Summary.—Strongly acidic solutions of osmium(VIII) are reduced directly to the +3 state at dropping mercury electrodes. Less strongly acidic solutions give an additional wave, corresponding to the intermediate formation of osmium(IV). At *p*H values above about 5, there is also a third wave representing the formation of osmium(VI). Data are given for the half-wave potentials and diffusion current constants of these waves under a wide variety of conditions.

In cyanide media osmium is chemically reduced to the +6 state, and polarograms of the resulting solutions show two waves attributed to the reduction scheme VI → III → II. The polarographic characteristics of osmium(II) and (III) in cyanide media are briefly discussed. Cyanide media are better suited than any others yet investigated for the determination of osmium by polarography or coulometry at controlled potential.

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The Mechanism of Chemisorption: Benzene and Cyclohexane on Nickel, and the Catalytic Hydrogenation of Benzene

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Magnetization–volume adsorption isotherms have been obtained for benzene and for cyclohexane on nickel–silica catalysts up to 150°. Results also have been obtained for hydrogen admitted over pre-adsorbed benzene or cyclohexane, and *vice versa*. Benzene and cyclohexane are chemisorbed on nickel by a minimum six and eight site attachment, respectively. Chemisorbed benzene must be desorbed before hydrogenation. Hydrogenation from the vapor phase or van der Waals phase may be observed down to about -25°. Hydrogen chemisorbed with a heat of adsorption of less than about 12 kcal. per mole is removable by benzene at room temperature. The participation of d-electrons in a functioning catalyst has been demonstrated by direct observation of magnetization changes attendant on the removal of chemisorbed hydrogen from a nickel surface by benzene molecules from the van der Waals phase.

Introduction

The purpose of this work was to extend our studies of surface reactions through use of the changes of magnetization which occur when gases are chemisorbed on finely divided nickel.[1] The systems studied were benzene, cyclohexane, and several combinations of benzene or cyclohexane with hydrogen. The adsorbent was nickel–silica catalyst.

Experimental

Magnetization–volume isotherms, and magnetizations as a function of time, were obtained on the volumetric adsorption apparatus and low frequency a.c. permeameter previously described.[2] Considerable improvement in convenience and precision was gained by placing the secondaries coaxial along the axis of the primary solenoid which was enlarged to 5100 turns. This arrangement made it possible to reduce the samples and to make measurements at any desired temperature without disturbing the relation between sample and secondaries. Convenience also was improved by placing an automatic Toepler pump in the gas handling system and a Varian G-10 (10 mv.) recorder after the Hewlett–Packard 400-D millivoltmeter in the electrical circuit. The primary was operated at 0.76 amp. stabilized 60 cycle a.c. at about 200 v. The secondary e.m.f. for a typical reduced sample at room temperature averaged about 5 to 10 mv. The zero reading in the absence of any sample was less than 0.1 mv. and was highly reproducible. The sensitivity of this device is such that the chemisorption of 0.01 cc. of hydrogen per g. of nickel in about 5 g. of catalyst produces a perceptible change of secondary e.m.f. Additional precision, if needed, could be obtained by improvement of temperature control in the sample, and by increased stabilization of primary current, and of back e.m.f. used to extend the zero in the recorder circuit.

Catalyst samples were either a Universal Oil Products Co. nickel-kieselguhr containing 52.8% Ni, or a coprecipitated nickel–silica containing 37.5% Ni. Details concerning these catalysts, which are referred to below as "U.O.P." or as "coppt.," respectively, were given in earlier papers.[2,3] Reductions were performed *in situ* for 12 hr. at 360° in flowing hydrogen, followed by evacuation at 10^{-6} mm. for 2 hr., and cooling *in vacuo* to the temperature of measurement. All isotherms were run in about 0.05 mm. of helium, to promote heat transfer. Measurements were made on 6 to 8-g. samples, in a dead space as determined with helium of about 10 cc. (S.C.).

Electrolytic hydrogen was purified by a Deoxo unit, followed by silica gel at -196°. Helium was passed over copper–asbestos at 600° and then over silica gel at -196°. Cyclohexane was Fisher Reagent Grade. Benzene was a specially purified sample obtained through the courtesy of Dr. W. Keith Hall of the Mellon Institute. Benzene and cyclohexane were introduced to the catalyst as required from a 500-cc. reservoir at a maximum pressure of 60 mm. The pressure of these two vapors over the catalyst samples was always a small fraction of a mm. except for those measurements made at 150°.

