HYDROGENATION OF AMIDES TO AMINES

Sir:

A useful process for the reduction of amides to amines has apparently not been described. Guerbet [*Chem. Zentr.*, II, 623 (1899)] reported the formation of ethylamine from acetamide (Na + ROH), but Bouveault and Blanc [*Compt. rend.*, **138,** 148 (1904)] obtained alcohols as the chief product from amides under similar conditions. Mailhe [*Bull. soc. chim.*, [3] **35,** 614 (1906)] reported the formation of ethyl and dimethyl amines from acetamide and of propyl and dipropylamines from propionamide in the vapor phase ($Ni + H_2$), but no details as to yields or purity of products were given.

The transformation $RCONH_2 + H_2 \longrightarrow RCH_2NH_2 + H_2O$ does not take place readily and is likely to go incompletely because the water formed in the reaction hydrolyzes unchanged amide with the formation of acid and ammonia, which may deactivate a catalyst. It has now been found possible to bring about this reaction over copper–chromium oxide under 100 to 300 atm. of hydrogen at 175 to 250°. It has been found advantageous to use dioxane as a reaction medium since thereby the water formed in the reaction is diluted and the hydrolysis of the amide is negligible. (Raney nickel should *not* be used with dioxane at 250°.)

Lauramide, heptamide, α-phenylbutyramide, furoamide and tetrahydrofuroamide have given yields of from 40 to 70% of the corresponding primary amines. The chief side reaction is the formation of secondary amines, which were isolated in yields of 25 to 50%. For example, 54 g. of α-phenylbutyramide in 125 ml. of dioxane with 10 g. of copper–chromium oxide under 250 atm. of hydrogen was hydrogenated in two hours at 250°, and 36 g. of 2-phenylbutylamine and 13 g. of di-2-phenylbutylamine obtained. The method has also been applied to the hydrogenation of substituted amides, *e. g.*, N-laurylpiperidine, N-sebacylpiperidine, mono- and di-N-β-phenylethyl lauramide, mono- and di-N-amyl lauramide, N-cyclohexyl lauramide, N-β-phenylethyl heptamide and N-phenyl lauramide. The yields of secondary or tertiary amines were from 70 to 95% except from the last mentioned compound [*cf.* Folkers and Adkins, THIS JOURNAL, **54,** 1152 (1932)]. The amides referred to above were prepared by the reaction of anhydrous ammonia or amines with an ester at 250°. The amide has also been prepared in place; *e. g.*, high yields of amines were obtained by the hydrogenation of ammonium laurate.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WIS.

HOMER ADKINS
BRUNO WOJCIK

RECEIVED DECEMBER 20, 1933

POSSIBILITY OF INTERCHANGE BETWEEN DEUTERIUM GAS AND HYDROGEN IN COMPOUNDS

Sir:

In some studies on the reaction between deuterium and hydrogen, it was necessary to determine if interchange took place between the deuterium in the gas phase and the hydrogen atoms in ordinary water when deuterium–hydrogen mixtures were stored over water and also if the concentration of deuterium in the gas phase was affected by the stopcock grease which was present in our apparatus. A 425-cc. Pyrex bulb was fitted with a three-way stopcock at the top and a stopcock at the bottom connecting with a leveling bulb. The bulb was filled with distilled water and then all but 35 cc. of the water displaced by adding, through one arm of the upper stopcock, a deuterium–hydrogen mixture obtained by electrolysis of heavy water. Both stopcocks were closed and the apparatus shaken for several minutes to saturate the water in the bulb with gas. The pressure in the bulb was about 1.1 atm. A sample of gas was then removed through the second arm of the upper stopcock leaving the gas in the bulb at atmospheric pressure. The bulb was kept at room temperature and shaken occasionally for nineteen days. At the end of this time, a second sample of gas was removed by displacement with water. Mass spectrographic analysis of the samples showed the first to contain 2.29% deuterium and the second 2.30%.

This result shows that the concentration of deuterium–hydrogen mixtures in contact with water in clean glass vessels remains constant if precautions are taken to avoid preferential solubility, diffusion and the presence of metallic surfaces [Horiuti and Polanyi, *Nature*, **132,** 819 (1933)], and that the result reported by Oliphant [*Nature*, **132,** 675 (1933)] cannot be interpreted as being an interchange between the deuterium in the gas phase and the hydrogen atoms in the water without the aid of a catalytic surface other than the glass wall of the containing vessel.