

Summary

1. The ortho-para conversion of hydrogen over the iron catalysts has been studied as a function of the temperature, pressure, time of contact and presence of various poisons. Kinetic expressions consistent with the observed data have been obtained.

2. The poisoning effects of activated adsorption of hydrogen on the -190° para-ortho hydrogen conversion over platinum and nickel have also been noted. This poisoning effect constitutes very strong evidence that the activated adsorption of hydrogen by nickel, platinum and iron is in part at least a surface phenomenon.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Adsorption of Hydrogen by Iron Synthetic Ammonia Catalysts

BY P. H. EMMETT AND R. W. HARKNESS

Some of the experimental results obtained in the course of a study¹ of the ortho-para interconversion of hydrogen over iron synthetic ammonia catalysts required for their interpretation more detailed information than was available relative to the adsorption of hydrogen by the iron catalysts. The rates and amounts of adsorption as a function of pressure between 25 and 760 mm. and of temperature between -195 and 450° have therefore been determined and are reported in the present paper. The results combined with the ortho-para interconversion studies already described establish definitely the existence of two types of activated adsorption² (type A and type B) of hydrogen on iron in addition to the usual physical adsorption.

Experimental

The adsorption apparatus was the one used by Emmett and Brunauer.³ By means of a trap cooled in liquid air and placed in the line leading to the catalyst, all hydrogen used for reduction purposes was kept free of traces of stopcock grease, water vapor, etc. The dead space in the catalyst system was determined in the usual manner with purified helium. Ten cc. of catalyst was used in the adsorption measurements. The system with the catalyst at 450° could be pumped down to 2×10^{-4} mm. in about an hour. After each adsorption run the catalyst was reduced for about an hour at 450° and was then evacuated for from one to three hours.

The doubly promoted iron synthetic ammonia catalyst (931) contained 1.59% potassium oxide and 1.3% aluminum oxide as promoters. The

preparation, reduction and properties of this type of catalyst have been described many times previously.⁴ The pure iron catalyst was No. 973, another sample of this same catalyst having been used by Benton and White⁵ in their adsorption experiments.

Results

Typical adsorption isotherms for hydrogen on catalyst 931 at -195 and -183° are shown in Fig. 1. Equilibration occurred practically instantaneously both in adsorption and in desorption

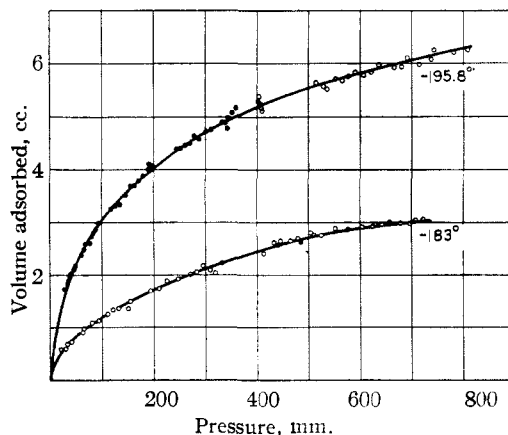


Fig. 1.

runs. The adsorption decreased quite rapidly with increasing temperature, as is evident from the 760 mm. isobar of Fig. 4, the calculated heat of adsorption being about 2000 calories per mole of hydrogen. This value is typical of physical adsorption; Benton and White obtained 1600 calories for the heat of adsorption on pure iron catalyst 973.

(1) Emmett and Harkness, *THIS JOURNAL*, **57**, 1624 (1935).

(2) Harkness and Emmett, *ibid.*, **56**, 490 (1934).

(3) Emmett and Brunauer, *ibid.*, **56**, 35 (1934).

(4) Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925); Almquist and Crittenden, *ibid.*, **18**, 1307 (1926).

(5) Benton and White, *THIS JOURNAL*, **54**, 1820 (1932).

At about -78° , an activated adsorption attained an appreciable rate. In the course of several hours the adsorption value reached about 7 cc. at 1 atmosphere pressure in contrast to 2.5 cc. occurring at 1 atm. and -183° (see Fig. 4). From rate curves of Fig. 2 for -78.5 , -87.6 and -96.5° taken under conditions that were as nearly as possible reproducible, the apparent energy of activation calculates to be about $10,400 \pm 1000$ calories per mole of hydrogen adsorbed, the time required for the adsorption of 2 cc. of hydrogen being used in the calculations.

