is equivalent to the formation of a barium alkyl, or a barium ion-carbanion pair. The second possibility involves "dissociative" adsorption on a barium atom and it may be schematically written as

$$Ba + CH_2 = CH_2 \longrightarrow (CH_2{=}CH)^-Ba^{++}H^- \quad (2)$$

Reaction 1 can probably be ruled out, since it requires that exchange occur between hydrogen atoms in the ethylene and hydride ions in the catalyst, contrary to experiment (ref. 1). Reaction 2 does not imply such an exchange. Furthermore, since it involves conversion of metal into a kind of hydride, it is likely to occur preferentially at the dual sites in the metal–hydride interface, as discussed above. In the absence of additional information, reaction 2 is favored as representing the manner in which ethylene is adsorbed.

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[CONTRIBUTION FROM THE HOUDRY PROCESS CORPORATION]

The Catalytic Activity of Barium and Calcium Hydrides. I. An Exploratory Study

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A study has been made of the catalytic activity of barium and calcium hydrides. These hydrides are moderately active for ethylene hydrogenation, cyclohexane and isobutane dehydrogenation, pentene double bond isomerization, and hydrogen- and ethylene–deuterium exchange reactions. These catalysts show stable activity for the dehydrogenation of cyclohexane under elevated hydrogen pressure, and for the hydrogenation of ethylene at atmospheric pressure. Consideration of the types of reactions catalyzed indicates that the alkaline earth hydrides are typical hydrogenation–dehydrogenation catalysts, similar to transition metal catalysts such as nickel and platinum.

Introduction

The salt-like hydrides of barium and calcium have been little investigated from a catalytic viewpoint.

Pease and Stewart[1] have described the hydrogenation of ethylene over calcium hydride at 200°. The hydride appeared to be more active as a catalyst than metallic calcium; however, it was demonstrated that calcium hydride was relatively inactive toward ethylene in the absence of hydrogen.

Schmidt[2] stated that barium metal supported on quartz was moderately active for ethylene hydrogenation at 200°, but gave no experimental data.

In the present work the following reactions were found to be catalyzed by barium and calcium hydrides: (1) hydrogen–deuterium exchange; (2) ethylene hydrogenation and deuteration; (3) pentene double bond isomerization; (4) dehydrogenation of cyclohexene, cyclohexane and isobutane.

Experimental

Materials.—Calcium and barium hydrides were obtained from Metal Hydrides, Inc., as gray powder and lumps, respectively. They were obtained in 98–99% purity with oxygen and nitrogen said to be the chief impurities. Spectrographic analysis by the Houdry Laboratories indicated the absence of metals known to be hydrogenation catalysts, *i.e.*, nickel, platinum, etc., and reported the following metals present in trace amounts: calcium, magnesium, strontium and manganese in the barium hydride; magnesium, manganese, sodium, strontium and iron in the calcium hydride. Surface area measurements by the BET method indicated that the surface areas of these materials were <1 m.^{2}/gram.

Calcium hydride was also prepared from finely divided calcium metal of low "active metal" content supplied by the Ethyl Corporation.

Hydrogen was purified by passing over hot copper and then through dried silica–alumina (Houdry Type S-45) at −195°.

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

A special blend of ethylene and hydrogen was obtained from the Matheson Company and used after drying by passage through anhydrous calcium sulfate at −78°.

Isobutene was obtained from the Phillips Petroleum Company (Research Grade, >99.5%) and was used after drying by passage through anhydrous calcium sulfate at 0°. Pentene-1, Phillips Technical Grade, 95%, was used as received.

Cyclohexene and cyclohexane were obtained from the Phillips Petroleum Company; after purification, infrared analysis indicated a purity of >99%.

Methylcyclopentene (the isomeric mixture) was prepared by the isomerization of cyclohexene over Houdry Type S-45 silica-alumina catalyst. Infrared analysis indicated that a product containing 97% methylcyclopentene was obtained by this procedure.