Some further details of procedure are given below.

Results

All gas volumes taken up are given as cc. (S.C.) of gas or vapor per g. of nickel. It will be understood that for benzene and cyclohexane considerable quantities are physically adsorbed by the silica support.

Figure 1 shows magnetization–volume isotherms at 25° on U.O.P. catalyst. Three situations are represented: (1) hydrogen on the bare surface; (2) benzene on the bare surface (after re-evacuation at 360°); and (3) hydrogen on the surface which is already covered, in part, to the extent of 5.3 cc. (S.C.) of benzene vapor per g. of nickel. Results with a sample of copptd. catalyst were strictly comparable with those shown except that the volume of hydrogen adsorbed on the bare surface to 1 atm. pressure is somewhat greater.

In our first work with the Faraday balance[1] we failed to observe any effect of benzene on the magnetization of nickel. This failure is seen now to

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(1) P. W. Selwood, T. R. Phillips and S. Adler, THIS JOURNAL, **76**, 2281 (1954).

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

(3) P. W. Selwood, *ibid.*, **79**, 3346 (1957).

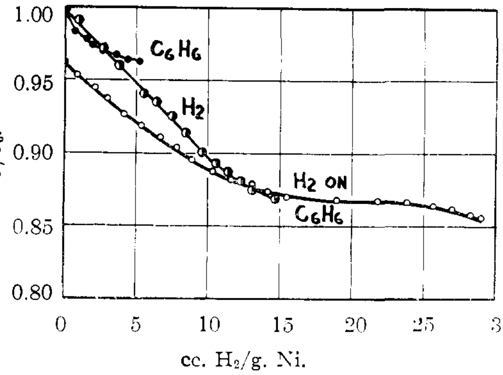


Fig. 1.—Magnetization–volume isotherms at 25° for hydrogen, for benzene and for hydrogen over benzene; all on nickel–kieselguhr.

have been due to the lower sensitivity of the Faraday balance, and to the small total effect produced by benzene as compared with hydrogen.

Figure 2 shows magnetization–volume isotherms on copptd. catalyst at 25° for the following three situations: (1) hydrogen on a bare surface up to a pressure of 0.01 mm. corresponding to 13.1 cc. H_2, obtained by adding hydrogen in increments as shown to 1 atm., then pumping out for a few min.; (2) benzene added over the surface already covered, in part, with 13.1 cc. H_2, the total volume of benzene vapor (S.C.) added being 9.0 cc.; and (3) hydrogen admitted over the surface already covered with benzene and hydrogen as stated above, to a pressure of 257 mm. corresponding to 32.7 cc. of H_2.

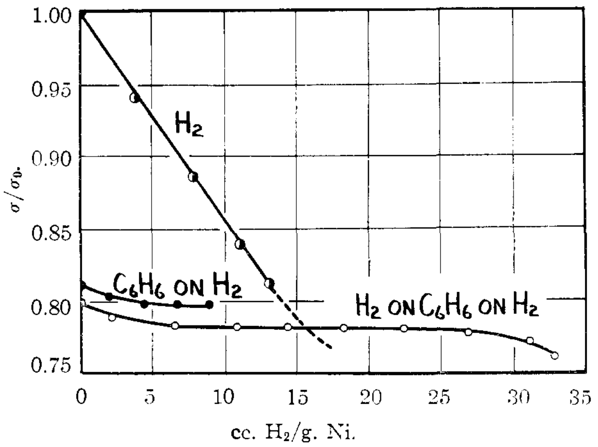


Fig. 2.—Magnetization–volume isotherms at 25° for hydrogen to 0.01 mm. pressure, for benzene over hydrogen, and for hydrogen over benzene over hydrogen; all on nickel–silica.

All points shown in Fig. 2 were attended with negative thermal transients. During the second addition of hydrogen these were fairly strong and were produced, no doubt, by the heat of hydrogenation. The pressure of the hydrogen over the sample also decreased rather slowly after each admission during this run. This doubtless was due to the rather slow rate of hydrogenation at room temperature. Each point was taken after a wait of about 20 min.

Runs similar to those shown in Fig. 2 were made on a sample of U.O.P. catalyst. The results were the same except that the first addition of hydrogen was 10.7 cc., the benzene vapor was 7.7 cc., and the final uptake of hydrogen to 1 atm. was 30.6 cc.

