10^3 dynes per cm. from the crude relationship[8] that the surface tension of a solid is directly proportional to the hardness of the solid. It is, of course, widely acknowledged that any single value for the surface tension of a solid is an almost meaningless quantity. Also, the surface tension of a solid in bulk, even if it were known, does not correspond to the surface tension of a particle of the same solid of the size involved at the critical point.

The value of S_2/S_1 at the critical point is 180 obtained by extrapolation of the plot of log S_2/S_1 *vs.* time lag. The corresponding critical radius, 2.9×10^{-6} cm., is larger than the radius found[9] for sulfur, silver chloride and tetraphenylarsonium perchlorate but is of the same order of magnitude found for barium sulfate. The reasonableness of this value is nevertheless difficult to evaluate since the crystal structure of magnesium oxalate has not been determined but it is undoubtedly larger than the $(MgC_2O_4)_2$ suggested by the proposed mechanism. However, because of the uncertainties associated with the calculations based on the Thomson equation, the size of $(MgC_2O_4)_2$ is probably a more accurate value than 2.9×10^{-6} cm.

From the proposed mechanism, it is probable that the structure of the activated complex is similar to the product of the reaction and, therefore, the entropy of activation should be about the same as the ΔS for the over-all reaction. Measurements of the temperature dependence of the rate constant for the precipitation of magnesium oxalate, from which the entropy of activation may be calculated, are in progress.

NEW YORK, N. Y.

[8] M. L. Dundon and E. Mack, Jr., THIS JOURNAL, **45**, 2479, 2658 (1923); G. E. Boyd, "Surface Chemistry," A.A.A.S. 1941 Symposium, p. 128, 1943.

[9] V. K. LaMer and R. H. Dinegar, THIS JOURNAL, **73**, 380 (1951); F. R. Duke and L. M. Brown, Abstracts Division of Phys. and Inorg. Chem., A.C.S. March '53 Meeting, page 46P.

[CONTRIBUTION FROM HOUDRY PROCESS CO.]

The Catalytic Activity of Barium and Calcium Hydrides. III. Hydrogen Exchange with Some C_4 Hydrocarbons

BY LEON WRIGHT AND SOL WELLER

RECEIVED JUNE 28, 1954

A study has been made of the exchange of hydrogen between the C_4 hydrocarbons (*n*-butane, isobutane and isobutylene) and barium and calcium hydrides. Exchange proceeds much more slowly with the paraffins than with the olefin. Normal butane exchanges with the hydrides as readily as does isobutane, and all hydrogen atoms in the hydrocarbons are exchangeable. The primary hydrogen atoms in isobutane exchange more rapidly than the tertiary atom; this may be a steric effect. The exchange is interpreted in terms of a homolytic split of a carbon–hydrogen bond in the hydrocarbon, with the intermediate formation of a kind of metal alkyl and metal hydride.

Introduction

In recent years, considerable attention has been directed to the mechanism of interaction of hydrocarbons with both acidic and metallic catalysts. Of the many approaches to this problem, hydrogen exchange reactions have been particularly useful in supplying information on the nature of the catalyst–hydrocarbon complex.

Hydrogen exchange with butanes over oxide catalysts has been reported by Hansford, Waldo, Drake and Honig[1] and Hindin, Mills and Oblad[2]; over metal catalysts by Thompson, Turkevich and Irsa[3]; and in sulfuric acid by Otvos, Stevenson, Wagner and Beeck.[4] Hansford, *et al.*, and Hindin, *et al.*, found that isobutane exchanges with deuterated silica–alumina cracking catalyst at 60–150°, whereas *n*-butane does not exchange under these conditions. Similar results are obtained with sulfuric acid at 25°.[4] Thompson, *et al.*, studied the exchange of normal and isobutane with deuterium over a Fischer–Tropsch catalyst (Co–ThO_2–MgO–SiO_2) at 183°. In contrast to the results with acid catalysts, they found that both butanes exchanged to about the same extent. In unpublished work at the Houdry Laboratories, Mills[5] has found that both normal and isobutane exchange over a deuterated supported platinum catalyst at 28–100°.