Apparatus and Procedure.—All static experiments were carried out by the use of high vacuum technique. Dynamic experiments were carried out with a procedure allowing evacuation of the catalysts during the pretreatment period. The general experimental procedure used was as follows: a measured amount of catalyst was evacuated under 10^{-5} mm. at 200 or 300° for a fixed period. The metered stream of hydrocarbon, and in some cases hydrogen or hydrogen and deuterium, was then passed over the catalyst at reaction temperature; after various on-stream periods, gas and/or liquid samples were taken for analysis by gas density, mass spectrometer, infrared spectrometer or silica gel adsorption.

High pressure experiments were carried out in an isothermal reactor previously described.[3]

Results and Discussion

Hydrogen–Deuterium Exchange.—In view of the results reported by Pease and Stewart it was anticipated that the alkaline earth hydrides would be able to activate molecular hydrogen. If this were the case, gaseous deuterium might also exchange with bulk hydride at elevated temperatures. It was found that no exchange occurred at 100° over calcium hydride, even after 17 hours. However, when the same sample of calcium hydride was pumped overnight at 200°, and then charged with an atmosphere of deuterium at 200°, considerable exchange occurred after one hour and appreciably more after six hours. From the data in Table I one can make the following observations: (1) only a fraction of the hydrogen in the calcium hydride

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(1) R. N. Pease and L. Stewart, THIS JOURNAL, **47**, 2763 (1925).

(2) O. Schmidt, *Chem. Revs.*, **12**, 363 (1933).

(3) H. Heinemann, G. A. Mills, J. B. Hattman and F. W. Kirsch, *Ind. Eng. Chem.*, **45**, 130 (1953).

participated in the exchange; (2) this fraction increased with increasing reaction time; and (3) within experimental error, the fraction that did exchange came to complete isotopic equilibrium with the deuterium ($K_{\text{Theor.}} = 3.4$ at 200°). These results are consistent with the interpretation that hydrogen near the surface exchanges rapidly with gaseous deuterium, but that participation of all the hydride hydrogen in the exchange is limited by the time required for diffusion of hydride ions from the interior to the surface.

TABLE I

DEUTERIUM EXCHANGE WITH CALCIUM HYDRIDE AT 200°

Charge: 16.8 mmoles calcium hydride; 1.7 mmoles deuterium.

Reaction time, hr.	Gas anal., mole % D_2	H_2	HD	K^a	Atom % D
1	56.3	6.8	36.9	3.6	74.8
6	3.0	71.2	25.8	3.1	15.9
∞	..	..	..	(3.4)	(10.1)

[a] $K = (\text{HD})^2/(\text{H}_2)(\text{D}_2)$.

The hydrogen–deuterium exchange reaction was studied as a function of temperature over calcium and barium hydrides. Although a threefold excess of barium hydride was used in these experiments, the results indicate that barium hydride is a more active catalyst than calcium hydride under the same pretreatment conditions. Calcium hydride is an active catalyst at temperatures as low as 0°, and isotopic equilibrium in the gas phase is reached in one hour at temperatures of 50° or higher. Over barium hydride, equilibrium in the gaseous phase is attained in one hour even at −78°. The loss of deuterium from the gaseous phase, especially marked at the higher temperatures, is the result of exchange between gaseous deuterium and the solid hydride. This effect is also more pronounced with barium than with calcium hydride, presumably because the rate of diffusion of hydride ion through the lattice is greater for the barium compound.

The Hydrogenation of Ethylene.—The hydrogenation of ethylene was studied over barium and calcium hydrides as a function of temperature. Experiments were made in a constant volume system with an approximately 1:1 mixture of ethylene and hydrogen. As one might predict from the hydrogen–deuterium exchange results, barium hydride appears to be a more active catalyst than calcium hydride for ethylene hydrogenation. The data in Table III indicate that barium hydride is about as active for ethylene hydrogenation at 0° as calcium hydride is at 150–200°. The hydrogenation did not go to completion over calcium hydride at 200°; however, it was essentially complete at 150°. This difference was apparently due to a poisoning or inhibition of the reaction by the products, since experiments with large catalyst ratios resulted in complete hydrogenation. Barium hydride pumped at 200° was relatively inactive for ethylene hydrogenation at −78° (Table III). However, a fresh catalyst sample pumped at 300° for 64 hours was very active for ethylene hydrogenation at −78°; complete hydrogenation was obtained after 75 minutes.

