REACTIVITIES OF NAPHTHENES OVER A PLATINUM RE-FORMING CATALYST BY A GAS CHROMATOGRAPHIC TECHNIQUE

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Received October 7, 1958

A micro-reactor coupled directly with a gas chromatographic analysis apparatus comparable to that of Kokes, Tobin and Emmett, was used to determine reactivities of thirty individual C_5–C_8 naphthenes. Tests were made over a platinum–alumina–halogen catalyst at 350° and atmospheric pressure, using excess hydrogen. It was found that cyclopentanes and 1,1-dimethylcyclohexane are converted to aromatics much more slowly than are ordinary cyclohexanes. To explain reactivities of cyclopentanes, it is supposed that cyclopentanes first dehydrogenate to olefins which then migrate to form carbonium ions on acidic sites. Skeletal isomerization of the carbonium ions to cyclohexyl structures is taken to be the slow step in the series of reactions leading to aromatic hydrocarbons. Relative rates of alternative paths are given by simple ratios for relative carbonium ion stabilities, multiplied by the number of possible paths. In this way, rates of aromatization and the amounts of specific aromatic isomers formed are explained. Two adjustable parameters suffice for fitting the data for 21 cyclopentanes.

Heterogeneous catalysis is recognized as one of the most difficult branches of chemical kinetics. Knowledge about the reaction intermediates is hard to obtain because these intermediates exist as transitory fractional monolayers on surfaces of ill-defined nature. In fact, the intermediates must in many cases consist of actual chemical compounds between the reacting molecules and groups of atoms of the solid, but unfortunately we seldom know the formulas or chemical properties of these compounds. In this situation, progress in understanding can only be made by systematically varying the catalyst, the reaction conditions or the reactants, and by establishing correlations between the observed reactions and the properties that are varied. The making of such studies has been greatly expedited by the gas chromatographic technique for catalysis, which has been described by Kokes, Tobin and Emmett.[1] In the following paragraphs we describe an application of this technique to the re-forming of a series of naphthenes. The data so obtained have led us to a theory which gives insight into the nature of this important type of catalysis.

The re-forming of gasolines for octane number improvement is today largely carried out over platinum–alumina–halogen catalysts. Some reactions in "Platforming" are described by Haensel and Donaldson.[2] The major conversion in this process is that of naphthenes (cycloalkanes) to aromatics. Among the reactions that occur, some, such as isomerization of paraffins and the conversion of methylcyclopentane naphthenes to aromatics, require an acidic catalyst function as well as metal dehydrogenation sites. Both types of site are present in the bifunctional platinum–alumina–halogen catalysts. Mills and co-workers[3] have shown that olefins are probable intermediates in conversions of cyclopentanes. It also has been demonstrated, by Mills,[4] and by Weisz and Swegler,[5] that the platinum sites and the acidic sites can act independently, for paraffin isomerization and methylcyclopentane conversion are obtained with physical mixtures of platinum catalysts and acidic catalysts. This latter finding is consistent with the appearance of olefins in the vapor phase as intermediates. In none of this work, however, has a systematic series of hydrocarbons been investigated. With the aid of the gas chromatographic technique we have been able to study such a series, using very small amounts of the excellent pure hydrocarbon samples from the American Petroleum Institute. The results illustrate the great power of this method of investigation. The theoretical interpretation of the results indicates that the slow step in re-forming of cyclopentanes under our conditions is not the formation of the olefin intermediate nor the migration of this intermediate to the acid sites, but is the skeletal isomerization of the olefin at the acid site. Furthermore, there is quantitative satisfaction in the theory developed from these data.

Experimental

A micro-reactor was placed in the hydrogen line leading to a gas chromatographic column. This reactor contained one gram of catalyst, which gave a volume of nearly 2 cc. For an experiment the naphthene feed was injected as a small shot through a serum cap directly into the hydrogen stream prior to the reactor. The hydrogen served to carry the feed through the reactor, to maintain the catalyst in the proper condition, to hydrogenate the major fraction of the olefins as in normal re-forming, to carry all the products into the chromatographic column, and to elute the fractions from the column. The usual feed shot was 4–5 microliters, or about 3 mg. The hydrogen flow rate of 3 liters per hour gave a residence time in the catalyst zone of about 2 seconds. Temperature was varied from 300–400°, but for the most part only results at 350° are shown. Pressure was atmospheric plus the small amount of pressure drop through the column.

