

THE CONVERSION OF PARA HYDROGEN TO ORTHO HYDROGEN OVER IRON SYNTHETIC AMMONIA CATALYSTS

Sir:

From studies carried out by various authors [Bonhoeffer and Harteck, *Z. physik. Chem.*, **4B**, 113 (1929); A. Farkas, *ibid.*, **10B**, 419 (1930); **14B**, 371 (1931); Bonhoeffer and Farkas, *ibid.*, **12B**, 231 (1931); Taylor and Sherman, *THIS JOURNAL*, **53**, 1614 (1931)] it has generally been concluded that hydrogen becomes "activated" during its conversion on metallic surfaces from the para to the ortho form. This "activation" on tungsten and platinum in particular has been interpreted as a surface dissociation into adsorbed hydrogen atoms [Bonhoeffer and Farkas, and Farkas, *loc. cit.*]. In continuing the study that this Laboratory has been making of the mechanism of the catalytic synthesis of ammonia, it has seemed worth while to determine the conditions under which hydrogen molecules on iron synthetic ammonia catalysts become sufficiently activated to bring about the para-ortho conversion and to compare the rates of this conversion to the known rates of ammonia synthesis on the same catalysts.

The only references heretofore made to the activity of iron for the para-ortho conversion were by Bonhoeffer and Harteck (*loc. cit.*), who reported coarse iron to be inactive and pyrophoric iron to be capable of effecting only a relatively slow transformation at room temperature, the times of contact of the hydrogen and iron in neither case-being specified. The present experiments have been carried out by a flow method, a stream of 49:51 para-ortho hydrogen being passed over 5 cc. of an ammonia catalyst at various temperatures at a rate of flow of 50 cc. per minute. A pure iron catalyst prepared by the reduction in hydrogen at 450-550° of fused Fe₃O₄ has been used. It is much less active as an ammonia catalyst than some of the promoted varieties. Nevertheless, at a temperature of 40° it converts a 49:51 para-ortho mixture to a 27.6:72.4 mixture in the very short time of contact accompanying the above-mentioned flow. At -20, 0, 20 and 40°, the percentage conversions from the entering 49:51 to the equilibrium 25:75 mixture are 19, 42, 69 and 89%, respectively.

The extent to which hydrogen must be activated by the catalyst in the catalytic synthesis of ammonia from hydrogen-nitrogen mixtures is not at present known [see Frankenberger's article in Ullman's "Enzyklopädie der Technischen Chemie, 1928"]. It is well established, however, that on the catalyst used in the present experiments appreciable rates of ammonia synthesis are not obtained below 300-400°. Accordingly, from the present experiments if one assumes that the activation of hydrogen during its conversion by an iron catalyst from the para to the ortho form is a type that puts it in an active form so far as catalytic hydrogenations in

general are concerned, then one may conclude that the limiting factor in the synthesis of ammonia is not the rate of activation of the hydrogen but the rate at which the nitrogen molecule can be brought into a reactive form by the catalyst.

Benton and White [THIS JOURNAL, 53, 3301 (1931)] have pointed out that activated adsorption of hydrogen on a sample of this same iron catalyst begins between -78° and about 0° . The results obtained in the present research seem entirely consistent with their conclusion. The study of the kinetics and temperature coefficient of the para-ortho hydrogen conversion on various synthetic ammonia catalysts is being continued.

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THE ALLYLIC REARRANGEMENT OF CROTYL BROMIDE AND CROTYLMAGNESIUM BROMIDE

Sir:

In view of the recent appearance of an article by Gilman and Harris¹ on the allylic rearrangement of cinnamylmagnesium chloride, it seems advisable to present a preliminary report on the allylic rearrangement of crotylmagnesium bromide.

Using the method of Dillon, Young and Lucas² we have analyzed butenes obtained from the following steps: *trans*-crotonaldehyde \rightarrow crotyl alcohol \rightarrow crotyl bromide \rightarrow 2-butene. The 2-butenes obtained by the action of (a) zinc and aqueous alcohol on crotyl bromide and (b) dilute acid on crotylmagnesium bromide, both contained approximately 10% 1-butene. This was contrary to our expectations since crotyl bromide, according to the work of Prévost³ and Bouis⁴ should be free from α -methylallyl bromide and thus give pure *trans*-2-butene. The presence of 1-butene in these mixtures must be attributed to an allylic rearrangement of the crotyl bromide or of the Grignard reagent and the corresponding zinc compound. Recent work in this Laboratory on crotyl alcohol and work on 2-pentene-1-ol by Meisenheimer and Link⁵ indicates that an allylic transformation probably does occur during the preparation of the bromide. For example, the boiling ranges of different crotyl bromide preparations vary from 1–12° depending on the procedure used.

¹ Gilman and Harris, THIS JOURNAL, 53, 3541 (1931).

² Dillon, Young and Lucas, *ibid.*, 52, 1953 (1930).

³ Prévost, *Ann. chim.*, [10] 10, 147–181 (1928).

⁴ Bouis, *Bull. soc. chim.*, [4] 41, 1160 (1927).

⁵ Meisenheimer and Link, *Ann.*, 479, 260 (1930).