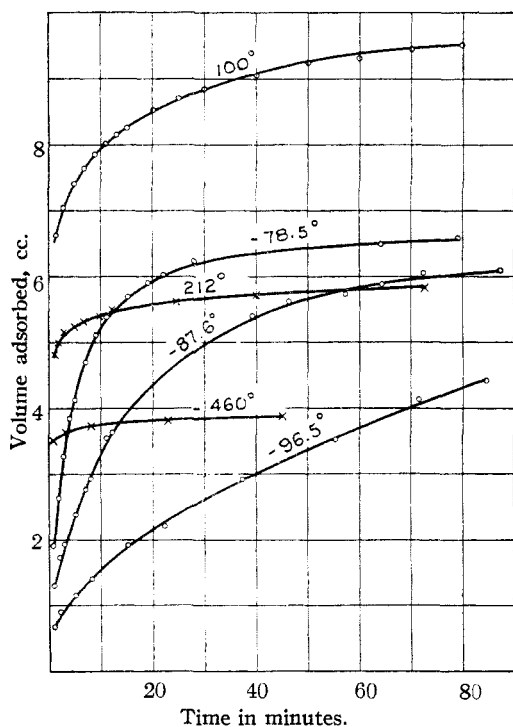


Fig. 2.

The rate of this type A activated adsorption was too low to permit isotherms to be determined at -78° . Even at -22° it was not possible to obtain complete reversibility at low pressures in a reasonable time. The heat of type A activated adsorption was therefore not obtained. Nevertheless the one atmosphere runs in the range -78 to 0° approached equilibrium sufficiently closely with respect to type A adsorption to permit the shape of the isobar to be determined. In run 22 shown on the isobar of Fig. 4, five minutes adsorption at 0° (22-a) was followed by thirty-seven minutes at -20° (22-b), forty-eight minutes at -72° (22-c), thirty-one minutes at -16° (22-d) and seven minutes at -64° (22-e).

At temperatures of 100° and above, another type of activated adsorption (type B) attained a conveniently measurable rate. A few typical rate runs for 100, 212 and 460° are shown in Fig. 2. This type B activated adsorption apparently occurred after an initial instantaneous type A adsorption. It was accordingly not practicable to obtain measurements on the temperature coefficient of the rate of type B adsorption.

Isotherms for the higher temperature type B adsorption at 350 and 400° were apparently reversible at pressures between 250 and 900 mm. They indicated energies of adsorption of about 8500 calories per mole of hydrogen. However, the value must be considered as only approximate for below 250 mm. due to incomplete equilibration the adsorption values obtained by a desorption equilibrium at 400° were about the same as those obtained by an adsorption approach at 350° .

It seemed of interest to obtain some information relative to the effect both of type A and of type B adsorption on the van der Waals adsorption of hydrogen and nitrogen on the iron catalysts. Accordingly, a nitrogen isotherm was taken at -183° , before and after the activated adsorption (type B) of 3.47 cc. of hydrogen at 100° (type A adsorption was largely removed by pumping with a Toepler pump). The two isotherms are shown in Fig. 3. Within experimental error no difference between the nitrogen isotherms before and after

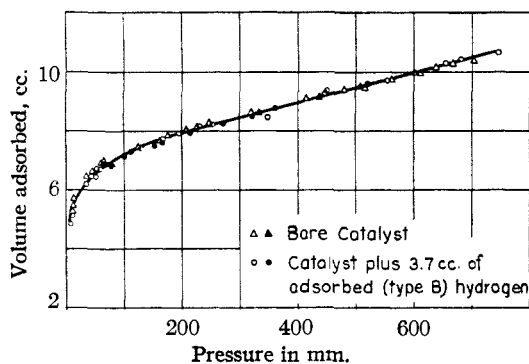


Fig. 3.

the hydrogen adsorption could be observed. Type B activated adsorption at 100° does however definitely decrease the physical adsorption of hydrogen at -183° . Thus the adsorption of 7.7 cc. (probably only 3 or 4 cc. of this being type B adsorption) of hydrogen at 100° decreased the physical adsorption 38% from 2.95 to 1.84 cc. in run 6. On the other hand, type A adsorption did not de-

crease the physical adsorption appreciably, 4.8 cc. of hydrogen adsorbed at -78° (type A) in run 7,⁶ causing the -183° van der Waals hydrogen adsorption to decrease from 2.94 to 2.8 cc. Run 40 showed 2.75 cc. of van der Waals adsorption both before and after 7.3 cc. of type A adsorption.