The results given in Figs. 1 and 2 show that benzene is hydrogenated readily over nickel at room temperature even though very little cyclohexane appears in the gas phase. A run was made to find the approximate lowest temperature at which hydrogenation could be detected. These results, shown in Fig. 3, were obtained by adding 5.6 cc. of benzene vapor to the bare U.O.P. sample at 19°. The sample was then cooled to −77°, after which hydrogen was added as shown up to 1 atm. pressure, corresponding to 13.0 cc. of H_2. The magnetizations shown in Fig. 3 for benzene and hydrogen are not directly comparable because the magnetization of the sample rises as the temperature is lowered.

Fig. 3

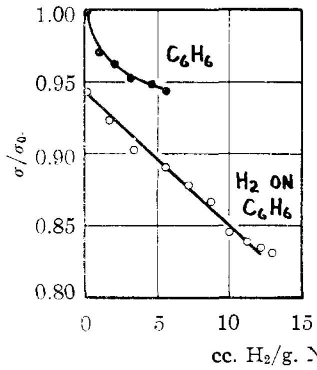


Fig. 5

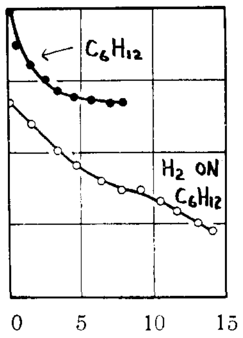


Fig. 3.—Magnetization–volume isotherms for benzene at 19° and for hydrogen over benzene at −77°; on nickel–kieselguhr.

Fig. 5.—Magnetization–volume isotherms at 25° for cyclohexane, and for hydrogen over cyclohexane; both on nickel–kieselguhr.

The magnetization–volume isotherm for hydrogen on bare nickel at −77° also was determined in connection with Fig. 3. The result was the same as that shown for hydrogen over benzene except that on the bare surface the volume of hydrogen adsorbed to 1 atm. pressure was 19.3 cc.

At the conclusion of the runs represented in Fig. 3 the sample was allowed to warm up. A significant uptake of hydrogen was observed in the neighborhood of −25°.

Figure 4 represents a continuous recording of magnetization *vs.* time during the removal of hydrogen from the nickel by benzene. A sample of U.O.P. catalyst was reduced and evacuated in the usual way. A few drops of benzene had been sealed into a side-arm near the sample and had been kept frozen at −77° throughout the reduction and evacuation steps. To prevent contamination with water the benzene had been placed "up-wind" of the sample. The sample was now covered with hydrogen up to a pressure of 794 mm. After equilibrium had been reached the benzene was allowed to melt and to diffuse into the sample where

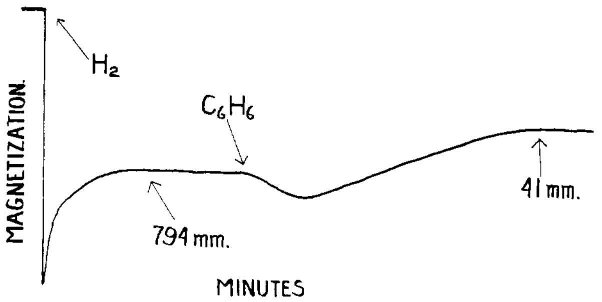


Fig. 4.—Magnetization *vs.* time showing the increase of magnetization attendant on the hydrogenation of benzene while the nickel-kieselguhr is actually functioning as a catalyst. The total elapsed time in this experiment was about 40 min. The temperature was 27°.

it was, of course, hydrogenated. Throughout the operation the system was closed so that no further access of hydrogen was permitted except for that (*ca.* 10 cc.) in the dead-space. This was not sufficient to hydrogenate all the benzene, so that the pressure over the sample slowly fell to a few cm. During this process the carbon tetrachloride bath surrounding the sample was held at 27°, within 0.1°.

It will be observed that the magnetization first fell slightly owing, no doubt, to the heat of hydrogenation, after which the magnetization slowly rose as the benzene molecules progressively removed hydrogen atoms from the surface.

Some of the interpretations given below require a knowledge of how cyclohexane behaves on a nickel surface. Figure 5 shows magnetization–volume isotherms on U.O.P. catalyst at 25° for: (1) cyclohexane on a bare surface; and (2) hydrogen on a surface which already has been covered, in part, with 7.9 cc. of cyclohexane vapor. The volume of hydrogen taken up, by this sample, to 1 atm. in the presence of cyclohexane was the same, namely, 14.0 cc., as in the absence of cyclohexane. The final magnetization of the nickel was also the same in these two cases.

