7. It has been shown that sintering of copper catalysts affects the low temperature activity of copper in the ortho–para conversion by no means so adversely as it affects the rate of hydrogenation of ethylene.

PRINCETON, N. J.

The Catalytic Exchange Reaction between Deuterium and Water

BY HUGH S. TAYLOR AND H. DIAMOND

In some experiments using the thermal conductivity method of analysis of deuterium–hydrogen mixtures, it soon became apparent that deuterium, when passed through a purification train containing platinized asbestos, might be contaminated with relatively large quantities of the light isotope. Similar effects were noted with deuterium standing in contact with chromium oxide gel. The phenomenon has been subjected to a detailed study involving also several other catalysts. It has been shown that the heavy isotope may be replaced by hydrogen due to a catalytic exchange reaction between deuterium and water retained by the contact material.

Experimental Procedure

Method of Analysis.—The thermal conductivity micro-method of analysis developed by Farkas and Farkas[1] was employed, with minor modifications of technique with respect to cell construction. The cell employed was of Pyrex glass containing a platinum wire 50 mm. long and 0.01 mm. in diameter. It was doubled around a coiled spring to keep it taut and fastened at both ends to tungsten leads sealed directly into the glass. A jacket surrounding the leads was evacuated to eliminate convection currents and so minimize fluctuations in the heat conduction along the leads. The vessel was immersed well below the surface of a liquid air bath during experiments. We are indebted to Dr. N. R. Trenner for invaluable assistance in the construction of the thermal conductivity cell.

The cell wire was calibrated in terms of resistance, rather than temperature, using a Wheatstone bridge arrangement. To attain the requisite two temperatures T_1 and T_2, greater than that of the liquid air bath surrounding the conductivity cell, two adjustable external resistances yielded heating currents of 14.4 and 15.3 milliamperes with current from a 6-volt battery. The pressure of gas studied was in the neighborhood of 7×10^{-2} mm. accurately adjusted in the case of each sample so as to give, with the lower current, a wire temperature T_1 equivalent to a wire resistance of 32.3 ohms. The variation of T_2 with each sample when the higher current was used defined the deuterium content of the gas, as already made clear by Farkas and Farkas. Access to the cell of water, mercury vapor,

grease and other impurities was prevented by means of traps immersed in liquid air or solid carbon dioxide.

Materials.—The preparation and characteristics of the catalyst materials used in this work have already been detailed in an earlier paper.[2] The hydrogen gas too was of similar origin and purity. The deuterium gas was generated by electrolysis from deuterium oxide, d^{25}_4 1.1079, using NaOD as electrolyte, freed from oxygen by contact with a glowing platinum wire and from water vapor by a liquid air trap. In some experiments the gas was diffused through a heated palladium tube but this precaution was subsequently found to be unnecessary.

Experimental Results

Chromium Oxide.—We present in Table I data on the composition of the gas in the dead space of a vessel containing 18.7 g. of chromic oxide gel at 184°, that of the gas desorbed from the gel surface and that from the buret from which deuterium was introduced to the catalyst. Four successive experiments (Nos. 1 to 4) were performed, in each of which 25 cc. (N. T. P.) of pure deuterium was adsorbed on the surface and subsequently completely desorbed between successive runs. There is evidence in these experiments of slow exhaustion of the water in the gel. The adsorbent was then allowed to take up approximately 450 cc. of deuterium at 350° in units of 50 cc., the adsorption of each unit being followed by desorption at the same temperature. Experiment 5 details the several isotopic concentrations for an immediately succeeding experiment analogous to those of the first four. Experiment 6 was next performed introducing the *light* isotope, H_2; the exchange reaction now took place in the reverse direction, obviously due to the deuterization of the adsorbent in the previous experiments.

The influence of temperature on the rate of exchange is shown in the data on Table II, using 1.75 g. of gel and deuterium as the gas introduced. In each experiment only a few cc. of gas was used.

(1) Farkas and Farkas, *Proc. Roy. Soc.* (London), **144A**, 467 (1934).

(2) Taylor and Diamond, THIS JOURNAL, **57**, 1251 (1935).

