

further concern with thermodynamic coupling would seem to be useless. Of what use it might be in conjunction with reaction mechanism remains an open question.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

## The Mechanism of Benzene Chemisorption on a Supported Nickel Catalyst

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A further study of benzene chemisorption on a nickel-kieselguhr catalyst by the low frequency a.c. permeameter magnetic method has shown, as previously reported, that the process takes place by the formation of approximately six bonds, up to a temperature of about 120°. This is assumed to mean flat, non-dissociative adsorption. At higher adsorption temperatures the number of bonds increases rapidly until at 200° substantially complete dissociation of the benzene molecule is achieved. These conclusions are supported by analysis of the saturated hydrocarbons obtained by flushing the adsorbed benzene with hydrogen and trapping the products. The conclusions are also confirmed by measuring the volume of hydrogen denied access to the surface by the presence of pre-adsorbed benzene, admitted to the catalyst at progressively higher temperatures.

### Introduction

In an earlier investigation by the low frequency a.c. permeameter method,<sup>1</sup> it was shown that benzene chemisorbed on silica-supported nickel is taken up primarily by the formation of six bonds. This suggests associative adsorption with the plane of the ring parallel to the nickel surface, although various other interpretations are not excluded by the magnetic data alone.

The maximum temperature of adsorption, in the earlier work, was 150°. In the present work the observations are extended to 200°, at which temperature extensive dissociative adsorption may be expected, and the conclusions reached by the magnetic method are confirmed through the use of several other lines of investigation.

### Experimental

Magnetization-volume isotherms were obtained as previously described.<sup>1</sup> All measurements were made on Universal Oil Products nickel-kieselguhr containing 52.8% of nickel. The reduction and evacuation of samples, together with purification of reagents have all been described.

Subsequent to several runs it was necessary to determine the products obtainable by flowing hydrogen over the adsorbent-adsorbate system. The hydrogenated products were selectively collected in cold traps for analysis in a mass spectrometer or, for some samples, by vapor phase chromatography. Conditions of adsorption and hydrogenation are given in connection with the data presented below.

In one series of experiments it was desired to estimate the area of nickel occupied by adsorbed benzene or its dissociation products. This was possible because benzene is not hydrogenated over nickel at -78°. The procedure was to determine the pressure-volume isotherm for hydrogen over the catalyst at -78°. The hydrogen then was desorbed by evacuation at 360°, following which a measured quantity of benzene was admitted to the surface. The sample then was cooled to -78° and another pressure-volume isotherm for hydrogen was obtained. The benzene, or its dissociation products, was thus shown to deny access of hydrogen to part of the nickel surface. The extent to which this denial of access occurred was, of course, a measure of the dissociative process which had occurred during chemisorption of the benzene. These experiments were performed over a considerable range of benzene adsorption temperatures.

In one experiment the benzene was adsorbed at a lower temperature, then heated, then cooled again to determine whether dissociative adsorption occurs primarily during the adsorption step or whether it may occur in a pre-adsorbed intact molecule if the temperature is raised.

### Results

Magnetization-volume isotherms for benzene on nickel are shown in Fig. 1. It previously has been shown<sup>2</sup> that the isotherms for hydrogen have a slope which is somewhat dependent on temperature even at temperatures well above those at which appreciable physical adsorption may take place. This effect seems to be related to the range of nickel particle diameters present in any catalyst sample. Whatever may be the reason for this behavior it is clearly necessary to compare the isotherm slope of any adsorbate with that of hydrogen at the same temperature, if accurate determination of the number of surface bonds per molecule adsorbed is required. Isotherms for hydrogen are, therefore, shown in Fig. 2. It will be noted that the slopes for benzene rise much more rapidly with increasing temperature of adsorption than do those of hydrogen.

Table I shows the effect of pre-adsorbed benzene on the volume of hydrogen which may be adsorbed by the nickel at -78° up to a pressure of 1 atm. The data are presented as (1) temperature at which benzene was admitted to the surface, (2) volume (s.c.) of benzene vapor adsorbed per g. of nickel, (3) volume of hydrogen (s.c.) adsorbed per g. of nickel at -78°, (4) volume of hydrogen (s.c.) denied access to the nickel and (5) molecules of hydrogen denied access to the nickel per molecule of benzene vapor adsorbed.