Figure 6 shows magnetization–volume isotherms on U.O.P. catalyst at 150°. At this temperature the catalyst is very active for the hydrogenation reaction, and the van der Waals adsorption is much less than at room temperature. Three isotherms are shown: (1) hydrogen on the bare surface; (2) benzene on the bare surface; and (3) cyclohexane on the bare surface. It was noted during the run on cyclohexane that the pressure rose a few mm. per hour owing, probably, to some dissociation.

Discussion

There can be no question that at room temperature, on the nickel catalysts described, both benzene and cyclohexane are chemisorbed. This is shown by the drop of magnetization which occurs, as shown in Figs. 1 and 5, when either of these vapors is admitted to a bare nickel surface. But the van der Waals adsorption is so great at room temperature that not much quantitative information may be obtained from these results.

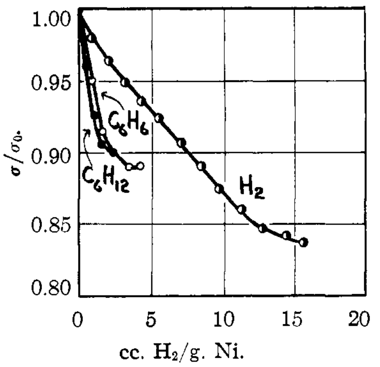


Fig. 6.—Magnetization–volume isotherms at 150° for hydrogen, for benzene, and for cyclohexane; all on nickel-kieselguhr.

At 150° the van der Waals adsorption is much diminished, and it is seen from Fig. 6 that the magnetic effect of adsorbed benzene is three to five times the effect of an equal number of hydrogen molecules. Similarly, the magnetic effect of cyclohexane is four to six times that of hydrogen. It will, of course, be noted that the volume of benzene or of cyclohexane which may be chemisorbed on the nickel surface is one-sixth to one-tenth the volume of hydrogen which may be chemisorbed.

In previous interpretations[2,3] we have assumed that each chemisorbed hydrogen atom forms one bond to nickel, and that the magnetic effect of a nickel–carbon bond is the same as that for a nickel–hydrogen bond. If these assumptions are correct then benzene is chemisorbed on nickel by a minimum six bond attachment and hence must lie flat on the surface in the Balandin sense excepting, of course, that chemisorption actually does occur. Similarly, cyclohexane is held by a minimum eight bond attachment which could mean dissociative adsorption in the boat form at four sites, plus the four dissociated hydrogens. For both benzene and cyclohexane it is probable that some further dissociation or fragmentation may occur, as it does for ethylene.

From Fig. 1 it will be seen that the incremental addition of hydrogen at room temperature to a surface already covered, in part, with benzene yields a magnetic change which has, at first, the same slope as that of hydrogen on a bare surface. This must mean that the first such additions of hydrogen are preferentially chemisorbed rather than used in hydrogenating the benzene. Use of any appreciable fraction of this hydrogen in hydrogenation would be reflected in a smaller initial slope for this magnetization–volume isotherm. Simple removal of the benzene as such, or as cyclohexane, without subsequent reoccupation of the vacated sites by hydrogen would cause a rise of magnetization. The alternative, of hydrogenation followed by dissociative adsorption of cyclohexane, might cause a slight decrease of magnetization but this process is almost identical with adsorption of hydrogen without change of the adsorbed benzene.

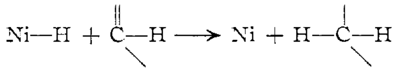
If, however, more hydrogen is added to the surface already covered, in part, with benzene it will be found, as in Fig, 1, that the isotherm becomes more nearly horizontal. As the volume of hydrogen taken up becomes large the magnetization change becomes negligible, showing that nickel–carbon bonds are being replaced by nickel–hydrogen bonds. The total volume of hydrogen taken up is just sufficient to cover the nickel surface and to hydrogenate all the benzene present. From Fig. 5 it is seen that the cyclohexane, like ethane,[3] cannot remain chemisorbed in the presence of abundant hydrogen.

