as 473.454 kcal./mole. The accuracy does not justify the correction outlined by Washburn.[12]

On investigation after heat of combustion determinations using the compounds discussed previously, the sample bulb was found either fused or more often shattered. After symmetrical dimethylhydrazine combustions (about fifteen runs were attempted on this compound) the bulb was in some cases so badly shattered that it appeared powdered. This indicated a tendency for the latter sample to burn more violently. Such a tendency could explain the fact that only one combustion resulted in a reasonable carbon analysis. This determination alone is used to calculate the value reported here; however, all other values lay within 1% of this mean.

The errors are estimated on the basis that the correction for unburned benzoic acid is good to only 20.0% of its value, and that compared to this, all other errors are negligible. As a matter of fact the deviation from the mean is roughly proportional to this correction. Accordingly, the average deviation from the mean is given as the error.

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[12] E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 529 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Some Catalytic Exchange and Hydrogenation Reactions of Acetylene and Ethylene[1,2]

BY JOHN E. DOUGLAS AND B. S. RABINOVITCH

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A series of experiments on the hydrogenation and exchange of acetylene and ethylene on nickel catalysts has provided the following information. (1) Contrary to previously published results, exchange between ethylene molecules has been found to occur. (2) Isomerization of *trans*-ethylene-d_2 takes place more rapidly than exchange. (3) Acetylene is adsorbed on the catalyst in part as a carbon complex and self-hydrogenates to ethylene. (4) Acetylene exchanges rapidly with itself and with residual hydrogen on the catalyst. (5) Addition of deuterium to acetylene at −80° yields a preponderance of *cis*-ethylene-d_2. (6) Hydrogenation of acetylene by one-step addition appears to be ruled out. The results are discussed.

In connection with a study of the thermal *cis–trans* isomerization of ethylene-d_2 a supply of *cis*-ethylene-d_2 was desired. Preparation by the catalytic addition of deuterium to acetylene appeared highly feasible. Farkas and Farkas[3] have pointed out that the catalytic addition of hydrogen to disubstituted acetylenes yields the *cis*-ethylenic derivative in large preponderance (except for those cases where the *cis*-isomer is highly unstable) and they suggested an explanation. Sheridan[4] has also suggested a similar mechanism. Moreover, Farkas and Farkas[5] found that during the platinum-catalyzed addition of deuterium to acetylene to form ethylene, exchange was slight as judged by the return of light hydrogen to the gas phase.

The catalytic synthesis of *cis*-ethylene-d_2 on palladium was attempted by Arnett and Crawford[6] who obtained a mixture of all possible deuteroethylenes. We also attempted the catalytic preparation on nickel using experimental conditions believed to be conducive to formation of a pure *cis* product. However, only mixtures of all possible deuteroethylenes were obtained.

To clarify this finding, a series of qualitative experiments on the catalytic hydrogenation and exchange reactions of acetylene and ethylene was undertaken, together with some related work on more general aspects of these reactions.

Experimental

Materials.—Deuterium was prepared by electrolysis of 99.8% D_2O, obtained on U. S. Atomic Energy Commission allocation. The acetylene was Matheson purified grade and was purified further by conventional methods. The ethylene was Matheson C.P. grade, used without further treatment. Dideuteroacetylene was prepared by the distillation of D_2O over a pure grade of calcium carbide. Mass spectrographic analysis showed that 1% of C_2HD was present. A sample of asymmetric-ethylene-d_2, containing 6.5% ethylene-d_1, was obtained from Dr. R. G. Inskeep of the University of Minnesota. *trans*-Ethylene-d_2 was prepared by reducing dideuteroacetylene with chromous chloride.[7] Mass spectrographic analysis showed the product to be 98.8% ethylene-d_2; the infrared spectrum showed no *cis*- or asymmetric-ethylene-d_2 and 1% ethylene-d_1 was the major impurity. Ethylene-d_4 was obtained by the addition of deuterium to acetylene-d_2 on a nickel catalyst previously flushed with the reagents. Mass spectrographic analysis showed the product to be 97.4% pure with 1.5% ethylene-d_3 and 0.8% ethane-d_6 as the major impurities.