Another result, which we believe to be of significance, is that in every case represented in Table I the slope of the magnetization-volume isotherm for hydrogen on a surface covered in part by benzene was the same as that on a bare nickel surface. This was true in spite of the fact that the total volume of hydrogen which could be taken up by the nickel was diminished substantially by the presence of pre-adsorbed benzene.

It is well known that adsorbed hydrocarbon molecules and their dissociation products are often quite difficult to remove by hydrogenation *in situ*. In spite of this enough product was obtained to confirm the conclusions reached on the basis of the

(1) P. W. Selwood, *THIS JOURNAL*, **79**, 4637 (1957).

(2) P. W. Selwood, *ibid.*, **78**, 3893 (1956).

TABLE I  
EFFECT OF PRE-ADSORBED BENZENE ON THE ADSORPTIVE CAPACITY OF NICKEL FOR HYDROGEN AT  $-78^{\circ}$ , TO 1 ATM. INFLUENCE OF BENZENE ADSORPTION TEMPERATURE

(1) $C_6H_6$ admission temp., $^{\circ}C$ .	..	25	25	100	100	110	125	200	200
(2) Cc. $C_6H_6/g.Ni$	..	2.45	1.05	2.4	1.05	1.05	1.7	1.2	1.05
(3) Cc. $H_2/g.Ni$		15.3	9.0	12.4	10.4	10.2	9.6	9.8	7.0
(4) $H_2$ , cc., denied access	0	6.3	2.9	4.9	5.1	5.7	5.5	8.3	9.1
(5) $H_2$ , mole, denied per $C_6H_6$ , mole, adsorbed	..	2.6	2.8	2.0	4.9	5.4	3.2	6.9	8.6

magnetic methods. The results are summarized in Table II.

Two runs were made in an attempt to determine whether dissociation could occur in a benzene molecule already adsorbed in the associative mode. Sufficient benzene was admitted to the bare nickel at  $103^{\circ}$  to lower the magnetization by 4.5%. The sample was heated at  $160^{\circ}$  for 1 hr. and then cooled again to  $103^{\circ}$ . The magnetization was found to have been diminished a total of 9.0%.

TABLE II  
SUMMARY OF HYDROGENATION EXPERIMENTS

Temp. $C_6H_6$ adsorption, $^{\circ}C$ .	100	200
Vol. (s.c.) $C_6H_6$ adsorbed, cc.	2.08	2.0
Temp. $H_2$ passage, $^{\circ}C$ .	100	200
Time $H_2$ passage, min.	30	30
Vol. (s.c.) vapor recovered, cc.	2.0	2.45
Composition vapor recovered, %	$\geq 95$ cyclohexane	12.5 benzene 3.7 cyclohexene? 67.5 cyclohexane 15 lower mol. wts.

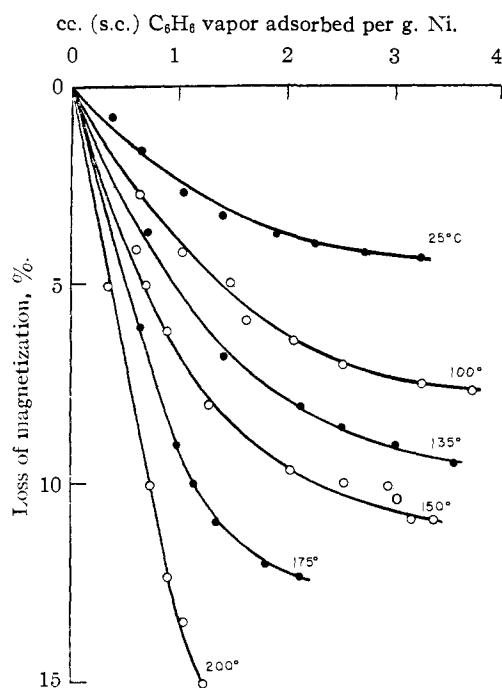


Fig. 1.—Magnetization-volume isotherms for benzene on nickel-silica over a range of adsorption temperatures. In the range  $150^{\circ}$  to about  $190^{\circ}$ , the magnetization is a function of the time, owing to progressive dissociation of the adsorbed benzene. The data shown represent the magnetization after thermal transients have disappeared but before secondary dissociation has progressed very far except for the results at  $200^{\circ}$ .