TABLE I

EXCHANGE REACTION ON Cr_2O_3 AT 184°

Expt.	1	2	3	4	5	6
Residual gas over catalyst, %	85.5 H	77.5 H	58 H	93 H (?)	60 H	67 H
Gas desorbed, %	98.5 H	97.5 H	92.5 H	87 H	41 H	45.5 H
Gas from buret, %	100 D	100 D	100 D	100 D	100 D	100 H

TABLE II

INFLUENCE OF TEMPERATURE ON THE EXCHANGE
REACTION AT Cr_2O_3 SURFACES

Temp. of catalyst, °C.	Time of contact	Composition of off-gas, %
313	0.1 sec.	95 H
116	0.1 sec.	100 D
116	10 min.	66 H
116	19 min.	69 H
0	110 min.	5 H
0	12.5 hrs.	11 H

The small amount of conversion was due to slowness of reaction and not to exhaustion of the available light isotope on the surface since immediately succeeding experiments at 100° showed conversions to the light isotope of 39.5, 47 and 51% in three, nine and fifteen minutes, respectively.

Zinc Oxide.—With a 0.96-g. sample, successive experiments, similar to those recorded in the preceding table, using pure deuterium, gave at a working temperature of 410 ± 5° the following decreasing conversions to light isotope, each after five minutes contact time: 87, 59, 35, 17, 13, 9, 6% H. Since the samples of gas taken were approximately equal to those introduced to chromium oxide, it is evident that the hydrogen source is exhausted much more rapidly in the case of zinc oxide. The results show, however, the tenacity with which adsorbed water vapor may be held,[3] no hydrogen gas having come into contact with the catalyst in the course of its preparation.

The exchange reaction was reversed by substituting hydrogen for deuterium, a 100% hydrogen giving an off-gas of only 66% H_2 in the first run. After several such treatments the conversion of deuterium to hydrogen was correspondingly increased. The reaction involved is hence reversible. To establish definitely the role of water as a reactant a little water vapor was introduced to zinc oxide which had been exhaustively treated with deuterium until no hydrogen appeared in the off-gas at 410°. In a new set of experiments using deuterium successive samples after five minutes of contact at 410° showed 77, 63, 50, 38 and 18% H. Such re-

(3) Cf. Taylor and Sickman, THIS JOURNAL, **54**, 602 (1932).

plenishment with water vapor and exhaustion of hydrogen supply by deuterium and the reverse processes could be repeated at will.
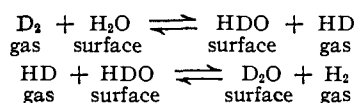
Zinc Chromite.—This substance showed qualitatively the same behavior as the oxide. At 427° the off-gas for five minutes contact was 75.5% H. In succeeding experiments with one minute contact the values were 53, 27.5, 13 and 7.5% H using deuterium and then 71, 95.5, 99.5% H using hydrogen.

Alumina.—Only the reaction between deuterium and light water was studied in this case. At 200° successive experiments showed 78 and 24% H in the off-gas. In this case it was found that water vapor introduced to the catalyst at this temperature did not noticeably increase the hydrogen production at 200°. That much water was present, however, became apparent on heating to 300°. Large amounts of liquid were evolved and subsequent successive experiments with five minute contact times gave 97 and 94% H, while two further experiments with ten minutes contact gave 97 and 95.5% H. Further experiments at this temperature showed that this preparation, like chromium oxide, has a high reserve of water vapor in its structure for the conversion reaction.
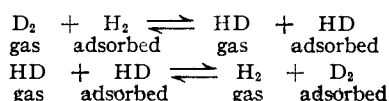
Platinized Asbestos.—A sample of this material converted pure deuterium to 85% H in five hours at 375°. The reaction was much slower than in the other cases studied, pointing to a less available water content of the asbestos fiber. This also can be exhausted, for the contact mass produced no further change in deuterium when examined after 14 liters of deuterium gas had been passed over the mass at 300°.

