

drogen peroxide solutions.²³ The kinetics of the reaction are accounted for by assuming reactions (6) and (8) to be much more rapid than (2), (3) and (4) and applying the "steady-state" hypothesis as regards HO₂SCN to the latter three reactions. The resulting rate law is

$$R = \frac{1}{3} \left(\frac{dx}{dt} \right) = k_2(\text{H}_3\text{O}^+)(\text{SCN}^-)(\text{H}_2\text{O}_2)^2 / [(\text{H}_2\text{O}_2) + k_4/k_3(\text{HCN})] \quad (g)$$

where x is the total $[(\text{H}_2\text{O}_2) + (\text{S}(\text{CN})_2)]$ as is determined by the iodometric technique (method A). It is seen that this expression corresponds exactly with (f) which was deduced above from iodometric rate data, provided $\alpha = k_4/k_3 = 2$ and is more or less temperature independent, an entirely reasonable expectation.

The similarity between SCN^- and halide ion has been mentioned in regard to reactions 1 and 2. It is of interest that studies of the peroxide/iodide reaction^{24,25} over a wide pH range lead to the rate expressions

(23) A. G. Mitchell and W. F. K. Wynne-Jones, *Trans. Far. Soc.*, **52**, 824 (1956).

$$R = k_1(\text{I}^-)(\text{H}_2\text{O}_2) \quad (\text{high pH})$$

$$R = k_2(\text{H}_3\text{O}^+)(\text{I}^-)(\text{H}_2\text{O}_2) \quad (\text{low pH})$$

These are identical in form with the expressions deduced in our studies for initial rates of the peroxide/thiocyanate reaction *in absence of HCN*. Furthermore, above an ionic strength of about 0.1, neither k_1 or k_2 of the iodide processes vary appreciably²⁴ with μ , again corresponding with our findings. However, the analogy is seen to break down completely in the acid-catalyzed thiocyanate reaction as soon as (HCN) becomes appreciable. The expected product on the basis of the halide comparison is $(\text{SCN})_2$, a species for the presence of which no evidence whatsoever could be adduced in our work.

Financial support of portions of this study through Contract No. AT(30-1)-1578 between the U. S. Atomic Energy Commission and the University of Buffalo is gratefully acknowledged.

(24) H. A. Liebhafsky and A. Mohammad, *THIS JOURNAL*, **55**, 3977 (1933); *J. Phys. Chem.*, **38**, 857 (1934).

(25) F. Bell, R. Gill, D. Holden and W. F. K. Wynne-Jones, *J. Phys. Coll. Chem.*, **55**, 874 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY, NEW YORK 32, N. Y.]

The Activation of Molecular Hydrogen by Platinum¹

BY ALVIN I. KRASNA

RECEIVED JULY 14, 1960

The activation of molecular hydrogen by platinum has been studied by means of the *ortho-para* hydrogen conversion and the exchange reaction between hydrogen and deuterium oxide. The reaction between hydrogen and water has been shown to be a gas phase reaction. With 100% D₂O as solvent, there was no *para* hydrogen conversion and D₂ was produced in greater quantities than HD. The data indicate that platinum catalyzes a homolytic split of the hydrogen molecule. The mechanism of the platinum catalyzed activation of hydrogen is compared with the enzyme catalyzed reaction.

In 1933, Horiuti and Polanyi² observed that platinum black catalyzed an exchange reaction between water and deuterium gas. They concluded that the deuterium gas is converted to ions by the catalyst which exchange with the protons of the water. Eley and Polanyi³ compared the platinum black catalyzed *ortho-para* hydrogen conversion and exchange reaction between deuterium and water and found that the rate of the conversion reaction was two to three times that of the exchange reaction. They suggested that the rate determining process in both reactions was the splitting of the hydrogen molecule to ions or atoms in a strongly polar state. There was no evidence for a preliminary equilibrium between the hydrogen molecule and hydrogen atoms and the differences in the rates of the two reactions were attributed to the differences in the energies of hydrogen compared to deuterium. When the platinum black catalyzed exchange reaction and *para* hydrogen conversion

between 80% D₂O and *para* hydrogen was studied by Farkas,⁴ the conversion was found to proceed more slowly than the exchange. It was suggested that the dissociation of hydrogen was the rate limiting step and that ions, not atoms, are produced which exchange with the deuterium ions of the water more rapidly than the discharge of two ions and the subsequent recombination to normal molecules.⁵

During the course of the investigation of the mechanism of action of the enzyme hydrogenase, certain of the reactions catalyzed by the enzyme were also studied when catalyzed by platinum. This paper describes these findings, and although many of the reactions catalyzed by the enzyme and platinum are quite similar, the mechanism of hydrogen activation is different in these two systems.