Catalysts.—Nickel catalysts supported on kieselguhr were prepared by calcination of nickel nitrate followed by reduction in hydrogen at 400°.[8] They contained 17 to 19% Ni. A nickel wire catalyst was prepared by cutting 1400 cm. of #18 Ni wire into 1-cm. lengths which were treated alternately with O_2 and H_2 at 330°. Catalysts were regenerated by oxidation in O_2 at 500° followed by reduction in the usual manner. Prior to use, a catalyst was evacuated at room temperature or at 400° as indicated in the tables of results. Catalysts of palladium-on-kieselguhr were made by passing hydrogen through a suspension of kieselguhr-in-palladium chloride solution. The palladium content varied from 7 to 14%.

Apparatus and Procedure.—A conventional glass vacuum apparatus was employed. Apiezon M stopcock grease was used. No special precautions were taken to keep mercury or grease vapor away from the catalyst.

Flow Experiments.—Reactants were placed in a mixing bulb and allowed to flow over a catalyst at the desired rate and pressure. The catalyst was contained in a water-

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(1) Presented before the Northwest Regional Meeting of the American Chemical Society, Seattle, June, 1951.

(2) Abstracted from a portion of a thesis to be submitted by John E. Douglas in partial fulfillment of the requirements for the Ph.D. degree at the University of Washington.

(3) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **33**, 837 (1937).

(4) J. Sheridan, *J. Chem. Soc.*, 133 (1945).

(5) A. Farkas and L. Farkas, THIS JOURNAL, **61**, 3396 (1939).

(6) R. L. Arnett and B. L. Crawford, *J. Chem. Phys.*, **18**, 118 (1950). We thank Prof. Crawford for communicating his results to us prior to publication.

(7) W. Patterson and V. du Vigneaud, *J. Biol. Chem.*, **123**, 327 (1938).

(8) F. De Pauw and J. C. Jungers, *Bull. soc. chim. Belg.*, **57**, 618 (1948).

cooled annulus 5.5 cm. long, 1.5 cm. o.d. and 0.9 cm. i.d. Condensable products were collected in liquid nitrogen traps.

Static Experiments.—Experiments with nickel-kieselguhr catalyst in 3-g. quantities were carried out in reactor tubes approximately 28 cm. long and 2.8 cm. i.d., fitted with a stopcock and standard taper joint. For nickel wire experiments, a reactor of similar type having a net volume, after packing, of 14 cc. was used. A reactor tube was maintained at a desired temperature by an appropriate bath or furnace.

Infrared analyses were made with a Beckman Model IR-2 spectrophotometer using the frequency assignments of Arnett and Crawford.[8] Intensity calibrations were made using the acetylenes and ethylenes referred to above; C_2HD, C_2H_3D and C_2HD_3 intensities were estimated from mass spectrographic analysis of impurities in the other ethylenes. *cis*-$C_2H_2D_2$ was estimated from thermally isomerized *trans*-$C_2H_2D_2$. It should be noted that when many deuterated ethylene species were present in a sample, the overlap of the numerous absorption bands posed serious interference problems so that only semi-quantitative analyses were possible.

Mass spectrographic analyses of products were made with a model 21-103 Consolidated spectrograph. Statistical considerations, as well as the results of the analysis of ethylene, ethylene-d_2 and ethylene-d_4, were employed in estimating the two deuteroethylenes not available in pure form for calibration purposes. Ethanes were estimated from A.P.I. data and simple statistical considerations.

Results and Discussion

Early Attempts to Prepare *cis*-Ethylene-d_2.—Ten flow experiments on nickel and palladium catalysts (evacuated at room temperature) were made. The $C_2H_2:D_2$ ratio was varied from 1:1 to 24:1. Pressure in the catalytic chamber was varied from 3.5 to 60 cm. while space velocities range from 50 to 0.08 sec.$^{-1}$. No catalyst was used for more than three runs. Unreacted acetylene was removed from ethylene product by absorption in alkaline mercuric cyanide and ammoniacal silver nitrate solution, a treatment which was shown not to cause exchange of the deuteroethylenes.