Hydrocarbons.—The naphthenes used were all from the American Petroleum Institute.[6] For the most part, these have been prepared by the A.P.I. Project 45.[6] Gas chromatographic analyses verified the high purities of these samples.

Catalyst.—The platinum–alumina–halogen catalyst was ground and sieved to 40–60 mesh. Since the activity of a fresh catalyst changes rapidly, it was stabilized by use with a sulfur-containing feed at 400° before the experiments were done. All the runs were made with a single catalyst charge. Its activity was periodically measured by feeding 1,1-dimethylcyclohexane under standard conditions and was found to be virtually constant.

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(1) R. J. Kokes, H. Tobin, Jr., and P. H. Emmett, *J. Am. Chem. Soc.*, **77**, 5860 (1955).

(2) V. Haensel and G. R. Donaldson, *Ind. Eng. Chem.*, **43**, 2102 (1951).

(3) G. A. Mills, H. Heinemann, T. H. Milliken and A. G. Oblad, *ibid.*, **45**, 134 (1953).

(4) G. A. Mills, *Advances in Catalysis*, **IX**, 639 (1957).

(5) P. B. Weisz and E. W. Swegler, *Science*, **126**, 31 (1957).

(6) American Petroleum Institute, Standard Samples of Hydrocarbons, Chemical and Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh 13, Penna. See also publications of A.P.I. Project 45, by C. E. Boord and co-workers.

Chromatographic Column.—A U-shaped glass column 1.8 m. long and 6 mm. i.d. was used. It was packed with 30–100 mesh firebrick coated with an ester prepared from dinitrodiphenic acid and C_5-C_6 oxo alcohols. The ratio of support to column liquid was 100/40. This column was used at 120°. It had excellent stability and good selectivity for separation of saturates and aromatics. Toluene emerged just after the highest boiling C_8 naphthenes. The detector made use of the ionization by Sr-90 β-rays. An integrating recorder was employed. With the radiological detection, the area of an elution peak is directly proportional to the weight of the component, and detailed calibration is not necessary.[7]

Results

Data for cyclohexanes treated at 350° are given in Table I. The dehydrogenation to the expected aromatic compound was 96–100% complete, except with 1,1-dimethylcyclohexane. The latter compound reacted only to the extent of 34% and gave almost exclusively *o*-xylene. The low reactivity of 1,1-dimethylcyclohexane was expected from the fact that the geminal dimethyl grouping blocks direct dehydrogenation to an aromatic.

TABLE I

CONVERSIONS OF CYCLOHEXANES OVER PLATINUM–ALUMINA–HALOGEN CATALYST

Temperature 350°; excess H_2 at slightly above atmospheric pressure

Compound	B.p., °C.	Wt. % of total effluent: Unconverted	Wt. % of total effluent: Reaction products
Cyclohexane	80.7	4	Benzene 96
Methylcyclohexane	100.9	2	Toluene 98
Ethylcyclohexane	131.8	0	Ethylbenzene 100
1-*cis*-2-Dimethylcyclohexane	129.7	0	*o*-Xylene 100
1-*trans*-2-Dimethylcyclohexane	123.4	0	*o*-Xylene 100
1-*trans*-3-Dimethylcyclohexane	124.5	0	*m*/*p*-Xylene 100
1-*cis*-4-Dimethylcyclohexane	124.3	0	*m*/*p*-Xylene 100
1,1-Dimethylcyclohexane	119.5	66	Toluene 1.3; *o*-xylene 32.7 (calcd. *o*-xylene 44)

Results from C_5–C_7 cyclopentanes are summarized in Table II. Conversions to aromatics varied from 1.4 to 25% and there were traces of cracking. Data for C_8 cyclopentanes are given in Table III. These were converted to the extent of 3 to 43.6%, but again amounts of cracking were quite small except for isopropylcyclopentane, for which cracking was 15.4%.

When it was possible, extensive *cis–trans* isomerization occurred in both C_7 and C_8 compounds. Some data on the *cis–trans* isomerizations are collected in Table IV. It appears that in many cases an equilibrium was reached. The *cis–trans* isomerizations are very much faster than isomerizations involving the shift of a methyl group from one carbon to another. This is consistent with the theory developed below.

