^{14}\text{C}$ benzene/benzene irreversibly adsorbed (%)	100	30	30	70
Ratio $^{14}\text{C}$ benzene/total benzene (%)	100	16	30	70

In order to study the role of the different species of adsorbed benzene in the reaction, we have also used the labeling properties of  $^{14}\text{C}$  in several sequences as shown in Table 2.

For the first sequence we adsorbed labeled benzene and after establishment of vacuum, only radioactive product remains irreversibly adsorbed on the catalyst (case I). In cases II and III, we repeated the same process, then nonlabeled benzene was admitted many times until all the radioactive exchangeable benzene was removed. If some reversibly adsorbed nonlabeled benzene is left on the catalyst, we have case II. If the reversibly adsorbed benzene is evacuated, we have case III. Case IV represents the opposite situation to case III: nonlabeled benzene is introduced first, then labeled benzene is admitted and evacuated until all the nonlabeled exchangeable benzene is removed. The distributions of labeled benzene in the adsorbate before hydrogenation for the different cases are shown in Table 2.

In all the cases, when hydrogen is admitted, the loss of weight is proportional to the cyclohexane evolved and the increase of the gas phase radioactivity is due to labeled cyclohexane evolved.

In cases I, II and IV where the quantity of adsorbed benzene is identical, the kinetics of weight variation and of total pressure decrease under 6 Torr of hydrogen pressure are the same as shown in Fig. 6, but the kinetics of gas phase radioactivity are different as illustrated in Fig. 7. Curves

1, 2 and 3 are the kinetics of hydrogenation of irreversibly adsorbed (case I), irreversibly adsorbed nonexchangeable benzene (case III), and irreversibly adsorbed exchangeable benzene (case IV), respectively. If only exchangeable benzene plays a prominent role in hydrogenation, we could expect a rapid rise of radioactivity followed by a plateau in case IV and the situation would be the reverse in case III. We do not observe such behaviour. The radioactivity evolution of the gas phase is proportional to the mass evolution (Fig. 8). This fact seems to indicate that the two

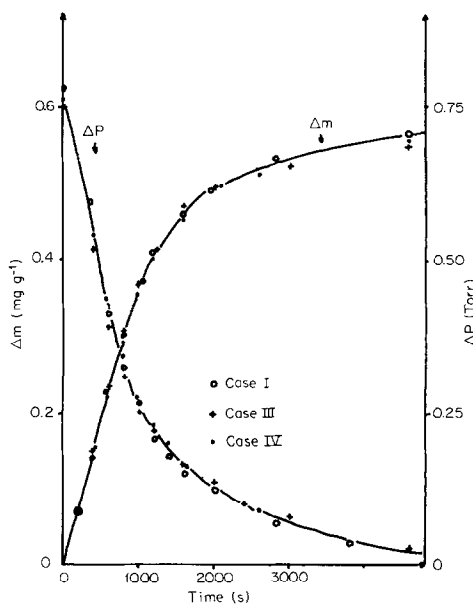


FIG. 6. Kinetics of weight variation and of total pressure decrease during benzene hydrogenation in cases I, III and IV.

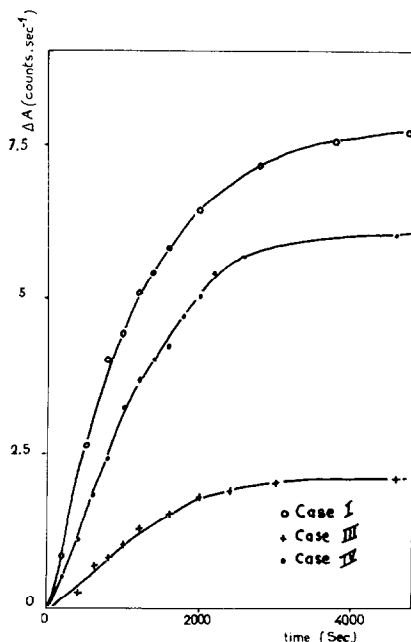


FIG. 7. Kinetics of gas phase radioactivity increase during benzene hydrogenation in cases I, III and IV.

species of irreversibly adsorbed benzene play the same role in the reaction.