In every run a mixture of all possible deuteroethylenes was obtained, as well as ethane and polymerized material. Analyses indicate that *cis*- and *trans*-ethylene-d_2 were formed in excess of simple statistical equilibrium, the two species accounting for equal percentages (approximately 20 or 25%) of total ethylene products. No significant difference in product proportions resulted from the variation of experimental conditions. Little difference in composition of products was found between palladium and nickel catalysts.

Exchange and Hydrogenation Experiments.—A number of exchange and hydrogenation experiments were performed, of which the most relevant are summarized in Tables I and II. Percentages quoted are averages, in most cases, of several runs.

Summary of Results.—The following results are embodied in Table I: (1) Exchange occurred between ethylene molecules on nickel catalysts. The exchange was rapid at room temperature on a kieselguhr-supported catalyst (Ni–k), prepared by final evacuation at 400° (Expts. 3-7, 5-8, 5-9), and was slower on a heated wire (Ni–w) (Expts. 6-1, 6-8). Half-time for hydrogenation of an equimolar hydrogen–ethylene mixture at 25° was found to be around 3 hr. on Ni–w and less than one minute on Ni–k. Acetylene inhibited interethylenic exchange (Expt. 1-9). (2) *trans–cis* isomerization of ethylene was found to proceed more rapidly than interethylenic exchange on both Ni–k and Ni–w (Expt. 1-0, 5-8, 5-9, 7-3). (3) As expected from the well-known self-hydrogenation of ethylene on nickel films, ethylene-d_4 yielded ethane-d_6 on Ni–k (Expt. 7-5). (4) Ethylene did not exchange or react appreciably with the hydrogen remaining on Ni–k from its preparation if the catalyst had been evacuated at 400° (Expts. 4-1, 7-5, 5-8, 5-9); however, interaction of ethylene with hydrogen on Ni–k evacuated at room temperature was appreciable (Expt. 7-8).

The following results are embodied in Table II: (5) Acetylene-d_2 was found to self-hydrogenate on Ni–k, forming a mixture of deuterated ethylenes, predominately ethylene-d_4 (Expt. 7-1). (6) Acetylene exchanged much more extensively than did ethylene with hydrogen left on a Ni–k catalyst which had been evacuated at 400° (Expt. 7-1) (*cf.* result 4). (7) Appreciable inter-acetylenic exchange occurred at temperatures as low as −80° on Ni–k previously evacuated at 400° (Expts. 4-6, 5-7). This result was independent of exchange of acetylene-d_2 with hydrogen already on the catalyst since Expt. 0-7 shows that the amount of exchange of acetylene-d_2 with a catalyst evacuated at room temperature was much less than the exchange found in Expts. 4-6 and 5-7. (8) The addition product of deuterium to acetylene on Ni–k at −80° contained a preponderance of *cis*-ethylene-d_2 (Expt. 5-2). When the temperature of deuteration was lowered from 25° to −80°, *cis* increased greatly, *trans* was unchanged and ethylene exchange products declined in relative amount (*cf.* Expts. 5-2 with early attempts to prepare *cis*-ethylene-d_2. (9) At −80° on Ni–k, the product of the addition of an equimolar hydrogen–deuterium mixture to acetylene was little changed if the hydrogen and deuterium were first allowed to equilibrate on a Ni–k catalyst to form hydrogen deuteride (Expts. 5-3 and 5-5). (10) Exchange occurred simultaneously during deuteration of acetylene on Ni–k (Expt. 2-7).

Reactions of Ethylene.[9]—Result 1 concerning exchange between ethylene molecules on nickel catalysts may be interpreted in terms of the dissociation mechanism of Farkas[9b] or the mechanism of Beeck.[10] According to the former mechanism, proposed to explain the hydrogenation and exchange reactions of ethylene, the initial adsorption step is (an asterisk presents a bond to the catalyst)

$$H_2C{=}CH_2 \xrightarrow{Ni} H_2C{=}\overset{*}{C}H + \overset{*}{H} \qquad (1)$$

In Beeck's work on films, where self-hydrogenation of ethylene was found to occur, the model for four-site adsorption is

$$H_2C{=}CH_2 \longrightarrow H\overset{*}{C}{=}\overset{*}{C}H + 2\overset{*}{H} \qquad (2)$$

Both mechanisms postulate donation of hydrogen to the catalyst. This hydrogen may subsequently bring about inter-ethylenic exchange as found here.

