[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Exchange between Ammonia and Deuterium on Catalytic Iron Surfaces

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The interaction of deuterium with hydrogen-containing compounds has now attained to a problem of considerable importance in the study of catalytic surfaces. The existence of an exchange reaction on such surfaces defines, to a degree hitherto unattainable, the nature of the association of the adsorbed reactants with the surface. Already hydrogen gas, water vapor, and unsaturated hydrocarbons have been thus studied in their reactions with deuterium at nickel, copper, platinum and chromium oxide surfaces.[2] In further prosecution of such studies we have examined the interaction of ammonia and deuterium on the surface of synthetic ammonia catalysts composed of iron promoted by an alumina-potash admixture.

In an earlier paper[3] we have shown that the ultraviolet absorption spectra of the deutero-ammonias are sufficiently definite and diverse to lend themselves to a study of progressive substitution of deuterium in ammonia or of hydrogen in deutero-ammonia. In the earlier work we examined the exchanges produced between ammonia and deuterium atoms produced by photosensitized decomposition of molecular deuterium using excited mercury. In the following paragraphs we record the results of a similar study using deuterium and ammonia in presence of an $Fe-K_2O-Al_2O_3$ catalyst at ordinary temperatures and also in an empty quartz reaction vessel at temperatures up to 300°.

Experimental.—In a quartz cylindrical vessel with plane parallel faces, 35 mm. in diameter, with a cylinder length of 4 cm., we have sealed up a mixture of 6 parts of ammonia and 15 parts of deuterium, under 21 cm. of mercury. This mixture was allowed to stand, first for seventeen days at room temperatures, and then for three days at 300°. The quartz vessel, before use, was rigorously dried by baking and evacuation and the gases used were similarly subjected to careful desiccation. Absorption spectra of the gas mixture were obtained, using a hydrogen discharge tube and a Hilger E-1 spectrograph, at the beginning of the experiment, also prior to and immediately after the heating process at 300°. In such a clean quartz vessel there was no observable change in the absorption spectrum of the ammonia, indicating the absence of any deuterium exchange with ammonia under these conditions of temperature and vessel surface.

In a similar quartz vessel, 50 mm. in diameter with plane faces and cylinder length of 1 cm., we placed in a quartz appendage a synthetic ammonia catalyst ($Fe-K_2O-Al_2O_3$). This was reduced *in situ* for a prolonged period and precautions were taken to ensure completeness of reduction and the removal of all traces of water vapor produced in the process. After intensive reduction and evacuation, a mixture of 20 parts of ammonia and 25 parts of deuterium at a total pressure of 45 cm. of mercury was introduced into the reaction vessel. The gases were subjected to careful desiccation, the ammonia being finally distilled into the reaction vessel from sodium, and the deuterium filled into the system through liquid air traps. The technique employed in introducing the gases and sealing the reaction system was especially designed to minimize, as far as was readily practicable, any introduction of water vapor; the sealed system represents, in our view, as dry a system as can be obtained without adopting the specialized technique of those who have studied the subject of intensive desiccation. Ultraviolet absorption spectra were taken of the reaction mixture, one-half hour, six hours, twenty-three hours, forty-seven hours and seventy-two hours after the filling and sealing of the reaction vessel which was held at room temperature. A further exposure was made of the gas mixture after a further month of standing. Already after twenty-three hours, the development of deutero-ammonia bands was evident on the spectral plates. After seventy-two hours it was apparent that the deutero-ammonias represented approximately 25% of all the ammonias present. A month later the spectra revealed well developed bands of all the several ammonias, NH_3, NH_2D, NHD_2 and ND_3.

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[2] (a) Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2**, 362 (1934); (b) Farkas, Farkas and Rideal, *Proc. Roy. Soc.* (London), **146**, 630 (1934); (c) Taylor and Diamond, THIS JOURNAL, **56**, 1821 (1934); (d) Horiuti, Ogden and Polanyi, *Trans. Faraday Soc.*, **30**, 663 (1934); (e) Horiuti and Polanyi, *ibid.*, **30**, 1164 (1934).

[3] Taylor and Jungers, *J. Chem. Phys.*, **2**, 452 (1934).

Discussion.—The contrast between the negative results with the quartz vessel and the positive results when a reduced iron catalyst was present in the reaction system establishes definitely that deuterium exchanges slowly with ammonia on an iron catalyst even at room temperatures. The negative results with the quartz vessel alone even at 300° assure us that traces of water vapor are not the cause of the observed exchange. Rather must this be attributed to the nature of the adsorption processes occurring between both ammonia and deuterium and the iron catalyst surface. We ascribe the exchange to the existence of the adsorbed gases on the surface in the form of dissociated fragments, atoms in the case of deuterium and at least NH_2 and H fragments in the case of ammonia. We conclude that, even at room temperatures, on an active iron catalyst of the type employed, activated adsorption of ammonia, dissociative in type, is freely occurring. Further, since the deutero-ammonias produced pass freely into the gas phase, it is evident that all of the operations $NH_{3(gas)} \rightleftarrows NH_{2(ads)} + H_{(ads)}$; $D_{2(gas)} \rightleftarrows 2D_{(ads)}$; $NH_{2(ads)} + D_{(ads)} \rightleftarrows NH_2D_{(gas)}$ and the corresponding processes for more complete deuterium substitution of ammonia, are all occurring freely *even at room temperatures*. It is evident, therefore, that such processes will proceed with great rapidity at the higher temperatures obtaining in ammonia synthesis and that they cannot be expected to be rate-determining steps in such synthesis. We do not know any reason why the further dissociative adsorption processes $NH_{2ads} \rightleftarrows NH_{ads} + H_{ads}$ and $NH_{ads} \rightleftarrows N_{ads} + H_{ads}$ should be any slower than the one involving the change from NH_3 to NH_2 and H. If this is so they are likewise not significant rate-determining steps in the synthesis or decomposition of ammonia. Such lines of reasoning lead by processes of elimination to the conclusion that it is the process $N_{2gas} \rightleftarrows 2N_{ads}$ which is rate-determining in ammonia synthesis on such iron catalysts; this conclusion from isotope chemistry is in best agreement with evidence of entirely different character.[4]

The exchange reaction between deuterium and ammonia on an iron surface is one further illustration of the delicacy of isotope chemistry in revealing the nature of the adsorptive association between surface adsorbent and adsorbate. As in the case of hydrogen and deuterium exchange studied by Gould, Bleakney and Taylor,[2a] the study of isotope exchange reveals activated adsorption of ammonia in a temperature range where the usual measurements of adsorption are unable to distinguish between van der Waals and activated adsorption. The ammonia–deuterium exchange on iron is, however, a slower process than the hydrogen–deuterium exchange on nickel or chromium oxide on which latter the hydrogen–deuterium exchange is also more rapid than the deuterium–water exchange under comparable conditions.[2c] The sensitivity of the technique prompts the belief that it offers an excellent tool in the examination of activated adsorption not only of unsaturated hydrocarbons[2d,2e] but even of saturated hydrocarbons. Experiments in this direction have already been undertaken.

Summary

1. The exchange reaction between deuterium and ammonia occurs on an active synthetic ammonia iron catalyst even at room temperatures.

2. This exchange reaction does not occur on fused quartz surfaces even at 300°.

3. The bearing of these observations on the problem of kinetics in ammonia synthesis is discussed.

4. The study of such exchange reactions is shown to be a most sensitive criterion for detection of activated adsorption on catalytic surfaces.

PRINCETON, N. J. RECEIVED FEBRUARY 4, 1935

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(4) Emmett and Brunauer, THIS JOURNAL, 55, 1738 (1933).