The implication from the results shown in Fig. 1 is that benzene may be hydrogenated over nickel at room temperature but that the hydrogenation must proceed from the van der Waals phase, and that chemisorbed benzene cannot be hydrogenated directly without prior desorption. For hydrogenation to take place it is necessary for the catalyst surface to be adequately covered by hydrogen, that is to say, for the nickel-hydrogen bond to be sufficiently attenuated by the presence of ample chemisorbed hydrogen. It will be clear, also, that although there is no doubt about the benzene being hydrogenated under the conditions of this experiment, yet the strong van der Waals adsorption will preclude any significant appearance of cyclohexane in the gas phase.

Figure 3 shows that the hydrogenation reaction does not proceed at −77°, and that the chemisorbed benzene is able, at this temperature, to deny some, but not all, of the surface to hydrogen. We may conclude that the failure to react at −77° is due to the inability of hydrogen to displace benzene, and probably also to the low mobility of the van der Waals benzene at this temperature. A perceptible reaction occurs in the neighborhood of −25° and higher.

Further evidence supporting the views expressed above is found in Fig. 2. It is seen that partial coverage of the nickel by hydrogen is able to deny almost all the surface to benzene. That is to say, only a slight chemisorption of benzene occurs at room temperature in the presence of 0.01 mm. pressure of hydrogen. But under these circumstances no hydrogenation occurs. If any appreciable hydrogenation occurred at this stage then the subsequent addition of more hydrogen would cause a large drop of magnetization. This large drop is not observed. It must be concluded that in the presence of tightly bound hydrogen the benzene remains in the van der Waals phase.

If now more hydrogen is added it is used, except for the first cc. or two, in hydrogenating the benzene. This process continues until all the benzene is hydrogenated, after which a small additional quantity of hydrogen is chemisorbed on the nickel surface. The precise details of these several steps will, of course, depend on the amount of hydrogen initially used to cover the surface, and on the amount of benzene admitted. But the mechanism which emerges is clearly that benzene is hydrogenated directly from the van der Waals phase by impingement on a nickel-hydrogen surface. The reaction



$$\mathrm{Ni{-}H} + \overset{\|}{\underset{\diagdown}{\mathrm{C}}}\mathrm{{-}H} \longrightarrow \mathrm{Ni} + \mathrm{H{-}}\overset{|}{\underset{\diagdown}{\mathrm{C}}}\mathrm{{-}H}$$

can occur only when the Ni–H bond has been weakened by the presence of enough hydrogen to approach complete surface coverage. A very rough estimate from Fig. 2 and published heats of chemisorption,[4,5] as a function of surface coverage, on similar systems, suggests that hydrogen chemisorbed with the liberation of more than 12 kcal. per mole would not be removable by benzene at room temperature. At the ordinary hydrogenation temperature of say 150° it appears that the surface is normally almost completely covered by hydrogen, that a considerable fraction of that hydrogen is removable by benzene, and that the benzene is thus hydrogenated directly from the gas phase. In actual catalytic practice it is, needless to say, an indispensable aid that the removed hydrogen is at once replaced by fresh hydrogen.

These considerations suggest a possible method for demonstrating directly the electronic state of the catalyst, or at least of the d-band electron concentration, while the catalyst is actually functioning as such. As shown in Fig. 4, it is essential for this demonstration that there should be an abundance of hydrogen on the surface, but that the gas phase hydrogen should be held to a minimum. Then, as benzene molecules take hydrogen from the surface, replacement from the gas phase leads to a fall of pressure and some of the nickel surface is left bare. This causes a rise of magnetization as electrons are drained out of the d-band by the departing hydrogen. It is believed that this is the first direct observation of d-electron participation in a functioning catalyst.

One further point which may be mentioned in connection with Fig. 5 is that the addition of hydrogen to a surface already covered, in part, with cyclohexane gives, at first, mere chemisorption of the hydrogen. One might say that the hydrogen ignores the cyclohexane. But as surface congestion increases, the hydrogen is able to displace the cyclohexane. It will be noted that over a small concentration range the Ni–C bonds broken are approximately equal in number to the Ni–H bonds formed. The final state is simply a surface covered in the usual manner with chemisorbed hydrogen, the cyclohexane being relegated to the van der Waals phase.

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[4] G. C. A. Schuit and N. H. DeBoer, *Rec. trav. chim.*, **72**, 909 (1953).

[5] E. L. Lee, J. A. Sabatka and P. W. Selwood, THIS JOURNAL, **79**, in press (1957).