General Discussion

The experimental observations recorded in the preceding pages, it is believed, establish the existence of an exchange reaction between deuterium gas and water retained by the contact material

$$D_2 + H_2O \rightleftharpoons HDO + HD$$
gas surface surface gas
$$HD + HDO \rightleftharpoons D_2O + H_2$$
gas surface surface gas

and other reactions of this type. The only other conceivable explanation would relate to a displacement by deuterium of adsorbed hydrogen from the chromium oxide, zinc oxide or platinized asbestos, thus

$$
\begin{array}{cccc}
D_2 & + \ H_2 \ \rightleftharpoons & HD & + \ HD \\
\text{gas} & \text{adsorbed} & \text{gas} & \text{adsorbed} \\
HD & + \ HD \ \rightleftharpoons & H_2 & + \ D_2 \\
\text{gas} & \text{adsorbed} & \text{gas} & \text{adsorbed}
\end{array}
$$

and so forth. This hypothesis is, however, at once eliminated in the case of zinc oxide and alumina, since no hydrogen was used in the preparation of these materials. It is not very plausible in the case of chromium oxide either, as only a very slow effect was observed at 0°. The work of Gould, Bleakney and Taylor[4] shows that hydrogen–deuterium mixtures are completely equilibrated with respect to hydrogen deuteride formation in one hour at this temperature; one would expect a displacement of this order of velocity if the present process involved only adsorbed hydrogen and deuterium gas. The part played by water is also made obvious by the fact that the exchange reaction was renewed on addition of water to a partially deuterized zinc oxide surface. It is of interest to note that the original water supplies of the chromium oxide and alumina gels were exhausted much less rapidly than in the case of zinc oxide and zinc chromite, which were obtained from more compact crystalline precipitates (oxalate and chromate, respectively). Kohlschütter[5] estimated the water in the chromium oxide gel as 0.6 H_2O/Cr_2O_3 and that it was 50% deuterized in the experiments described above.

The earliest communication in reference to the deuterium–water reaction was that of Oliphant,[6] who reported an exchange between the pure substances left standing in a glass vessel for six weeks, but this result has since been questioned.[4] Farkas and Farkas[7] showed that the reaction $D_2 + H_2O$ $\rightleftharpoons HDO + HD$ goes three times as fast as D_2 $+ H_2O \rightleftharpoons D_2O + H_2$. From measurements at high temperatures they calculate an energy of activation of 60,000 calories, and on extrapolation to room temperature a collision efficiency of 10^{-45} is obtained; they therefore conclude that there must have been present in the system studied by Oliphant an impurity which catalyzed the reaction. Horiuti and Polanyi[8] observed that

the exchange takes place in one hour at room temperature between deuterium and ordinary water containing dissolved sulfuric acid if platinum black or palladium black is suspended in the liquid; they postulate an ionic mechanism corresponding to the electromotive process of the hydrogen electrode: the catalyst adsorbs hydrogen and ionizes it; the ions then enter the solution while an equal quantity of H^+ and D^+ is simultaneously deposited on the surface; ionization being rapid, diffusion of hydrogen to the platinum is the rate-determining step. The efficiency of nickel has also been demonstrated.[9]

A mechanism of this type is obviously not applicable to the gas–solid systems studied in the present research; one pays attention instead to the nature of the adsorption occurring. Since hydrogen is adsorbed in activated form on the hydrogenation catalysts, chromium oxide, zinc oxide, and zinc chromite at all the temperatures investigated, it is doubtless this process which is responsible for the exchange. In the case of the dehydration catalyst, alumina, the reaction may be accounted for by assuming that the water at least was present in the activated form.[10] An exchange associated with activated adsorption of at least one of the reactants would be quite in harmony with general chemical behavior at surfaces of this type. The reaction velocity is thus determined by the rate of the adsorption–desorption process.

Since the communication of this paper similar exchange effects with water in quartz glass at high temperatures and with hydrogen occluded in fine wires have also been published by Farkas and Farkas.[11]

Summary

1. A rapid exchange reaction has been observed at high temperatures between deuterium gas and water retained by the catalytic materials: chromium oxide, zinc oxide, zinc chromite, alumina and platinized asbestos.