TABLE II

HYDROGEN–DEUTERIUM[a] EXCHANGE OVER CALCIUM AND BARIUM HYDRIDES[b]

(300 mm. H_2–D_2, 1 hr. reaction time)

Temp., °C.	Gas anal., mole % Calcium hydride H_2	HD	D_2	Barium hydride H_2	HD	D_2
200	47.7	41.9	10.4	94.0	5.6	0.4
150	30.4	47.9	21.7			
100	27.4	47.8	24.8	70.2	26.5	3.3
50	27.0	47.2	25.8			
0	35.1	31.1	33.8	30.4	47.2	22.4
−78				29.3	45.8	24.9

[a] Charge analysis: 49.9% H_2, 0.8% HD, 49.3% D_2. [b] Seventeen mmoles (1 cc.) of calcium hydride, 54 mmoles (3 cc.) of barium hydride, evacuated 17 hours at 200° prior to charging with H_2–D_2.

TABLE III

THE HYDROGENATION OF ETHYLENE[a] OVER CALCIUM[b] AND BARIUM[c] HYDRIDES—STATIC SYSTEM

Catalyst hydride	Temp., °C.	Sample taken after (min.)	Gas anal., mole % C_2H_6	C_2H_4	H_2
Calcium	200	150	71.4	11.0	17.6
Calcium	150	420	93.6	0.9	5.5
Calcium	25	Inactive	..	..	..
Barium	200	30	75.1	23.9	0.5
Barium	100	25	79.2	20.5	0.3
Barium	0	210	77.0	22.5	0.5
Barium	−78	420	8.4	50.6	41.0

[a] Charge analysis: 51.8% H_2; 48.2% C_2H_4 for calcium hydride. 42.0% H_2, 55.8% C_2H_4, 1.6% C_2H_6 for barium hydride. [b] Thirty-four mmoles (2 cc.) of calcium hydride evacuated 17 hours at 200°. [c] Seventy-two mmoles (4 cc.) of barium hydride evacuated 17 hours at 200°.

The Deuteration of Ethylene.—The interaction of hydrogen and olefins over platinum and nickel catalysts has been investigated by numerous workers[4] with the objective of determining the mechanism of the hydrogenation of olefins. This problem has yet to be resolved satisfactorily, although some of the details have been worked out.[5] In order to better compare the alkaline earth hydrides with known hydrogenation catalysts, a brief study was made of the reaction of a 1:1 mixture of deuterium and ethylene over calcium hydride at 150° and over barium hydride at −78°. The data in Table IV indicate relatively clean reactions, ethane and deuterated ethanes being the main products. No deuterated ethylenes were obtained even when residual ethylene was found in the product gas. In a separate experiment, ethane was found not to exchange with calcium deuteride at 150°. These results imply that the addition of deuterium to the olefin and the redistribution reaction in the deuteroethanes occurred prior to the desorption of any hydrocarbon species. At low temperatures the deuteration occurs *via* a mechanism such that the mixture of deuteroethanes contains dideuteroethane in amounts greater than statistical equilibrium. These results closely parallel those obtained with nickel and platinum catalysts,[5c,d] and, in general, agree with

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(4) General Reference, *Discs. Faraday Soc.*, No. 8 (1950).

(5) (a) G. H. Twiggs, *ibid.*, No. 8, 152 (1950); (b) T. I. Taylor and V. H. Dibeler, *J. Phys. Colloid Chem.*, **55**, 1036 (1951); (c) J. Turkevich, D. O. Schissler and A. P. Irsa, *ibid.*, **55**, 1078 (1951); (d) J. N. Wilson, J. W. Otvos, D. P. Stevenson and C. D. Wagner, *Ind. Eng. Chem.*, **45**, 1480 (1953).