Experiments not tabulated were done at 300 and 400°. Even at 300° dehydrogenation of cyclohexanes was 95% or more, except for values of 89% for ethylcyclohexane, 78% for methylcyclohexane, 64% for cyclohexane and only 13% for 1,1-dimethylcyclohexane. Conversions of the cyclopentanes under the same conditions were less than 5%, except for a value of 7.7% for isopropylcyclopentane. Thus it is possible that an analytical method for distinguishing cyclopentanes from cyclohexanes could be based on the dehydrogenation reaction over a platinum catalyst at about 300°. Such an analysis would put geminally substituted cyclohexanes largely into the cyclopentane group. At 400° the cyclohexanes were 100% converted, except for 1,1-dimethylcyclohexane, 93.7%. At this temperature conversions of cyclopentanes ranged from 6 to 76%. Clearly, 300° is better for an analytical scheme.

Discussion

It is well known that platinum re-forming catalysts are bifunctional, for they display characteristics that can be attributed to metal sites and other characteristics that can be attributed to acid sites (halogen on alumina). It has been shown many times that simple dehydrogenation reactions, such as the conversion of cyclohexane to benzene, require only the participation of metal sites. Other typical re-forming reactions, however, such as conversion of methylcyclopentane to benzene, or the isomerization of *n*-heptane, require action of sites of both types. In these reactions olefins formed on the metal sites presumably migrate to the acid sites where the isomerization occurs. It often has been thought that the low concentration of olefins, or the slow migration of the olefins, sets a limit to the rate of reactions requiring coöperation of both sites. However, our results demonstrate that the rate-controlling step, under our conditions, is the isomerization at the acid site. This is most clearly shown by the great difference in rate of reaction of different cyclopentanes. It is reasonable to think that rates of dehydrogenation to olefin are about the same for all these cyclopentanes. Likewise, equilibrium concentrations of olefins, and rates of migration to the acid sites, should be relatively constant. We are left with isomerization as the crucial slow step. This conclusion has consequences that are well borne out by the experimental results.

Cyclohexanes, except for the geminally substituted members like 1,1-dimethylcyclohexane, can be directly dehydrogenated to aromatics on the metal sites. They are converted rapidly at 350° and atmospheric pressure, with no change in carbon skeleton, to almost the full extent permitted by equilibrium, which is essentially 100%. We need no further theory for these compounds.

Cyclopentanes, on the other hand, must be isomerized before they can be dehydrogenated to aromatics. The same applies for the geminally substituted cyclohexanes. The isomerization occurs on the acid sites, and is closely akin to isomerizations that take place on acidic cracking catalysts. The reactions on cracking catalysts can be explained by reactions of postulated intermediate species called carbonium ions held on a surface adjacent to a counter-ion. The carbonium ions split and rearrange according to definite rules.[8] Similar rules applied to the isomerizations of the cyclopentenes on the acid sites of reforming catalysts explain reactivities and predict the major products. This is further evidence that the isomerization is the slow step.

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(7) C. H. Deal, J. W. Otvos, V. N. Smith and P. S. Zuco, *Anal. Chem.*, **28**, 1958 (1956); H. Boer in D. H. Desty, "Vapor Phase Chromatography" Butterworths Scientific Publications, London, 1956.

(8) B. S. Greensfelder, H. H. Voge and G. M. Good, *Ind. Eng. Chem.*, **41**, 2573 (1949).

TABLE II

CONVERSIONS OF C_5–C_7 CYCLOPENTANES OVER PLATINUM–ALUMINA–HALOGEN CATALYST

Temperature 350°; excess H_2 at slightly above atmospheric pressure

		Products, wt. % of effluent					
			Benzene		Toluene		
Compound	B.p., °C.	Unconverted	Obsd.	Calcd.	Obsd.	Calcd.	Other
Cyclopentane	49.3	99.3	..	..	..	..	[b]
Methylcyclopentane	71.8	96.0	2.6	1.4	..	..	[c]
Ethylcyclopentane	103.5	74.0	..	..	25.0	21.9	[d]
1,1-Dimethylcyclopentane	87.8	98.0	..	..	2.0	2.7	..
1-*cis*-2-Dimethylcyclopentane	99.5	97.1[a]	..	..	2.9	2.7	..
1-*trans*-2-Dimethylcyclopentane	91.9	96.1[a]	..	..	3.9	2.7	..
1-*cis*-3-Dimethylcyclopentane	90.8	98.6[a]	..	..	1.4	2.7	..
1-*trans*-3-Dimethylcyclopentane	91.7	98.5[a]	..	..	1.5	2.7	..

