COMMUNICATIONS TO THE EDITOR

GRIGNARD REAGENTS FROM DIALKYL SULFATES

Sir:

In a study of some of the reactions of di-*n*-butyl sulfate it was found that this compound reacts with *n*-butylmagnesium bromide according to the equation: $(n\text{-}C_4H_9)_2SO_4 + n\text{-}C_4H_9MgBr \longrightarrow n\text{-}C_4H_9MgOSO_2OC_4H_9 + n\text{-}C_4H_9Br$. This indicated that dialkyl sulfates might form Grignard reagents directly and this has been found to be the case. Diethyl sulfate reacts readily with magnesium in dry ether to give a slightly soluble Grignard reagent as follows: $(C_2H_5)_2SO_4 + Mg \longrightarrow C_2H_5Mg(C_2H_5)SO_4$. This with benzaldehyde gave a good yield of phenylethylcarbinol. Di-*n*-butyl sulfate similarly formed a compound which hydrolyzed readily to give *n*-butane. So far as we are at present aware this type of Grignard reagent has not been studied heretofore.

The investigation upon the preparation and properties of di-*n*-butyl sulfate will be published shortly. Work upon the Grignard reagents from dialkyl sulfates is still in progress.

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Received June 5, 1933 Published August 5, 1933

CONVERSION OF ORTHO TO PARA HYDROGEN OVER PROMOTED IRON SYNTHETIC AMMONIA CATALYSTS AT −190°

Sir:

The catalytic conversion of ortho to para hydrogen at about −190° has now been reported for a number of catalysts. It is generally recognized that the mechanism of the low temperature conversion, whatever be its nature, is quite different from that involved in the high temperature conversion (from 0 to 500°). The experiments on a promoted iron catalyst to be summarized briefly in the present letter afford several additional contrasts between the characteristics of the high and the low temperature conversion.

The adsorption of hydrogen by a promoted iron synthetic ammonia catalyst was found to inhibit markedly the activity of the latter toward the ortho-para conversion at −190°. Thus at a space velocity of 12,000 practically 100% conversion of a 25:75 to a 47:53 para-ortho mixture could be obtained if the freshly reduced sample was degassed at 450° and cooled to −190° in helium; whereas if the sample was cooled in hydrogen from 450°, it was found capable of effecting only a 12% conversion at −190°. Furthermore, exposing a sample of helium-cooled catalyst to hydrogen at 100° and 760 mm. pressure for 5, 15, 30, 60, 120 and 200 minutes resulted in the catalyst being able to effect 43, 20, 16, 15, 10 and 15% conversion, respectively, at −190°; similar exposure of a sample to hydrogen at 200° for 15, 30 and 60 minutes left the catalyst able to effect a 32% conversion in each case. These data combined with measurements that have been made on the rate and amount of hydrogen adsorbed by the catalyst at 100 and 200° appear to indicate definitely that the activated adsorption of hydrogen at the higher temperatures is primarily a surface adsorption and not a solution within the iron sample. If this inhibitive effect of high temperature hydrogen adsorption on the low temperature conversion activity of metal catalysts proves to be a general one, it should be a useful tool for differentiating between the adsorption of gases by catalyst surfaces and solution within metal catalysts.

Permitting the promoted catalyst to take up oxygen between room temperature and 450° almost eliminates its high temperature activity toward the para-ortho conversion but only slightly impairs the activity toward the conversion at −190°. Since the iron oxide that would be formed first by the reaction of oxygen and iron is magnetite (Fe_3O_4), the retention of activity at −190° by the partially oxidized catalyst is perhaps not surprising for as Bonhoeffer, Farkas and Rummel [*Z. physik. Chem.*, **B21**, 225 (1933)] and Taylor and Diamond [THIS JOURNAL, **55**, 2613 (1933)] have suggested, the low temperature conversion may be associated with magnetic characteristics of the catalyst surface.

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RECEIVED JUNE 19, 1933 PUBLISHED AUGUST 5, 1933

THE LOW TEMPERATURE ABSORPTION SPECTRUM OF PEPSIN

Sir:

Preliminary measurements indicate that pepsin has an absorption band in the ultraviolet in the region 2600–2900 Å. If the pepsin is cooled, say to −100°, then it is found that this wide band is "resolved" into a number of sharp, narrow bands. At the present time it appears probable that certain of these bands may be correlated with activity.

It has also been found that proteins such as serum albumin and egg albumin show narrow band formation at low temperatures. It seems that there is a difference in the temperature required to produce the narrow bands in the case of the albumins and that of pepsin; apparently a lower temperature is necessary for pepsin.

The apparatus used in the low temperature work is very simple and is