Experimental

The platinum oxide and platinum tetrachloride were purchased from Baker and Co., Newark, N. J. Deuterium gas and 99.9% D₂O were purchased from the Stuart Oxygen Company on allocation from the Atomic Energy Commission.

(4) A. Farkas, *ibid.*, **32**, 922 (1936).

(5) The literature on the exchange reactions has been reviewed by T. I. Taylor in "Catalysis," Vol. V, P. H. Emmett, Editor, Reinhold Publishing Co., New York, N. Y., 1957, p. 257.

(1) This investigation was supported by grants from the National Science Foundation (NSF G-9587), Office of Naval Research (ONR 26602), Atomic Energy Commission (AT (30-1) 1803), and the National Institutes of Health (E-2839). Reproduction of this article in whole or in part is permitted for any purpose of the United States Government.

(2) J. Horiuti and M. Polanyi, *Nature*, **132**, 819 (1933).

(3) D. D. Eley and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1388 (1936).

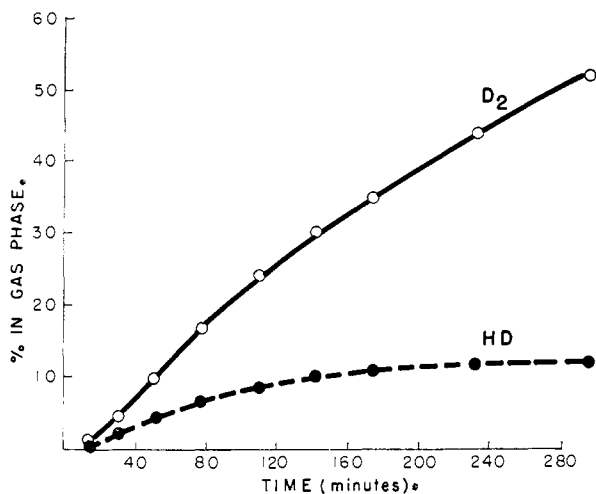
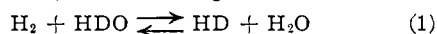


Fig. 1.—Exchange reaction in 100% D₂O. The flask contained 0.72 mg. of PtO₂, 46.4 mg. of Na₂HPO₄, 57.4 mg. of KH₂PO₄ and 5.0 ml. of D₂O; the buffer concentration was 0.15 M and the pH 6.6; the gas phase was hydrogen. Similar results were obtained with 5 mg. of PtO₂.

All the experimental methods have been previously described in detail.⁶ All reactions were carried out at 25°.

Results and Discussion

Platinum oxide or platinum tetrachloride was suspended in 10% D₂O in an atmosphere of H₂ in order to study the exchange (reaction 1) under



conditions identical to those used for the enzyme hydrogenase.⁶ The reaction was extremely fast and equilibrium was reached in a very short time. The reaction was too rapid to permit accurate kinetic measurements but a first order rate constant of about 0.03–0.06 min.⁻¹ was estimated. The parahydrogen conversion in H₂O was also very fast and was about two to three times more rapid than the exchange reaction. The rates of these two reactions were independent of the concentration of platinum oxide in the range 0.5 mg. to 20 mg.

When these same reactions were catalyzed by the hydrogenase of *Proteus vulgaris*, it was found⁶ that the maximum rate constant obtainable was 0.0065 for the exchange reaction and 0.010 for the para hydrogen conversion. At these rates, the diffusion of hydrogen into solution is the rate limiting step. If the platinum catalyzed reactions take place in solution as they must with the bacteria, the rate limiting step should be the diffusion of hydrogen into solution and the rate should be the same as the maximum rate obtained with the bacteria. The fact that the rates of the reactions are many times more rapid with platinum would suggest that platinum is catalyzing a reaction between hydrogen and water vapor and this gaseous reaction is not limited by diffusion of hydrogen into liquid water.