2. Of these substances, chromium oxide and alumina gels possess the largest available water content.

3. The reverse reaction between hydrogen and the heavy water of a partially deuterized surface has also been demonstrated.

(4) Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2**, 362 (1934).
(5) Kohlschütter, *Z. physik. Chem.*, **A170**, 300 (1934).
(6) Oliphant, *Nature*, **132**, 675 (1933).
(7) Rideal, *Proc. Roy. Soc.* (London), **144A**, 19 (1934).
(8) Horiuti and Polanyi, *Nature*, **132**, 819, 931 (1933).

(9) Horiuti and Polanyi, *ibid.*, **134**, 378 (1934).
(10) Taylor and Gould, THIS JOURNAL, **56**, 1685 (1934).
(11) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **31**, 821 (1935).

4. The variation of reaction velocity with temperature was determined approximately in the case of chromium oxide.

5. A mechanism is provided by the activated adsorption of hydrogen which occurs on chromium oxide, zinc oxide and zinc chromite; on alumina,

it is probably the water which is activated.

6. The existence of this exchange is important, since it may cause unintentional replacement of deuterium by the light isotope in a reaction mixture.

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The Electron Affinity of Free Radicals. VII. Triphenylboron and Tri-α-naphthylboron

BY HENRY E. BENT AND MAURICE DORFMAN

The title of this paper is open to the criticism that triphenylboron should not be classed as a free radical, analogous to triphenylmethyl. The electronic formula indicates that the three electrons of boron are all utilized in forming non-polar bonds with three phenyl groups and therefore the molecule would appear to be saturated and not capable of association. Molecular weight determinations indicate that no association occurs.[1] On the other hand, there are chemical reactions of boron compounds which would indicate that this compound is comparable to a free radical. The close parallel between C_2H_6 and $C(C_6H_5)_3$ on the one hand and B_2H_6 and $B(C_6H_5)_3$ on the other is perhaps not very significant. In the case of addition of sodium, however, there seems to be close similarity between triphenylboron and triphenylmethyl. Both compounds add sodium from dilute amalgam and in both cases the sodium is removed by mercury.[2] In the case of triphenylmethyl the free-energy change for the reaction has been determined, but in the case of triphenylboron only qualitative experiments have been reported. It seemed very desirable, therefore, to study triphenylboron quantitatively, especially so in view of the fact that in the case of triphenylmethyl the reaction may be considered to involve the addition of an electron to complete a group of eight electrons, while in the case of triphenylboron the addition of an electron results in only seven electrons around the boron atom. As might be expected the results reported below indicate that there is a much greater tendency to form the group of eight. The results give a measure of the difference between these two reactions.

(1) Krause and Dittmar, *Ber.*, **63**, 2347 (1930).

(2) (a) Krause and Polack, *ibid.*, **59**, 777 (1926); (b) Bent, THIS JOURNAL, **62**, 1498 (1930).

Triphenylboron

In several respects the behavior of triphenylboron is quite different from that of triphenylmethyl. Shaking triphenylboron with 40% amalgam produced the sodium addition compound rapidly and quantitatively. However, shaking the addition compound with mercury or dilute amalgam gave quite erratic results. This was finally traced to a very slow reaction, requiring months for substantially equilibrium conditions to be established. The final data given in Table I were obtained from runs some of which were shaken for four months, the equilibrium being approached from both sides.

The second peculiarity of triphenylboron was the anomalous color observed when the sodium addition compound was shaken with mercury or dilute amalgam. The sodium addition compound has a very decided yellow color and could be recrystallized repeatedly in a closed system without alteration in the intensity of the color. However, when part of the sodium was removed by shaking with dilute amalgam or with mercury the color entirely disappeared. Analysis of the ether solution showed that not more than 70% of the sodium had been removed and therefore one would have expected a very decided color. Similar results were obtained when the equilibrium was approached from the other side. A dilute amalgam would introduce as much as 20% of an equivalent amount of sodium without the appearance of any color in the solution. That decomposition was not taking place was definitely proved by first preparing the sodium addition compound with 40% amalgam, then removing part of the sodium with mercury, and finally again shaking the solution with 40% amalgam. A very close check on the amount of triphenylboron taken originally