Result 4 shows that result 1, as well as all our ethylene work performed on Ni–k evacuated at

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[9] For reviews of this subject see: (a) R. Greenhalgh and M. Polanyi, *Trans. Faraday Soc.*, **35**, 520 (1939); (b) A. Farkas, *ibid.*, 906; (c) D. D. Eley, *Discussions of the Faraday Society*, No. 8, 99 (1950); (d) T. I. Taylor and V. H. Dibeler, *J. Phys. Colloid Chem.*, **55**, 1036 (1951).

[10] (a) O. Beeck, *Rev. Modern Phys.*, **17**, 61 (1945); (b) *Discussions of the Faraday Society*, No. 8, 118 (1950).

TABLE I

EXCHANGE EXPERIMENTS WITH ETHYLENE

Expt. No.	Reactants	Conditions[a]	Catalyst[b]	Results[c]
1-9	*t*-$C_2H_2D_2$ + C_2H_2, 6 cm.:6 cm.	Static, 15 min. C_2H_2 admitted first	Ni, once used for exchange of *t*-$C_2H_2D_2$, then pumped at room temp.	No exchanged ethylenes
4-1	C_2D_4, 0.8 cm.	Static, 2 min.	Ni, fresh, pumped at 400°	No exchanged ethylenes; no analysis for ethanes
7-5	C_2D_4, 0.8 cm.	Static, 15 min.	Ni, fresh, pumped at 400°	80% C_2D_4; 1% C_2HD_3; 19% C_2D_6 (mass spect. anal.)
7-8	C_2D_4, 0.8 cm.	Static, 15 min.	Ni, fresh, pumped at room temp.	Mixed deuteroethanes: C_2D_6:C_2HD_5:$C_2H_2D_4$:$C_2H_3D_3$::2.1:1.8:1.1:1.1; analysis for deuteroethylenes not possible (mass spect. anal.)
3-7	C_2H_4 + C_2D_4 1.5 cm.:0.7 cm.	Static, 2 min.	Ni, fresh, pumped at 400°	Over 50% exchange
1-0	*t*-$C_2H_2D_2$	Flow	Ni, fresh, pumped at room temp.	65% of *trans* removed to form all possible deuteroethylenes; *cis* formed in excess of statistical equilibrium
5-8	*t*-$C_2H_2D_2$, 2 cm.	Static, 15 min.	Ni, fresh, pumped at 400°	80% of *trans* removed to form all possible deuteroethylenes; *cis* formed in excess of statistical equilibrium
5-9	*t*-$C_2H_2D_2$, 2 cm.	Static, 15 min.	Ni, fresh, flushed with D_2, pumped at 400°	No detectable difference from 5-8
6-1	C_2H_4 + C_2D_4 13 cm.:13 cm.	Static, 3 hr., 300°	Ni wire, fresh, pumped at 300°	90% exchange, mixed deuteroethylene product
6-8	*t*-$C_2H_2D_2$, 27 cm.	Static, 3 hr., 200°	Ni wire, fresh pumped at 300°	50% exchange, mixed deuteroethylene product
7-3	*t*-$C_2H_2D_2$, 27 cm.	Static, 3 hr., 100°	Ni wire, fresh, pumped at 300°	10% *trans*-$C_2H_2D_2$ removed; *cis*-$C_2H_2D_2$ principal product
7-9	C_2H_4 + D_2, 9 cm.:3.5 cm.	Static, 5 min.	Ni, fresh, pumped at 400°	Ethylene residue: 70% C_2H_4; 30% deuteroethylenes, predominantly C_2H_3D; no analysis for ethanes

[a] When temperature is omitted the experiment was performed at room temperature; flow experiments were performed at 10 cm. pressure and space velocity of 0.025 sec.$^{-1}$. [b] Ni refers to nickel–kieselguhr catalysts. [c] Compositions were determined by infrared analysis, except where mass spectral data are noted.