In Fig. 4 the approximate position of the 760 mm. isobars for the three types of adsorption are shown. The dotted portions represent the regions in which no adsorption runs were made because of the slowness of one of the two types of adsorption occurring in each of these regions. All runs in the region -196 to -140° made on the degassed catalyst are shown. The volume of type A adsorption in the -78 to 0° region was quite sensitive to the duration and temperature of the preliminary evacuation. About 12 runs ranging from 1 to 25% lower than the curve have been omitted for the sake of clarity. All runs in the temperature range 100 to 460° are shown in Fig. 4, the 6 points at 100° being for runs 6, 8, 13, 17, 19, 23 and those at about 450° for runs 10, 15, 16, 24, 25 and 26.

In an endeavor to ascertain whether the general shape of the 760 mm. isobar was characteristic of iron catalysts or was in some way due to the promoters, several adsorption measurements were made on a 10-cc. sample (about 20 g.) of catalyst 973. At -183 , -78 and 100° the catalyst adsorbed 1.2, 2.9 and 2.6 cc. before sintering and 0.4, 0.9 and 0.9 cc. after several hours of sintering at 500° . These values indicate an isobar of the type found for catalyst 931.

Discussion

In a previous communication² it was pointed out that studies of the catalytic ortho-para interconversion of hydrogen together with adsorption measurements, which have been described in detail in the present paper, lead unambiguously to two conclusions: (1) that in the iron-hydrogen system two types (A and B) of what Taylor⁷ has termed "activated" adsorption exist and (2) that a considerable portion of both types must be adsorption on the surface and not solution within the

(6) Both of these nitrogen isotherms were taken after the catalyst had been partially oxidized due to a break in the reaction vessel (at the end from 44) and then reduced. Subsequent experience makes it probable that the -183° nitrogen adsorption before this accident would have been somewhat higher.

(7) Taylor, *THIS JOURNAL*, **53**, 578 (1931).

metal catalysts. Because the ortho-para conversion studies have been published in a separate paper it may be well to summarize briefly the specific nature of the experimental evidence that permits these conclusions to be drawn.

The first of the above conclusions is almost self-evident even if judged solely by the adsorption isobar of Fig. 4 and the adsorption characteristics of both type A and type B adsorption given in connection with Figs. 1, 2 and 3. Both A and B adsorptions conform to Taylor's⁷ definition of activated adsorption, for these are slow, temperature sensitive processes occurring well above the temperature at which van der Waals adsorption occurs. The manner in which the amount of activated adsorption between -80 and 0° decreases

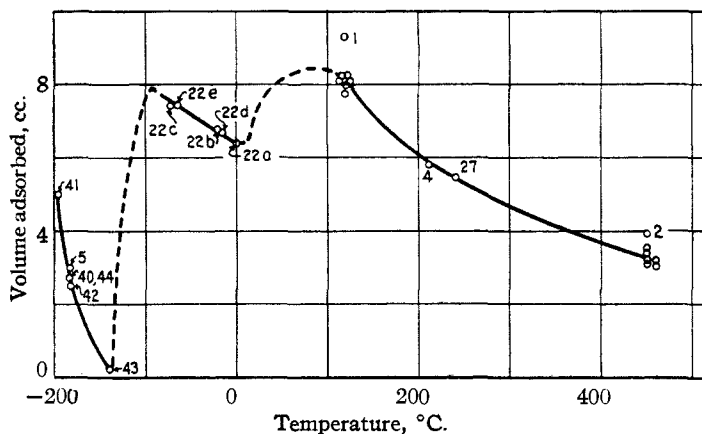


Fig. 4.

with increasing temperature is unmistakable evidence that the type B adsorption which first attains a conveniently measurable rate at about 100° is distinct from that occurring between -78 and 0° . Final confirmation of a difference in the two types of activated adsorption was furnished by their relative poisoning capacities¹ for the ortho-para conversion, type B activated adsorption (100°) being about eight times as poisonous per unit volume of gas adsorbed as the type A adsorption (-78°) for the para-ortho conversion at -190° .

The "surface" referred to in the second of the above conclusions may be defined simply as that portion of the catalyst that is sufficiently accessible to permit instantaneous equilibration with respect to van der Waals adsorption of gases such as hydrogen or nitrogen at liquid air temperature. The slow sorption of hydrogen by iron in the temperature range -100 to 0° (type A) was shown to

be taking place in part at least on the surface by the fact that 0.16 cc. of it on 0.25 cc. of catalyst 931 was able to cause a 20% decrease in the activity of the latter for the -190° ortho-para hydrogen conversion.¹ Incidentally, it is interesting to note that the observed rate of adsorption in this temperature range agrees well with the rate that one calculates by assuming that every molecule striking the surface with the observed energy of activation becomes adsorbed. A comparison of the observed rates with those calculated for energies of activation of 10,000 and 11,000 calories is shown in Table I.