This experiment was repeated under these conditions: initial and final temperature,  $106^{\circ}$ ; heating at  $200^{\circ}$  for 1 hr., magnetization loss, 18%.

In view of the result given above an attempt was made to observe dissociation or fragmentation of the adsorbed benzene as a kinetic process. In this experiment 1.15 cc. (s.c.) of benzene vapor per g. of nickel was admitted to a freshly reduced and evacuated sample at  $85^{\circ}$ . This caused a loss of magnetization corresponding to the associative mode of adsorption. The sample now was heated to  $176^{\circ}$  and held there for 12 hr. The loss of magnetization

occurring as a function of time is shown in Fig. 3. It should be emphasized that this loss was not that caused merely by raising the temperature but that it occurred after the constant temperature of  $176^{\circ}$  had been reached.

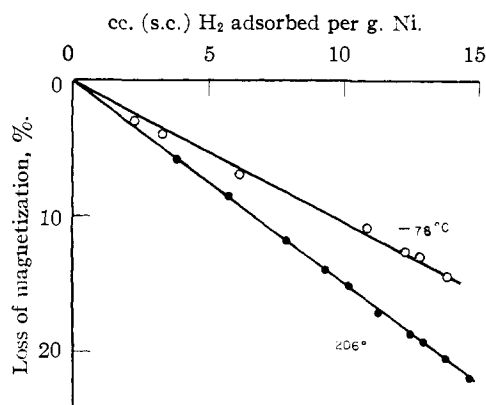


Fig. 2.—Magnetization-volume isotherms for hydrogen on nickel-silica at  $-78^{\circ}$  and at  $206^{\circ}$ .

### Discussion

The procedure necessary and the assumptions involved in finding the number of surface bonds formed by an adsorbed molecule have been described.<sup>3</sup> In brief, it is necessary to divide the initial (low coverage) slope of the magnetization-volume isotherm by that of hydrogen. If molecular hydrogen is correctly assumed to dissociate and to form two surface-hydrogen bonds, then the ratio so found gives the number of bonds formed by any adsorbate. Our present understanding of the phenomenon is that by "number of bonds formed" we mean "number of metal atoms bonded" by the adsorbate molecule or its dissociation products.

Following this procedure, we present in Fig. 4 the number of bonds formed per molecule of benzene as a function of the temperature of the adsorbent. The number of bonds formed averages about six up to an adsorption temperature in the neighborhood of  $130^{\circ}$ . As the adsorption temperature is raised

(3) P. W. Selwood, Preprint No. 88, Second International Congress on Catalysis, Paris, July 4-9, 1960.

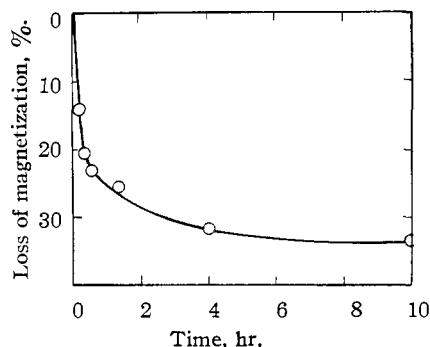


Fig. 3.—Fractional loss of magnetization with time for benzene adsorbed on nickel-silica at 100° then quickly heated to 176°. The results show that rate studies of dissociation by an adsorbed molecule *in situ* are possible; further corrections are necessary before rate constants and activation energies may be calculated.

further, the number of bonds formed increases rapidly, reaching about eighteen at 200°.

These results clearly suggest that up to about 130° the benzene lies flat, forming six bonds by associative adsorption, with probable loss of aromatic character. This view has received tentative support from infrared absorption spectrum observations<sup>4</sup> and it is supported by kinetic studies of benzene over platinum.<sup>5</sup>

But as the adsorption temperature rises above about 130°, it is clear that dissociation or fragmentation or both must occur.