[a] *cis–trans* isomerization occurred, but is not counted as conversion. [b] 0.7% *n*-pentane formed. [c] 1.4% *n*-hexane formed. [d] 1.0% *n*-heptane formed.

TABLE III

CONVERSIONS OF C_8 CYCLOPENTANES OVER PLATINUM–ALUMINA–HALOGEN CATALYST

Temperature 350°; excess H_2 at slightly above atmospheric pressure

		Products, wt. % of effluent							
			Ethylbenzene		*m/p*-Xylene		*o*-Xylene		
Compound	B.p., °C.	Unconverted	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Other
n-Propylcyclopentane	130.9	73.2	26.4	21.9	0	0	0	0	[b]
Isopropylcyclopentane	126.4	56.4	0	0	0	0	28	43.8	[c]
1-Methyl-1-ethylcyclopentane	121.5	79.9	1.1	1.4	3.4	0	15.6	21.9	
1-Methyl-*cis*-2-ethylcyclopentane	128.1	81.4[a]	2.5	1.4	8.5	10.9	7.6	10.9	
1-Methyl-*trans*-2-ethylcyclopentane	121.2	82.0[a]	1.7	1.4	9.1	10.9	7.5	10.9	
1-Methyl-*cis*-3-ethylcyclopentane	121.1	83.4[a]	0.2	1.4	16.4	21.9	0	0	
1-Methyl-*trans*-3-ethylcyclopentane	121.1	70.3[a]	0.3	1.4	29.4	21.9	0	0	
1,1,2-Trimethylcyclopentane	113.7	95.6[a]	0	0	3.4	1.4	0.9	2.7	
1,1,3-Trimethylcyclopentane	104.9	97.0[a]	0	0	2.4	2.7	0.6	1.4	
1-*cis*-2-*cis*-3-Trimethylcyclopentane	123.0	95.3[a]	0	0	2.8	1.4	1.9	2.7	
1-*cis*-2-*trans*-3-Trimethylcyclopentane	117.5	95.1[a]	0	0	2.9	1.4	2.0	2.7	
1-*trans*-2-*cis*-3-Trimethylcyclopentane	110.2	96.7[a]	0	0	2.1	1.4	1.2	2.7	
1-*cis*-2-*trans*-4-Trimethylcyclopentane	116.7	95.9[a]	0	0	3.5	2.7	0.6	1.4	
1-*trans*-2-*cis*-4-Trimethylcyclopentane	109.3	95.4[a]	0	0	3.6	2.7	1.0	1.4	

[a] *cis–trans* isomerization occurred, but is not counted as conversion. [b] 0.4% toluene. [c] 0.2% methane, 15.2% octane.

TABLE IV

cis-trans ISOMERIZATION OF CYCLOPENTANES

The table shows the compositions of some recovered cyclopentanes after treatment at 350°

Compound treated	Composition of recovered material
Dimethylcyclopentanes	
1-*cis*-2	35% 1-*cis*-2; 65% 1-*trans*-2
1-*trans*-2	15% 1-*cis*-2; 85% 1-*trans*-2
Methylethylcyclopentanes	
1 *M*, *cis*-2 E	16% 1 *M*, *cis*-2 E; 84% 1 *M*, *trans*-2 E
1 *M*, *trans*-2 E	13% 1 *M*, *cis*-2 E; 87% 1 *M*, *trans*-2 E
Trimethylcyclopentanes	
1-*cis*-2-*cis*-3	60% 1-*trans*-2-*cis*-3; 30% 1-*cis*-2-*trans*-3; 10% 1-*cis*-2-*cis*-3
1-*cis*-2-*trans*-3	56% 1-*trans*-2-*cis*-3; 40% 1-*cis*-2-*trans*-3; 4% 1-*cis*-2-*cis*-3
1-*trans*-2-*cis*-3	72% 1-*trans*-2-*cis*-3; 24% 1-*cis*-2-*trans*-3; 4% 1-*cis*-2-*cis*-3
1-*cis*-2-*trans*-4	73% 1-*trans*-2-*cis*-4; 25% 1-*cis*-2-*trans*-4; 2% 1-*cis*-2-*cis*-4
1-*trans*-2-*cis*-4	83% 1-*trans*-2-*cis*-4; 16% 1-*cis*-2-*trans*-4; 1% 1-*cis*-2-*cis*-4