TABLE I
COMPARISON OF OBSERVED AND CALCULATED RATES OF
TYPE A ACTIVATED ADSORPTION

Temp.	Pressure, mm. (average)	Rate of adsorption (cc. per minute)		
		Observed during first minute	Calculated for ^a $E_1 =$ 10,000 cal.	Calculated for ^a $E_1 =$ 11,000 cal.
-63.9	25	2.3	4.6	0.4
-72.0	54	3.2	3.9	.3
-78.7	22	1.1	0.7	.05
-87.6	760	1.3	7.3	.5
-95.0	760	1.8	2.4	.15

^a Surface is taken to be 200,000 sq. cm. for 10 cc. of catalyst as judged from nitrogen isotherms at -183° .

The slow sorption of hydrogen by iron at and above about 100° is typical of processes that have frequently been designated as "solution."⁸ However, in the present studies two types of experimental results were obtained that cannot be reasonably attributed to solution within the metallic lattice or to "activated diffusion" into any cracks or crevices that are too small to fall within the above definition of surface. The results⁹ referred to are (1) the poisoning experiments^{1,10} by which type B adsorption at 100° was found strongly to inhibit the catalytic ortho-para conversion over iron at -190° , and (2) the marked decrease in van der Waals hydrogen adsorption at -183° caused by type B (at 100°) but not by type A (at -78°) activated adsorption. These results could, it seems, be caused only by type B adsorption, being to a large extent *on the surface* of the catalyst.

The second of the above experimental results constitutes a type of evidence already offered by

(8) Ward, *Trans. Faraday Soc.*, **28**, 399 (1932); Steacie, *J. Phys. Chem.*, **35**, 2112 (1931).

(9) The present experiments, of course, neither prove nor disprove the possible occurrence of some "solution" within the metal lattice concomitantly with types A and B activated adsorption *on the surface*.

(10) Harkness and Emmett, *THIS JOURNAL*, **55**, 3496 (1933).

Howard¹¹ in showing that activated adsorption of hydrogen on chromic oxide is a surface adsorption. This criterion is useful when positive. However, it must be used with caution, for apparently gas held on the surface by activated adsorption does not decrease the van der Waals adsorption of all gases alike. Thus, type B activated adsorption of hydrogen at 100° on iron is able to decrease the van der Waals adsorption of hydrogen at -183° by about 40% but has no effect whatever upon the van der Waals adsorption of nitrogen at -183° (Fig. 3).

Comparatively little work has been published relative to the adsorption of hydrogen by iron. Taylor and Dew¹² found at 0, 110 and 218° and one atmosphere pressure, adsorption values of 0.0074, 0.0028 and 0.194 cc. of hydrogen per gram of iron. Benton and White⁵ on a sample of a pure iron synthetic ammonia catalyst (973) found at 1 atmosphere pressure per gram of iron a physical adsorption of 0.044 cc. of hydrogen at -183° , a slight adsorption of 0.01 cc. at -78° , and 0.006 cc. of rapid adsorption at 0° followed by about 0.06 cc. of a much slower adsorption over a period of thirty-five days. They interpreted their results as probably indicating physical adsorption, activated adsorption and a slow "solution" process of some kind, though the possibility that the slow sorption of gas at 0° and above constituted a second type of activated adsorption was mentioned. Our results for the -183° adsorption on catalyst (931) (0.14 cc. per gram) agree with Benton and White's in general when due allowance is made for the fact that promoted catalyst (931) would be expected to have a surface several times as large as that of the pure iron catalyst (973) used by them. They differ, for some as yet unknown reason, however, in that the ratio of type A activated adsorption at -78° to the van der Waals adsorption at -183° is about ten times as great in our experiments as in those of Benton and White.

No definite conclusions can at present be drawn as to which type if either of the activated adsorptions of hydrogen on iron is atomic or ionic. It should be mentioned that two types of activated adsorption of hydrogen have recently been found by Taylor and Strother¹³ on zinc oxide. It is possible that numerous examples exist but have been overlooked due to failure to take experimental points at sufficiently small temperature intervals.

(11) Howard, *Trans. Faraday Soc.*, **30**, 278 (1934).

(12) Dew and Taylor, *J. Phys. Chem.*, **31**, 277 (1927).