For cases II and III, the slope of the straight line which represents the variation of gas phase radioactivity versus sample weight loss is similar, although reversibly adsorbed benzene is present in case II. This fact indicates that the reversibly adsorbed product does not play a role in the hydrogenation act.

## DISCUSSION AND CONCLUSION

One fraction of benzene is adsorbed reversibly and, for a given pressure, the amount fixed on the surface is independent of the volume of adsorbed hydrogen. The isotherm is of Freundlich type, in agreement with the results of other authors (32). This kind of adsorption does not play a role in hydrogenation as may be deduced from the slopes of curves II and III in Fig. 8.

The other fraction of benzene is irreversibly adsorbed and, for every such molecule, six hydrogen molecules have to be removed from the catalyst surface. As the adsorbate is exclusively hydrogenated to cyclohexane, we can deduce that there is no cracking of the carbon ring of the molecule. In these conditions, is this hydrogen coming from the surface or resulting from broken C-H bonds? For the first possibility, the hydrogen could escape after weakening of Ni-H bonds caused by action of the electrons of the chemisorbed complex through the intermediate agency of the metal. A steric effect is also possible. Freed sites would be able to fix a new amount of irreversibly adsorbed benzene. For the second eventuality a part of the hydrogen would be produced by breaking C-H bonds, according to the equation proposed by Tetenyi and Babernics (18) to

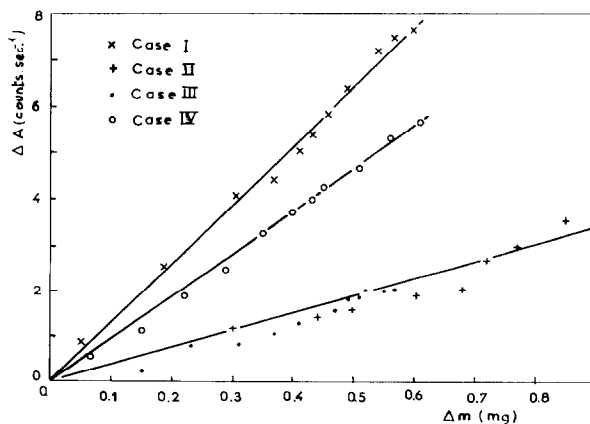
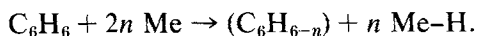


FIG. 8. Gas phase radioactivity as a function of adsorbed weight during benzene hydrogenation for the different cases shown in Table 2.



explain why a part of the labeled benzene cannot be exchanged by nonlabeled benzene and is only desorbed by hydrogenation:



Such an adsorbate will be called benzene A. These features have the advantage of explaining hydrogen and deuterium exchange between benzene and perdeuterobenzene molecules (23,33) and the high bound number value for benzene adsorbed on nickel at room temperature (21).

Nevertheless, this cannot concern the irreversibly adsorbed exchangeable benzene that will be called benzene B. It constitutes more than two thirds of the whole. Tetenyi and Babernics (18) suggest that this kind of adsorption is due to C-Ni interactions while one double bond or more disappear. The large number of hydrogen molecules escaping during adsorption fits in with an adsorption of the ring parallel to the surface.

Furthermore, if double bonds are broken, we should find a nonnegligible amount of cyclohexene and cyclohexadiene among hydrogenation products. Although hydrogenation of these reactants is rapid compared to benzene, one would observe traces of these compounds chiefly at low hydrogen pressures. We detected no traces of these products. It rather seems to us that we have an adsorbed complex where double bonds are statistically concerned either one after the other or all together, as in the case of a  $\pi$ -complex (34). In this model, the ring would be parallel to the surface.

When hydrogenation occurs, molecules are produced by benzene A and benzene B. If we consider Figs. 6 and 7, it seems that the rate-limiting step of the reaction is the same for the two kinds of chemisorbed benzene. In a fast step, we could have a partial hydrogenation of benzene A to give benzene B. In this eventuality, benzene A would not exist during adsorbate hydrogenation.

Therefore, we have to assume that benzene A, during adsorption, loses a fraction of its hydrogen which also becomes fixed on the surface. Formation of benzene A, rather than benzene B, would occur for a surface less occupied by hydrogen and it requires also that Ni sites near the adsorbed benzene have a strong affinity for hydrogen coming from broken C-H bonds.

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