In view of the difference existing in the exchange behavior of normal and isobutane over acid and metal catalysts, a study was undertaken of the exchange of butanes with barium and calcium hydrides in order to gain information as to the mode of interaction of these catalysts with hydrocarbons.

Experimental

Materials.—Calcium metal was obtained as a dark gray powder (100–200 mesh) from the Ethyl Corporation.

Deuterium of >99% purity was obtained from the Stuart Oxygen Company and used without further purification.

Calcium deuteride was prepared from the reaction of calcium metal and deuterium at 200–300°.

Barium deuteride was prepared from barium hydride (Metal Hydrides, Inc.) by exhaustive exchange with deuterium at 200–300°.

Normal butane, isobutane and isobutylene of research grade (>99.5%) were obtained from the Phillips Petroleum Company and were used after drying over anhydrous calcium sulfate at 25°.

---

[1] R. C. Hansford, P. G. Waldo, L. C. Drake and R. E. Honig, *Ind. Eng. Chem.*, **44**, 1108 (1952).

[2] S. G. Hindin, G. A. Mills and A. G. Oblad, THIS JOURNAL, **73**, 278 (1951).

[3] S. O. Thompson, J. Turkevich and A. P. Irsa, *ibid.*, **73**, 5213 (1951).

[4] J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, *ibid.*, **73**, 5741 (1951).

[5] G. A. Mills, private communication.

TABLE I

EXCHANGE OF ISOBUTYLENE AND ISOBUTANE WITH CALCIUM DEUTERIDE

300°, 36 mmoles CaD_2[a]

Run	Hydrocarbon		Time, hr.	Iso-C_4H_8	Iso-C_4H_{10}	Gas analyses (vol. %)[b]						
	Charged	Mmoles				D_1	D_2	D_3	D_4	D_5	D_6	D_7
1	i-C_4H_8	1.0	4	7.1	..	15.8	23.9	23.9	17.3	8.6	2.8	0.6
Statistical[c] distribution				3.9		15.5	27.2	27.4	17.2	6.9	1.7	0.3
2	i-C_4H_{10}	0.44	3	..	75.8	12.9	3.2	3.2	3.2	1.7	..	..
Statistical[c] distribution					59.8	31.6	7.5	0.8	0.1	0.008	..	..

[a] 36 mmoles calcium metal evacuated 20 hours at 300°, deuterated at 300° to the extent of 35% CaD_2. [b] % D_1 = % monodeuterohydrocarbon, etc. [c] Calculated from $D_n = (10!/n!(10-n)!)x^n(1-x)^{10-n}$ where D_n = mole fraction of the species D_n containing n deuterium atoms, x = mole fraction of hydrogen in the product gas.

TABLE II

EXCHANGE OF ISOBUTANE WITH BARIUM DEUTERIDE[a] AT 200°

Run	Time, hr.	Hydrocarbon, mmoles	Catalyst, mmoles	Gas analyses (vol. %)[b]							
				D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}
1	4	0.021	36	6.1	10.9	24.5	25.6	22.0	7.6	3.3	..
Statistical distribution				5.3	10.2	21.6	24.9	19.7	10.4	3.2	0.4
2	20	0.021	36	..	..	2.7	7.1	20.8	22.9	12.4	7.1
Statistical distribution				..	..	2.8	8.5	17.5	21.9	16.9	5.9

[a] Charged barium deuteride (97 atom % deuterium) in run 1 evacuated ten minutes at 200° prior to run 2. The initial pretreatment of the barium hydride sample prior to exchange with deuterium involved a twelve hour evacuation period at 300°. [b] % D_3 = % $C_4H_7D_3$, etc.