(13) Taylor and Strother, *THIS JOURNAL*, **56**, 587 (1934).

Summary

1. Two types of activated adsorption of hydrogen on iron synthetic ammonia catalysts have been found, type A occurring at a convenient rate at -90° and above, type B at 100° and above.

2. Evidence has been presented to show that both types of activated adsorption are in part at least adsorptions on the surface rather than activated diffusion into cracks or solution within the lattice.

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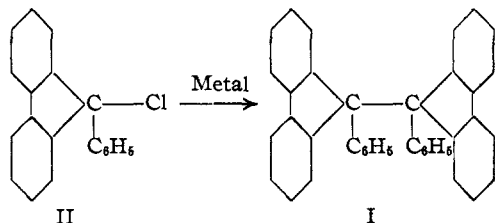
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Di-*p*-alkylphenyldibiphenyleneethanes. The Effect of the *p*-Alkyl Group on the Dissociation of the Ethane¹

BY L. E. SCHNIEPP AND C. S. MARVEL

Diphenyldibiphenyleneethane (I) has been reported to be undissociated in solution at ordinary temperatures, and to be unoxidized by air until the temperature is raised to above 200° .² However, if the treatment of phenylbiphenylene-methyl chloride (II) with a metal is carried out



in the presence of air, the hydrocarbon (I) is not obtained, but the peroxide forms in good yields.³ Schlenk and Herzenstein⁴ have also reported that the closely related hexaarylethane, in which biphenyl groups replace the simple phenyl groups in the above hydrocarbon (I), is likewise unexpectedly stable toward oxidation by air, and does not dissociate in benzene solution at room temperature. The unusual behavior of these hydrocarbons must be attributed to the extra ring system present in the biphenylene groups, since hexaphenylethane is easily oxidized in air and at room temperature in 0.08 molar solution in benzene is dissociated to the extent of 3.6%,⁵ and tetraphenyldibiphenyleneethane is even more easily oxidized, and exists as the free radical to the extent of 10–15%.⁶

In order to gain more information concerning

(1) For the first paper on this subject, see Copenhagen, Roy and Marvel, *THIS JOURNAL*, **57**, 1311 (1935).

(2) Schlenk, Herzenstein and Weickel, *Ber.*, **43**, 1753 (1910); Gomberg and Cone, *ibid.*, **39**, 2989 (1906).

(3) Gomberg and Cone, *ibid.*, **39**, 1461, 2957 (1906).

(4) Schlenk and Herzenstein, *Ann.*, **372**, 21 (1910).

(5) Ziegler and Ewald, *ibid.*, **473**, 163 (1929).

(6) Schlenk, Weickel and Herzenstein, *ibid.*, **372**, 1 (1910).

the dibiphenyleneethanes we have prepared three homologs of diphenyldibiphenyleneethane in which the *p*-hydrogen atoms of the phenyl groups are replaced by methyl, ethyl and *n*-propyl groups, respectively. The synthesis of these compounds involved well-known reactions. Fluorenone was treated with the *p*-alkylphenylmagnesium halide after the method of Ullmann and Von Wursterberger⁷ for the preparation of phenylbiphenylenecarbinol. The *p*-tolyl compound has previously been described by Kovache.⁸ The other carbinols could not be obtained in crystalline form. The carbinols were converted to chlorides by the method of Gomberg.⁹ The *p*-tolyl- and *p*-ethylphenyl derivatives crystallized easily and were converted to the ethanes by treatment with copper bronze. The *p*-*n*-propylphenylbiphenylenechloromethane did not crystallize, but it did react with methyl alcohol to give the methyl ether of *p*-*n*-propylphenylbiphenylenecarbinol which crystallized readily. This methyl ether was then cleaved with sodium amalgam to give sodium *p*-*n*-propylphenylbiphenylenemethyl which was converted to the desired ethane by treatment with tetramethylethylene bromide according to the general method devised by Ziegler and Schnell.¹⁰

None of the new ethanes were obtained in pure crystalline form. Their solutions in benzene were light yellow to red, and all were readily oxidized by air at room temperature to give the peroxides. It is thus evident that introduction of alkyl groups into the *para* position of the phenyl group in this class of hexaarylethanes increases

(7) Ullmann and Von Wursterberger, *Ber.*, **37**, 73 (1904).

(8) Kovache, *Ann. chim.*, [9] **10**, 210 (1918).

(9) Gomberg, *THIS JOURNAL*, **26**, 1516 (1904).

(10) Ziegler and Schnell, *Ann.*, **437**, 227 (1924).