The chief steps in the conversion of a cyclopentane to an aromatic are: (1) dehydrogenation to olefin on a metal site; (2) migration of the olefin to an acid site; (3) addition of a proton at the acid site to form a carbonium ion; (4) isomerization of the ion by carbon skeleton rearrangement; (5) release and migration of a new olefin; (6) dehydrogenation of the new olefin to an aromatic at a metal site. In this complex set of reactions, many carbonium ions have to be considered in steps 3 and 4. Simplifications result, however, from the facts that step 4 is slow and that many carbonium ions produce no new dehydrogenation products. But before we proceed with our analysis of step 4, some comment on the other steps is needed.

Dehydrogenation to olefin in step 1 is rapid. Evidence for this is found in the high rate of conversion of cyclohexanes, where cyclohexenes are presumably intermediates. We shall postulate that cyclopentenes are in equilibrium with cyclopentanes. We shall also postulate that the migration of step 2 is rapid, either through the vapor phase or across the catalyst surface. Step 3 is the initial formation of a carbonium ion. There are a number of possible carbonium ions of unchanged carbon skeleton. The high observed rate for double-bond shift isomerizations over cracking catalysts[9] and the rapidity of hydrogen exchange reactions in similar systems both suggest that equilibrium will prevail among these various ions of the same carbon skeleton. Since tertiary carbonium ions are most stable, secondary next, and primary least stable, we may take their abundances in that order. These values are used: *tertiary/primary carbonium ion ratio*, 32;

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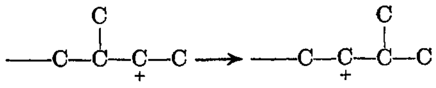
(9) H. H. Voge, G. M. Good and B. S. Greensfelder, *ibid.*, **38**, 1033 (1946).

secondary/primary carbonium ion ratio, 16.

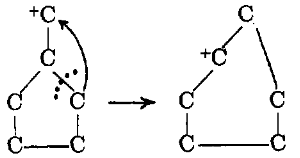
Steps 5 and 6 are fast for the same reasons that 1 and 2 are fast. They have no influence on product distribution. Step 6, the dehydrogenation of suitable olefins to aromatics, removes these olefins from the system, and thus permits more of the same structure to form. The completeness of this dehydrogenation reaction, determined by thermodynamics, causes aromatics to be the major products rather than isomerized naphthenes. If there is extensive cracking, lower paraffins can also be major products.

In step 4 several types of isomerization of the carbonium ion at the acid site can occur, as well as cracking. The new olefins that return to the metal sites may be dehydrogenated to aromatics or hydrogenated to paraffins or to isomerized naphthenes. We can expect some of each, but since cracking is not extensive under mild re-forming conditions, aromatics that can form readily will predominate as stable end products. Thus we can restrict attention to those ions and isomerizations that lead to aromatics. In the isomerization of a carbonium ion, a group attached to the carbon atom adjacent to the carbonium-ion carbon moves over to the carbonium-ion carbon. This shifting group is visualized as carrying a negative charge.



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

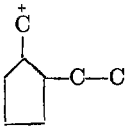
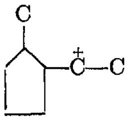
This shift is closely related to the beta fission rule that explains the products of catalytic cracking over acid catalysts.[8] The same type of shift can change a 5-ring to a 6-ring.



The 6-ring goes readily to an aromatic. The ring enlargement is essentially like one of the steps proposed by Pines and Shaw[10] to explain movement of a tagged carbon from the side chain to the ring in treatment of ethylcyclohexane over another bifunctional catalyst, nickel on alumina–silica.