Support for this suggestion is offered by the following experiment. Platinum oxide (5 mg.) was dried by heating under vacuum. This was

then shaken with 3% D₂–97% H₂. After 20 minutes, very little D₂ remained in the gas phase and HD appeared. However, the total deuterium that could be accounted for was only 1.5%. This suggests that an exchange reaction had occurred between D₂ and the water formed during the reduction of the PtO₂. When dry platinum oxide was shaken with para hydrogen, complete conversion took place within a few minutes. If dry PtO₂ was shaken with 700 mm. H₂ and 18 mm. D₂O vapor, 13% HD appeared in the gas. In all these experiments, no liquid water was visible. These observations would indicate that in the previous experiments where the platinum was suspended in water, the platinum catalyzed a gaseous reaction between hydrogen and water vapor on the surface of the platinum (which was both suspended in the liquid and clung to the walls of the flask above the liquid phase).

The extreme speed of the platinum catalyzed reactions made it difficult to obtain accurate kinetic data. When the experiments in aqueous solutions were repeated using 0.15 M phosphate buffer, pH 6.7, instead of distilled water, the rates of the reactions were decreased three to four times and the kinetics could easily be measured. (The bacterial cells gave the same rates whether suspended in buffer or distilled water.) Under these conditions the rates were somewhat dependent on the platinum oxide concentration in the range 1–5 mg., and the para hydrogen conversion was two to three times more rapid than the exchange reaction. Both reactions followed first order kinetics. There was very little difference in the rate of the exchange reaction whether the flask was shaken or not which would indicate that the reaction was a gaseous one as shown above.

Parahydrogen Conversion and Deuterium Exchange in 100% D₂O.—The conversion experiments described above were carried out with the catalyst suspended in H₂O. When the platinum oxide was suspended in 100% D₂O (containing phosphate salts to decrease the rate of the reaction) and shaken with parahydrogen, there was no conversion of parahydrogen (see Table I). The results obtained in H₂O are included for comparison. Farkas⁴ found that when platinum black suspended in 80% D₂O was shaken with parahydrogen, the conversion reaction proceeded more slowly than the exchange reaction. The absence of any parahydrogen conversion in D₂O was also observed with the hydrogenase of *Proteus vulgaris*.⁶

The rate of appearance of HD and D₂ when the exchange is carried out in 100% D₂O is shown in Fig. 1. It can be seen that D₂ is formed in much greater quantities than HD⁷ even in the very early stages of the reaction. The gases are not in equilibrium with respect to the reaction



With respect to the appearance of D₂ and HD, the platinum system is different from the enzyme system. With hydrogenase, the rate of HD for-

(7) The formation of HD during the platinum foil catalyzed exchange between a gas mixture of 66% D₂, 14% HD, 20% H₂ and H₂O vapor has been observed by K. Hannerz, *Acta Chem. Scand.*, **10**, 655 (1956).

(6) A. I. Krasna and D. Rittenberg, *THIS JOURNAL*, **76**, 3015 (1954).

TABLE I
PARAHYDROGEN CONVERSION BY PLATINUM OXIDE IN
D₂O AND H₂O

Each flask contained 5.0 mg. of PtO₂, 46.4 mg. of Na₂HPO₄, 57.4 mg. of KH₂PO₄ and 5.0 ml. of either D₂O or H₂O; the final buffer concentration was 0.15 M and the pH 6.6. The experimental details of this experiment are similar to those described in reference 6.

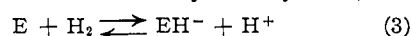
Time (min.)	Relative parahydrogen concentration ^a in D ₂ O	in H ₂ O
0	100	100
32	101	75
61	110	60
92	107	33
123	110	25
154	111	15
185	105	13

^a The relative parahydrogen concentration, P , is defined as $P = \frac{(P_t - P_\infty)}{(P_0 - P_\infty)} 100$, where P_0 , P_t and P_∞ are the percentages of parahydrogen at $t = 0$, t and at equilibrium, respectively.

mation is five times more rapid than D₂ formation with *Proteus vulgaris* and equal to the rate of D₂ formation with *Desulfovibrio desulfuricans*.⁸ In the enzyme case, the formation of HD in greater quantities than D₂ and the absence of parahydrogen conversion in D₂O was taken as evidence for the heterolytic split of the hydrogen molecule with