It should be pointed out that the adsorption temperatures given above represent the steady temperature of the adsorbent just prior to admission of the adsorbate. The heat of adsorption always raises the temperature of the adsorbent. In some cases this is a considerable amount and thus, while the magnetization isotherms are given at accurately determinable temperatures, there is always some uncertainty concerning the precise temperature at which the adsorbent reaches the surface. It is, of course, this temperature which determines the degree to which the adsorbed molecule may be dissociated.

The possible dissociation and fragmentation species derivable from benzene are so numerous that little may be gained by trying to relate the total number of bonds found to any particular species. Eighteen bonds could be formed by complete dissociation yielding six Ni-H bonds, plus twelve Ni-C bonds, leaving a saturated six-membered carbon ring intact. But eighteen bonds could also be an average formed by various species including H, CH, C<sub>2</sub>, C<sub>2</sub>H, C<sub>2</sub>H<sub>2</sub>, etc. Our conclusions from the magnetic data are therefore limited to the statement that the adsorption is primarily associative below 130°, above which dissociation becomes increasingly important.

This conclusion is supported by the experiments in which the adsorptive capacity of nickel for hydrogen was shown to depend on the temperature at which benzene was pre-adsorbed. Even though the precision is low, it is clear that a molecule of benzene

(4) R. P. Eischens, personal communication.

(5) R. C. Pitkethly and A. G. Goble, Preprint No. 91, Second International Congress on Catalysis, Paris, July 4-9, 1960. Also see discussion relative to Preprint No. 88 of the same Congress.

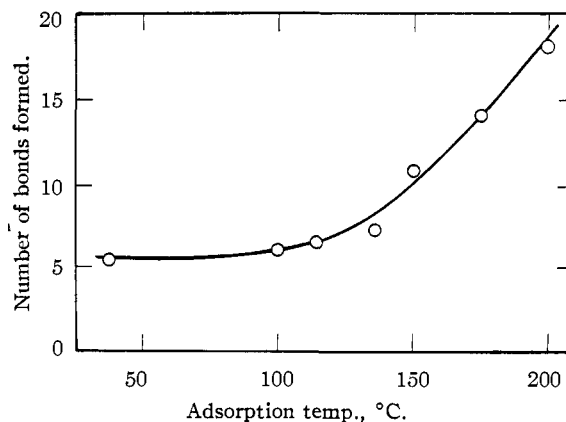


Fig. 4.—Average number of bonds formed by benzene adsorbed on nickel-silica as a function of adsorption temperature.

pre-adsorbed at 200° is able to deny access of two to three times as much hydrogen as is a molecule of benzene pre-adsorbed at room temperature.

Further evidence concerning these views is obtained from the hydrogenation experiments. Benzene adsorbed at 100° yields, on hydrogenation, substantially pure cyclohexane. This, in itself, does not exclude some form of dissociative adsorption with the ring structure remaining intact. But, together with the magnetic and other data, this result makes it virtually certain that the adsorption of benzene on supported nickel below about 130° is almost entirely associative.

Proof of some fragmentation, at higher temperatures, is also obtained from the hydrogenation experiments. But the fairly large fraction of cyclohexane found, even for an adsorption temperature of 200°, makes it clear that much of the benzene merely loses its hydrogen and that the carbon-carbon bonds are broken in only a moderate fraction of the adsorbed molecules. Extensive "carbiding," as observed for ethylene on nickel, apparently does not occur.

It is also clear that further dissociation may take place after adsorption, provided that the temperature is sufficiently high. The demonstration that the rate of such dissociation may be observed *in situ* appears to open a rather fruitful field for further study.

One final conclusion to be drawn from the isotherms for hydrogen at -78° over pre-adsorbed benzene is that quite extensive electronic involvement of surface nickel atoms (as by benzene) does not alter the mode of adsorption of hydrogen by nickel atoms which are, presumably, adjacent to those covered by benzene. This observation has some bearing on current discussions concerning the possible effect of the silica support on the distribution of electrons in the nickel. If a rather obvious change such as that produced by benzene affects only those nickel atoms bonded to benzene, then it is difficult to see how the silica could have much effect on any nickel atoms not actually touching silica and perhaps not even on those which are touching silica.

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