TABLE IV

REACTION OF DEUTERIUM[a] WITH ETHYLENE OVER BARIUM HYDRIDE AT −78° AND CALCIUM HYDRIDE AT 150°

Catalyst	Sample taken after min.	Gas anal., mole % C_2H_4	C_2H_6	C_2H_5D	$C_2H_4D_2$	$C_2H_3D_3$	$C_2H_2D_4$	C_2HD_5	C_2D
BaH_2[b]	90	24.8	..	10.2	61.6	3.1	0.2	..	..
Statistical distribution[d]			3.0	6.7	6.2	3.1	0.9	0.1	..
CaH_2[c]	60	..	14.2	31.4	31.6	12.7	6.3	2.8	0.8
Statistical distribution[d]			13.1	31.6	32.0	17.2	5.2	0.8	0.06

[a] Charge analysis: 48.1% C_2H_4; 50.7% D_2. [b] 180 millimoles (10 cc.) of barium hydride evacuated 65 hours at 300° prior to charging with C_2H_4 and D_2 at −78°; 17.9% residual deuterium in the gas phase after reaction. [c] 34 millimoles (2 cc.) of calcium hydride evacuated 17 hours at 200° prior to charging with C_2H_4 and D_2 at 150°. [d] Calculated from $D^n = 6!/n!(6-n)!\ \alpha n(1-\alpha)^{6-n}$ where D^n = mole per cent. of species containing n deuterium atoms; α = atom fraction of hydrogen in the product gas.

the observation that exchange is more rapid at 100–200° than addition, whereas addition is more rapid than exchange at temperatures below 0°. This change in reaction rate may be attributed to differences in the energies of activation for exchange and addition over the temperature range in question.[6]

The Hydrogenation of Ethylene–Dynamic System.—In order to conveniently study the stability and range of activity of barium and calcium hydrides, the hydrogenation of ethylene was studied in a flow system at 200°, a 45:55 hydrogen–ethylene mixture being used. Essentially complete hydrogenation of ethylene occurs at low gaseous space velocities (13–40 v./v./hr. for calcium hydride, and 29–342 v./v./hr. for barium hydride). At higher space velocities with calcium hydride, Fig. 1, the conversion to ethane falls off rapidly with increasing space velocity, whereas with barium hydride high conversions can be obtained at gaseous space velocities as high as 1000–1500 v./v./hr. (Fig. 2). The hydrogenation of ethylene was perceptible over barium hydride at 50° and a GHSV of 43 v./v./hr.; 11% ethane was obtained over a three-hour period.

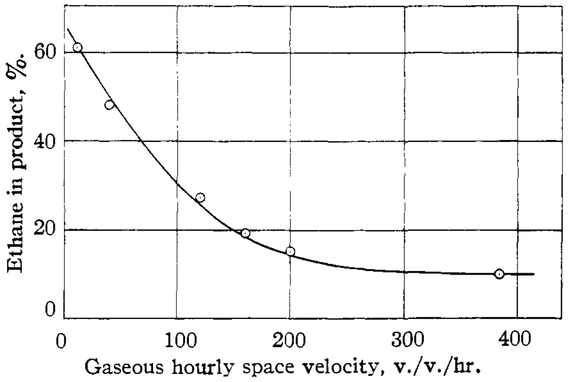

Fig. 1.—Hydrogenation of ethylene over calcium hydride at 200°.

The catalytic stability of these alkaline earth hydrides for hydrogenation appears to be good. The conversion remained constant over calcium hydride during a six hour period at 200° and a GHSV of 40 v./v./hr., and constant conversion was similarly obtained over barium hydride during a three-hour run at 340 v./v./hr. and 200°.