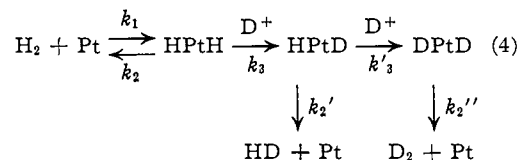
(8) A. I. Krasna, E. Riklis and D. Rittenberg, *J. Biol. Chem.*, **235**, 2717 (1960).

the formation of an enzyme hydride,⁶ *i.e.*



If the hydrogen molecule were split homolytically, only D₂ would be formed and very little HD.

Clearly, the activation of hydrogen by platinum is not due to a heterolytic split of the hydrogen molecule since D₂ is the predominant species. The mechanism of the platinum activation of hydrogen is probably an essentially homolytic one and can be represented by the equations



The hydrogen atoms on the platinum in the species HPtH are probably present in the ionic form as protons⁴ which exchange rapidly with the deuterons of the D₂O. The exchange of HPtD and DPtD with H⁺ is negligible in a system containing 100% D₂O. The data presented suggest that k_3 and k'_3 are much greater than k_2 , k_2' and k_2'' . This explains the large amount of D₂ formed, the small amount of HD and the absence of parahydrogen conversion in D₂O. This last fact by itself demonstrates that k_3 is very much larger than k_2 . The formation of HD might be due to reaction 2 even though it is not rapid enough to bring about equilibrium.

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS]

Fluorine 18 Exchange between Uranium Hexafluoride and Metal Fluorides¹

BY IRVING SHEFT, HERBERT H. HYMAN, RICHARD M. ADAMS AND JOSEPH J. KATZ

RECEIVED JULY 5, 1960

Uranium hexafluoride has been reported to form a compound 3 NaF·UF₆ with sodium fluoride. The fluorine exchange between UF₆ and NaF was undertaken to further investigate the nature of this addition compound. With the radioactive fluorine F¹⁸ in either the NaF or UF₆, exchange experiments indicate complete exchange for a compound of the composition 2 NaF·UF₆. In some experiments with more than one mole of UF₆ for three moles of NaF all the UF₆ was absorbed, and the extent of exchange indicated the compound 2 NaF·UF₆ was formed. Essentially no exchange occurs when gaseous UF₆ is passed through NaF¹⁸ at temperatures above which the solid addition compound forms. No compound was formed, and essentially no exchange occurred, between UF₆ and LiF, KF, ZrF₄ and AgF. No compound was identified in the case of CaF₂, but a significant amount of exchange was noted.

Introduction

Sodium fluoride has been used for many years to absorb hydrogen fluoride from uranium hexafluoride. Small amounts of uranium were often found trapped on the sodium fluoride. In 1946 Martin and Albers² reported the formation of stable complexes between uranium hexafluoride and a number of inorganic fluorides. Further work,³⁻⁶ primarily with the sodium fluoride complex, indi-

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. Martin and A. Albers, *Naturwissenschaften*, **33**, 370 (1946).

(3) H. Martin, A. Albers and H. P. Dust, *Z. anorg. u. allgem. Chem.*, **265**, 128 (1951).

(4) R. E. Worthington, United Kingdom Atomic Energy Authority, IGR-R/CA 200 (1957).

(5) G. I. Cathers, M. R. Bennett and R. L. Jolley, "Formation and Decomposition Reactions of the Complex UF₆·3NaF," Paper presented at the A.C.S. meeting, Spring 1957.

cated its composition to be 3 NaF·UF₆. A study of the exchange of fluorine between uranium hexafluoride and some of these inorganic fluorides was inaugurated in hopes of learning more about the nature of those complexes which were formed. Rapid exchange between fluorine atoms is good evidence for the introduction of fluorine atoms into the nearest neighbor coordination sphere of the uranium atom, while absence of such exchange can be taken as evidence that the uranium hexafluoride was incorporated mechanically into the metal fluoride. The use of radioactive F¹⁸ as a tracer for fluoride ion exchange is well established both in this Laboratory and elsewhere. The preparation, properties and some general considerations in the

(6) F. E. Massoth and W. E. Hensel, Jr., *J. Phys. Chem.*, **62**, 479 (1958).