TABLE III

EXCHANGE OF ISO- AND n-BUTANE WITH BARIUM HYDRIDE[a]

Run	Hydrocarbon		Catalyst, mmoles	Temp., °C.	Time hr.	Iso-C_4H_{10}	n-C_4H_{10}	Gas analyses (vol. %)[b]				
	Charged	Mmoles						D_1	D_2	D_3	D_4	D_5
1	Iso-C_4H_{10}	0.45	180	300	1	34.9	..	35.5	14.6	4.7	0.5	0.2
2	n-C_4H_{10}	.45	180	300	1	..	40.9	38.1	16.2	4.1	0.7	..
3	Iso-C_4H_{10}	.021	36	100	20	47.3	..	34.8	14.2	0.9	..	..
4	n-C_4H_{10}	.021	36	100	20	..	52.6	35.9	9.9	1.6	..	..

[a] Charged barium hydride evacuated 18 hours at 300° prior to exchange with deuterium (10 atom % deuterium) in run 1, catalyst evacuated ten minutes at 300° prior to run 2; charged barium deuteride evacuated twelve hours at 300° prior to deuterium exchange (93 atom % deuterium) in run 3, catalyst evacuated ten minutes at 100° prior to run 4. [b] % D_1 = % C_4H_9D, etc.

Methylpropane-1-*d* and methylpropane-2-*d* were obtained from Dr. S. G. Hindin of the Houdry Laboratories and, as determined by mass spectrometry, were of better than 98% isotopic purity. Details of their preparation have been described previously.[2]

Apparatus and Procedure.—All experiments were carried out using high vacuum techniques. The general experimental procedure was as follows: a measured amount of catalyst was evacuated under 10^{-5} mm. at elevated temperatures (200 or 300°) for a fixed period. A known amount of hydrocarbon was then admitted to the catalyst at reaction temperature; after the desired reaction time, the hydrocarbon was desorbed into a gas sample tube, cooled to −195° and analyzed by mass spectrometer. The technique used for analyzing the mixtures of deuterated isobutanes has been previously described.[2]

Experimental Results

The initial experiments in this study were concerned with the exchange of isobutane and isobutylene with calcium deuteride at 300°. Isobutylene exchanged at a rate rapid enough to reach isotopic equilibrium in the gas phase after four hours at 300° (Table I); isobutane, however, exchanged at a much slower rate, and deuterobutanes were obtained in non-statistical distribution.

Since it had been reported[1] that olefins catalyzed hydrogen exchange of isobutane over oxide catalysts, an experiment was carried out in which a mixture of 98.4% isobutane and 1.6% isobutylene was allowed to stand over calcium deuteride at 300°. Only the isobutylene exchanged, no catalysis of isobutane exchange being observed under the experimental conditions.

Isobutane was found to exchange more rapidly with barium hydride than with calcium hydride. Complete isotopic equilibrium in the gas phase was obtained within one hour at 300° when isobutane was exposed to partially deuterided (5.8 atom % deuterium) barium hydride, the catalyst:hydrocarbon ratio being 5:1.

Isobutane readily exchanges only nine of its ten hydrogens with silica–alumina at 60–150°.[1,2] It was accordingly of interest to determine if all ten hydrogens of isobutane would exchange over barium hydride. By exhaustively treating a sample of barium hydride with deuterium, a catalyst was obtained containing essentially only barium deuteride (97 atom % deuterium). When isobutane was allowed to stand over this catalyst at 200°, highly deuterated isobutanes were obtained, the 20-hour experiment producing 7.1% iso-C_4D_{10} (Table II). A duplicate four-hour experiment at 200° yielded essentially the same distribution of deuterated isobutanes as that shown for run 1, Table II.

The exchange behavior of the butanes over acid catalysts has been interpreted in terms of the formation of a carbonium ion complex with the catalyst.[1,2,4] When the present work was undertaken, it was considered possible that the alkaline earth hydrides could form a similar polarized complex with isobutane, and that in this system also, a difference in exchange rates between normal and isobutane could be expected. It was found, however, that the alkaline earth hydrides behave more like metals than like oxides; as the results of Table III show, when either normal butane or isobutane is allowed to stand over barium hydride at 100° or 300°, exchange occurs to approximately the same extent.