The rate of the series of reactions leading to a particular product will be given by the relative amount of the carbonium ion multiplied by one factor for the rate of the step 4 isomerization and another for the number of equivalent isomerization paths (statistical factor). As a simple assumption, we take the rate of isomerization as a constant (empirical factor) in this series of closely related compounds. For example, consider 1-methyl-2-ethylcyclopentane. The two ions that can produce aromatics are in the tabulation, with calculations. The empirical factor here is chosen to fit the average total aromatics formed from the trimethylcyclopentanes. The same empirical factor is used for all the cyclopentanes. Probably this is somewhat of an oversimplification for in certain isomerizations two successive rearrangements are necessary to produce a structure dehydrogenatable to an aromatic. This occurs when a 1,1-dimethylcyclohexane structure is formed by the primary isomerization, and then the final product is predicted to be *o*-xylene. However, use of additional rate factors for such cases introduces too many adjustable parameters.

EXAMPLE OF CALCULATION

Ion	Product	Relative amount of ion	Statistical factor	Empirical factor	Rate of formation
	Ethylbenzene	1	2	0.684	1.4
	*o*-Xylene	16	1	.684	10.9
	m-Xylene	16	1	.684	10.9

In Tables II and III the calculated amounts of various products are given for comparison with the experimental amounts. The average amounts of aromatics from various classes are summarized below.

AROMATIC CONTENTS OF PRODUCTS AT 350°

Compound or class	No.	Av. aromatics, % wt. Obsd.	Calcd.
Methylcyclopentane	1	2.6	1.4
Ethylcyclopentane	1	25	22
Dimethylcyclopentanes	5	2.3	2.8
n-Propylcyclopentane	1	27	22
Methylethylcyclopentanes	5	21	23
Trimethylcyclopentanes	7	4.1	4.1
1,1-Dimethylcyclohexane	1	34	44

In this summary table, only two adjustable parameters are involved, namely, 16/1 and 0.684. Conversions have been taken as proportional to rates, which is reasonable at conversion levels below 30%. The agreement between observed and calculated amounts is quite good considering the simplifications that have been introduced into the theory. The calculated value for 1,1-dimethylcyclohexane is also of the right order of magnitude. Isopropylcyclopentane is the only compound of the series in which a tertiary carbonium ion has been postulated. Because of the double isomerization necessary in converting isopropylcyclopentane to *o*-xylene, as well as because of the extensive cracking that occurred, the parameter of 32, used with this compound only, is probably too low. In other cases some double isomerization may account for appearance of a product not predicted, such as *m*-xylene from 1-methyl-1-ethylcyclopentane.

The aromatic products did not ever appear to be at equilibrium. At 350° the approximate equilibrium composition is 22% *o*-xylene, 50% *m*-xylene, 22% *p*-xylene, 6% ethylbenzene.

Re-forming is normally carried out at 20–40 atmospheres rather than at near atmospheric pressure as in these experiments. Nevertheless, the higher temperature of re-forming, about 480°, means that equilibrium olefin concentrations are not much different than at 350° and atmospheric pressure. There is no evidence of which we are

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[10] H. Pines and A. W. Shaw, *J. Am. Chem. Soc.*, **79**, 1474 (1957).

aware to say that the present picture would not hold under commercial re-forming conditions, although naturally the parameters will be somewhat different, and the isomerization step will be faster because of the higher temperature. Our conclusion that the isomerization step is rate limiting agrees with the evidence of Weisz and Prater[11] who found acid activity usually limited octane improvement in re-forming.

Acknowledgment.—We wish to thank the Bataafsche Petroleum Maatschappij for permission to publish this paper, Dr. H. Bau who designed and constructed the apparatus, and H. van Kranen for experimental work.

[11] P. B. Weisz and C. D. Prater, *Advances in Catalysis*, **IX**, 575 (1957).