TABLE II

EXCHANGE AND HYDROGENATION EXPERIMENTS WITH ACETYLENE[a]

Expt. No.	Reactants	Conditions	Catalyst	Results
0-4	C_2D_2, 12 cm.	Static, 30 min.	Kieselguhr only	No exchange
0-8	C_2D_2:H_2, 10 cm.:10 cm.	Static, 30 min.	Kieselguhr only	No exchange or hydrogenation
2-7	C_2H_2 + D_2, 5:1	Flow	Ni, fresh, pumped at room temp.	0.4% C_2HD in early products, increasing to over 1% in later product. Mixed ethylenes; early product 80% C_2H_4 + C_2H_3D
7-1	C_2D_2, 0.6 cm.	Static, 15 min.	Ni, fresh, pumped at 400°	Product analysis: (approximately 50% reaction), 10% C_2H_2, 45% C_2HD, 30% C_2D_4, 10% C_2HD_3, 41% $C_2H_2D_2$, (mass spect. anal.)
5-2	C_2H_2 + D_2 44 cm.:29 cm.	Static, 20 hr., −80°	Ni, fresh, pumped at 400°	Ethylene product: 50% *cis*-$C_2H_2D_2$, 20% *trans*-$C_2H_2D_2$, 15% C_2H_3D, 10% C_2HD_3, no analysis for acetylenes
5-3	C_2H_2 + H_2 + D_2 45 cm.:15 cm.:15 cm.	Static, 22.5 hr., −80°	Ni, fresh, pumped at 400°	Ethylene product: 10% *cis*-$C_2H_2D_2$, 15% *trans*-$C_2H_2D_2$, 20% C_2H_3D, 35% C_2H_4, no analysis for acetylenes
5-5	C_2H_2 + H_2 + D_2 + HD, 12 cm.:2 cm.:2 cm.:4 cm.	Static, 20.5 hr., −80°	Ni, fresh, pumped at 400°	Ethylene product: 10% *cis*-$C_2H_2D_2$, 10% *trans*-$C_2H_2D_2$, 25% C_2H_3D, 40% C_2H_4, no analysis for acetylenes
0-7	C_2D_2, 10 cm.	Static, 1 hr.	Ni, fresh, pumped at room temperature	2% C_2HD, 2% C_2H_2 formed
4-6	C_2H_2 + C_2D_2 10 cm.:10 cm.	Static, 2 min.	Ni, fresh, pumped at 400°	13% C_2HD formed
5-7	C_2H_2 + C_2D_2 5 cm.:5 cm.	Static, 5.5 hr., −80°	Ni, fresh, pumped at 400°	13% C_2HD formed; no ethylene analysis (small percentage)

[a] See footnotes to Table I.

400°, is independent of complication due to the presence of hydrogen on the catalyst, from its preparation.

Polanyi[9a] and Twigg[11] have advocated an associative mechanism for the hydrogenation and exchange of ethylene in which the adsorption step is

$$H_2C{=}CH_2 \xrightarrow{Ni} H_2\overset{*}{C}{-}\overset{*}{C}H_2 \qquad (3)$$

Conn and Twigg[12] have stated that intermolecular exchange of ethylene is to be expected on the basis of the dissociative mechanism. Their experimental finding that exchange did *not* occur between light and heavy ethylene on a nickel wire catalyst, even at temperatures above 300°, has been taken by them and others[9c] as strong argument against the dissociative mechanism and in favor of the associative mechanism. The negative result of Conn and Twigg was probably due to poisoning of the relatively small surface used by them.

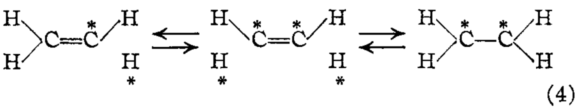
The slowness of intermolecular exchange relative to hydrogenation on the same catalyst (result 1) may be explained both by the relatively greater poisoning of the surface in the absence of added hydrogen, and by the reduction of the surface concen-

[11] G. H. Twigg, *Discussions of the Faraday Society*, No. 8, 152 (1950).