One point of similarity between the hydrides and acid catalysts was observed. Under mild conditions methylpropane-2-*d* was found to exchange much more slowly than does methylpropane-1-*d* with the catalyst hydrogen in barium hydride. Runs 3–6, Table IV, illustrate this behavior at 100 and 200°. This result is similar to that obtained with silica–alumina and sulfuric acid. At the higher temperature of 300°, however, both deuterobutanes exchanged extensively (runs 1 and 2, Table IV).

Table IV

Exchange of Methylpropane-1-*d* and -2-*d* with Barium Hydride[a]

Run	Hydrocarbon charged	Hydrocarbon, mmoles	Catalyst, mmoles	Temp., °C.	Time, hr.	Exchange,[b] %
1	1-*d*	0.054	144	300	1	98.4
2	2-*d*	.054	144	300	1	92.6
3	1-*d*	.021	36	200	1	9.0
4	2-*d*	.021	36	200	1	0
5	1-*d*	.021	36	100	20	6.6
6	2-*d*	.021	36	100	200	0

[a] Charged barium hydride, fresh catalyst in each run. The catalyst was evacuated one hour at 300° in each experiment. [b] % exchange = % C_4H_{10} in the product gas.

Since methylpropane-2-*d* does exchange with isopentane over silica–alumina catalyst,[2] a mixture of these hydrocarbons was allowed to stand over barium hydride at 200°. When the usual pretreatment of one-hour evacuation at 300° was used, no exchange occurred; however, over catalyst evacuated 17 hours at 300°, both methylpropane-1-*d* and -2-*d* exchanged with the catalyst, the -1-*d* isomer considerably more rapidly than the -2-*d*. Although small amounts of monodeutero isopentanes were also obtained, it was not possible to establish whether these resulted from direct exchange with the methylpropane-*d*, or from exchange with catalyst deuterium resulting from the rapid catalyst–methylpropane-*d* exchange.

Discussion

In general, olefins exchange at temperatures much lower than those required for paraffin exchange. However, the question of olefin participation in the exchange of paraffins has not been satisfactorily resolved, at least over oxide catalysts.[1,2] The present work indicates that isobutylene competes successfully for the catalyst surface (calcium deuteride) even if present only in small amounts (1–2%) relative to the isobutane. Thus, isobutylene appears not to catalyze the exchange of isobutane to any measurable extent.

The alkaline earth hydrides resemble metal catalysts in that all of the hydrogen atoms in isobutane are exchangeable with hydrogen in (on) the catalyst (Table II), and normal butane and isobutane exchange at essentially the same rate (Table III). The slow exchange of methylpropane-2-*d* relative to methylpropane-1-*d* (Table IV) has not thus far been reported for metal catalysts, but this may be due to failure to study the exchange under sufficiently mild conditions or short reaction times. The difference between these isomers over barium hydride is attributed to a steric effect: if both the carbon and the hydrogen (deuterium) atoms have to be adsorbed at the same time on adjacent catalyst sites, dissociative adsorption can occur with much less steric interference for the primary than for the tertiary carbon. The nature of the catalyst–hydrocarbon interaction cannot be accurately specified at this time. The authors prefer a mechanism in which a carbon–hydrogen bond in the hydrocarbon breaks homolytically, the alkyl and hydrogen atom fragments being adsorbed on adjacent metal sites to form a kind of metal alkyl and metal hydride.

Acknowledgment.—Mass spectrometric analyses were done by J. Terrell. The authors wish to express their appreciation to Dr. G. A. Mills and Dr. S. G. Hindin for many helpful discussions and to the Houdry Process Corporation for permission to publish this material.

Marcus Hook, Pennsylvania