HEATS OF ADSORPTION OF HYDROGEN ON A SINGLY PROMOTED IRON CATALYST

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Received September 15, 1958

Early work by Emmett and Harkness has indicated the presence of two types of chemisorption of hydrogen on iron catalysts. These types, designated as A and B, proceed fairly rapidly at temperatures around 0 and 200°, respectively. More recently Kummer and Emmett have shown that "singly promoted iron catalysts, unlike doubly promoted catalysts, rapidly catalyze the hydrogen–deuterium exchange reaction at −195°." On the basis of this observation and of the adsorption data for the hydrogen–iron system, these authors postulate a third kind of chemisorption, called Type C, occurring in the low temperature region. At Emmett's suggestion, we have undertaken the calorimetric measurement of the heats of adsorption of hydrogen on the singly promoted iron catalyst at temperatures selected to sort out the three types of chemisorption. We have achieved satisfactory calorimetric measurements at 0° and at −195°. At these two temperatures the heat values range from 16.5 to 8.0 (at 0°) and from 5.4 to 1.6 kcal. per mole (at −195°) for successive increments of hydrogen. Rather crude measurements at 200° indicate heats ranging from 27 to 15 kcal. per mole. In particular the calorimetric results at −195° confirm the prediction of Emmett and Kummer that the heat of Type C adsorption would be "considerably greater than that of the heat of adsorption of physically adsorbed hydrogen, but at the same time considerably smaller than the heat of adsorption of either Type A or Type B hydrogen adsorption."

Introduction

The work of Emmett and Harkness[1] has indicated the presence of two types of chemisorption of hydrogen on a doubly promoted iron catalyst and on a "pure" iron catalyst. These types designated as A and B were found to occur in the temperature ranges −78 to 0° and +100 to 460°, respectively. The evidence for types A and B chemisorption is based on the shapes of the isobars and also upon the relative poisoning effects of these two types on the ortho–para hydrogen conversion at −190°, Type B being a much more effective poison. In addition to the two chemisorption processes, there was a physical adsorption in the −195 to 183° range; however there was no evidence for any significant amount of chemisorption in this low temperature region.

More recently Kummer and Emmett[2] have extended the previous work to include a singly promoted iron catalyst and to test the activity of both the doubly and singly promoted catalysts for the hydrogen–deuterium exchange reaction as well as the ortho–para hydrogen interconversion. These investigators found that, unlike the doubly promoted catalyst, the singly promoted material could effect a rapid hydrogen–deuterium exchange at −195°. Moreover the singly promoted catalyst differed in another respect in that it was not poisoned for the ortho-para hydrogen interconversion at −195° by the presence of Type B adsorption. On the basis of these observations and of the adsorption data for the hydrogen–iron system Kummer and Emmett have suggested the existence of a third type of chemisorption, called Type C, on the singly promoted iron catalyst. On the basis of their observations, Kummer and Emmett conclude that the heat of binding of this third type of chemisorption "is apparently considerably greater than the heat of adsorption of physically adsorbed hydrogen but at the same time considerably smaller than the heat of adsorption of either Type A or Type B hydrogen adsorption."

At Professor Emmett's suggestion we have undertaken the calorimetric measurement of the heats of adsorption of hydrogen on the singly promoted iron catalyst at temperatures selected to sort out the three types of chemisorption. The temperatures selected were 0, 214 and −195° for Types A, B and C, respectively.

Experimental

Reduction of the Iron Catalyst.—The sample of singly promoted iron catalyst, designated as catalyst 198, was kindly supplied to us by Professor Emmett. This sample contained 5.50% Al_2O_3 and 70.73% Fe before reduction. The weight of this catalyst used in the calorimeter was 36.67 g. Approximately the same weight (36.12 g.) was used in the preliminary adsorption experiments. The specific surface area of the catalyst 198, as used in the preliminary experiments and computed from the nitrogen isotherm at −195° by the BET method, was 16.9 m.²/g. After the completion of the calorimetric work, the specific surface area of the sample was determined at 11.85 m.²/g.

Experience has shown[1-3] that the optimum conditions for activating these iron catalysts are achieved by reduction at 500° in a stream of pure hydrogen at high space velocity. For instance, Kummer and Emmett[2] used 1000 to 5000 cc. of hydrogen per hour per cc. bulk volume of catalyst. Special precautions are necessary to prevent traces of oxy-

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[1] P. H. Emmett and R. W. Harkness, *J. Am. Chem. Soc.*, **57**, 1624 (1935).

[2] J. T. Kummer and P. H. Emmett, THIS JOURNAL, **56**, 258 (1952).

[3] H. H. Podgurski and P. H. Emmett, *ibid.*, **57**, 159 (1953).