[12] G. K. Conn and G. H. Twigg, *Proc. Roy. Soc.* (*London*), **A171**, 70 (1939).

tration of hydrogen in the exchange experiments due to the simultaneous self-hydrogenation reaction (result 3 above).[10,13]

Our experiments do not permit us to undertake a detailed discussion of the reactions of the hydrogen donated to the catalyst upon ethylene adsorption. To speculate briefly about hydrogenation and exchange reactions of ethylene in general, it seems possible from the published literature that interpretation in terms of a single mechanism may be too great a simplification; several mechanisms, or a composite of them, may occur to some extent during the complete course of hydrogenation or exchange, with their relative importance depending upon conditions. An example of a possible "composite" mechanism which is allowed by the existing evidence would be an equilibrium such as[14]



(4)

Eventual polymerization (poisoning of the surface) would terminate reactions (4).

No conclusions concerning Result 2, that *cis–trans* isomerization occurs more rapidly than exchange, will be drawn now; however a kinetic study of these reactions is in progress.

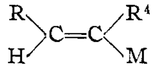
Reactions of Acetylene.—Result 5 shows directly that acetylene when admitted to a Ni–k catalyst will self-hydrogenate to ethylene. Self-reduction of acetylene indicates partial dehydrogenation of acetylene and adsorption as a carbon complex. Our results are in accord with the well-known poisoning of hydrogenation catalysts by acetylenes, attributed in part to a deposit of carbon. Result 5 is qualitatively independent of effects due to the presence of hydrogen on the catalyst, remaining from its preparation, inasmuch as the principal self-reduction product of acetylene-d_2 on a hydrogen-reduced catalyst was ethylene-d_4.

Result 7 concerning the occurrence of interacetylenic exchange on Ni–k may be accounted for by exchange of acetylene with hydrogen on the catalyst (Result 6). Exchange of acetylene-d_2 on a hydrogen-reduced catalyst is found to be more extensive in the presence of light acetylene than in its absence; presumably the light acetylene acts as a reservoir of hydrogen.

Result 8 shows that hydrogenation of acetylene conforms to the conclusion of Farkas and Farkas[3] concerning the stereochemistry of reduction of the triple bond. The apparent independence of the yield of *trans*-ethylene-d_2 on the temperature of deuteration of acetylene suggests that much of the *trans* compound arises from the isomerization of newly-formed *cis* product. This explanation is in conformity with Result 2.

The mechanism of *cis* hydrogenation suggested by Farkas and Farkas[3] involves the simultaneous addition of both atoms of a hydrogen molecule; however, Greenhalgh and Polanyi[9a] pointed out that for ethylene the condition of simultaneity is unnecessary. Addition of an equimolar mixture of hydrogen and deuterium to acetylene should yield *cis*-ethylene-d_2 and light ethylene primarily, if addition is by independent hydrogen and deuterium molecules. A statistical distribution of atoms would reduce the amounts of *cis*- and light ethylenes and increase the proportion of ethylene-d_1. Furthermore, the proportions of products should be unaffected by pre-equilibration of the hydrogen and deuterium. Result 9 shows that this is so.[15] This finding is similar to one obtained by Twigg for ethylene.[12] It will be recalled that hydrogen is not returned to the gas phase during deuteration of acetylene on platinum.[5] If it is assumed that there is no appreciable exchange between hydrogen and deuterium molecules during the reduction of acetylene on nickel, a mechanism in which both atoms of a molecule from a van der Waals layer are added simultaneously to the acetylene is ruled out. The mechanism of addition can be any which involves the production of atoms; the scrambling of these atoms on the surface is implied by the experimental results. Presumably, in the hydrogenation of acetylene, hydrogen once adsorbed on the catalyst is not returned to the gas phase.

If the half-hydrogenated state for acetylene may be represented by a model such as



cis hydrogenation is still to be expected. Such an intermediate preserves stereospecificity whether hydrogen atoms are added in pairs or not.

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(13) J. Aman, L. Farkas and A. Farkas, THIS JOURNAL, **70**, 727 (1948).

(14) D. D. Eley, (*Discussions of the Faraday Society*, No. 8, 34 (1950)) has stated that on nickel the right side of (4) is favored over the center and left side. His argument is not conclusive, however.

(15) It will be noticed that in both Expts. 5-3 and 5-5 the light hydrogen content of the products is larger than expected. This may be due to the fact that hydrogen remaining on the catalyst from its preparation enters into the product, or to faster reaction of hydrogen relative to deuterium as found by Farkas.[5]