The Isomerization of Olefins.—The isomerization of pentene-1 was studied over barium and calcium hydrides in a flow system at 150–475° and a liquid hourly space velocity of one v./v./hr. The distribution of products was determined by infrared analysis. Both catalysts were found to have good double bond isomerization activity (Table V). However, neither catalyst was effective for structural isomerization; only trace amounts of methylbutenes were obtained in the product.

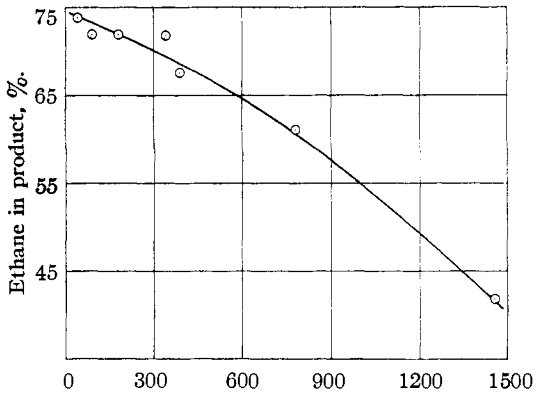

Fig. 2.—Hydrogenation of ethylene over barium hydride at 200°.

TABLE V

ISOMERIZATION OF PENTENE-1[a] OVER BARIUM AND CALCIUM HYDRIDES,[b] LHSV ≅ 1

Run no.	Temp., °C.	Hydride	Liquid product anal., % 1-C_5H_{10}	2-C_5H_{10} (*cis*)	2-C_5H_{10} (*trans*)	2Me-1-C_4H_8	2Me-2-C_4H_8
626	300	BaH_2	12.0	25.4	61.6	..	1.0
627-1	250	BaH_2	9.8	24.0	65.1	..	1.1
627-2	200	BaH_2	8.8	23.2	67.4	..	0.6
628-1	150	BaH_2	74.0	13.6	9.7	..	2.7
628-2	250	BaH_2	11.9	24.9	62.0	0.8	0.4
631-1	300	CaH_2	11.3	30.3	58.1	..	0.3
632-2	200	CaH_2	54.4	27.0	16.9	..	1.7
662-1	400	BaH_2	14.6	26.8	56.9	0.7	1.0
662-2	475	BaH_2	18.2	28.1	51.6	1.0	1.1

[a] All experiments except 627-2, 662 (30 minutes) were one-hour runs. Phillips technical grade—minimum 95 mole % pentene-1. [b] Seven cc. of barium (120 mmoles) or calcium hydride (119 mmoles) used in each experiment.

As a further test of the isomerization activity and selectivity of the alkaline earth hydrides, methylcyclopentene and cyclohexene were passed over barium hydride at 300–475° and a LHSV of 0.2 v./v./hr. The results of this study (Table VI) are in agreement with the pentene isomerization

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[6] A. Farkas and L. Farkas, THIS JOURNAL, **60**, 22 (1938).

TABLE VI

REACTION OF CYCLOHEXENE AND METHYLCYCLOPENTENE OVER BARIUM HYDRIDE[a] IN A DYNAMIC SYSTEM

Charge stock	Temp., °C.	LHSV, v./v./hr.	Liquid product,[b] mole %			Infrared anal.
			Benzene	Cyclohexene	Cyclohexane	
Cyclohexene	300	0.2	26.8	71.5	1.7	No C_5 ring compounds found
Cyclohexene	400	.2	90.7	8.4	0.9	
Cyclohexene	475	.2	92.0	7.5	0.5	
			Benzene	Methylcyclopentene	Methylcyclopentane	
Me-cyclopentene	300	0.3	..	95.2	4.8	No C_6 ring compounds found
Me-cyclopentene	400	.3	..	95.7	4.3	No C_6 ring compounds found
Me-cyclopentene	475	.3	..	95.7	4.3	

[a] 120 mmoles (7 cc.) of barium hydride used in each run; catalyst evacuated one hour at 200°, raised temperature to run temperature with helium passing over the catalyst. Helium (5.1/hr.) was used as a carrier in every run. [b] Analysis by mass spectrometer.

data; structural isomerization of one ring system to the other did not occur. Interestingly, cyclohexene did not disproportionate to benzene and cyclohexane as has been found for platinum catalysts under similar conditions.[7] The absence of disproportionation during the dehydrogenation of cyclohexene has been reported recently by Komarewsky and Erikson[8] for a vanadium oxide catalyst.

The Dehydrogenation of Isobutane and Cyclohexane.—The dehydrogenation of isobutane was studied over calcium hydride at 525° and atmospheric pressure in a flow system. The results given in Fig. 3 indicate that the dehydrogenation activity of calcium hydride is quite high initially but it rapidly decreases with time on-stream over the range of gaseous space velocity of 60–240 v./v./hr.

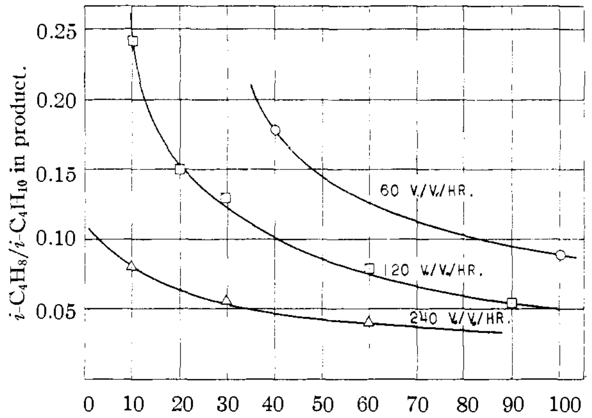

Fig. 3.—Dehydrogenation of isobutane over CaH_2 at 525°.

The dehydrogenation of cyclohexane was studied over barium hydride at 450–500° and atmospheric pressure in a flow system. Some dehydrogenation occurred at 450°, but the conversion to benzene was low even at 500° (7–17%). In order to evaluate the catalyst stability during dehydrogenation at elevated hydrogen pressures, calcium and barium hydrides were tested for cyclohexane dehydrogenation in an isothermal reactor[3] at 300 p.s.i., 950°F., H_2:C_6H_{12} mole ratio = 4:1, and a LHSV = 1–4 v./v./hr. At a LHSV of 1, 40% benzene was obtained over calcium hydride. At 4 space velocity, coarsely ground barium and calcium hydrides both gave a conversion of about 20%. A nine-hour run over calcium hydride showed no change in conversion during this period.

General Discussion

The reactions studied in this work demonstrate, within rather broad limits, the scope and applicability of the alkaline earth hydrides to hydrocarbon conversion processes. The results of this study indicate that the alkaline earth hydrides are pure hydrogenation–dehydrogenation catalysts resembling transition metal catalysts with respect to both the types of reactions catalyzed and the distribution of the hydrocarbon products. Recently, Trapnell[9] has also noted the similarity of barium and calcium metals to the transition metals from a study of the chemisorption of gases on evaporated films. The level of activity of the hydrides is rather low, however; while barium hydride has a catalytic activity considerably greater than that of calcium hydride, it is still much less active than platinum or nickel catalysts. The distribution of deuterated ethanes obtained from the deuteration of ethylene over barium hydride at −78° is similar to that obtained over nickel and platinum[5c,d] catalysts. The isomerization of 1-olefins over hydride catalysts also gives products of the same nature as that obtained from a nickel catalyst in the presence of hydrogen, *i.e.*, double bond migration occurs, but not skeletal isomerization.[5b]

Acknowledgment.—The authors wish to express their appreciation to the Houdry Process Corporation for permission to publish this material.

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[7] M. Ya Kagan and N. A. Shcheglova, *Zhur. Fiz. Khim.*, **23**, 1203 (1949).

[8] V. I. Komarewsky and T. A. Erikson, THIS JOURNAL, **75**, 4082 (1953).

[9] B. M. W. Trapnell, *Proc. Roy. Soc.* (*London*), **218**, 566 (1953).