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THE PREPARATION OF AMINES BY HYDROGENATING AMINATION OF ALDEHYDES AND KETONES

In order to avoid the difficulties inherent in the preparation of amines from alcohol and ammonia under high pressure, conditions for the hydrogenating amination of ketones and aldehydes were studied.

The aldehydes required for this process were obtained by dehydrogenation of the corresponding fractions from the isobutyl oil synthesis. This process permits to separate the aldehydes comparatively purely which is an advantage over the tedious separation of alcohols. According to the German patent 621629, hydrogenation in the presence of ammonia is carried out using metallic nickel as catalyst. Since catalysts of this type are easily poisoned and since, on the other hand, aldehydes contain impurities in the form of sulphur compounds, the hydrogenating amination in the presence of sulphur-resistant catalysts was attempted. The following aldehydes and ketones were converted into the corresponding amines using a sulphur-containing catalyst: Isobutyraldehyde, isocamylaldehyde, isohexylaldehyde, isoheptylaldehyde, acetone, methylethylketone, 5-methyloctanone-2 (C₉ ketone), isobutyrene.

Catalysts

Catalyst 118 This catalyst was used almost exclusively for the hydrogenating amination of aldehydes and ketones and represents a nickel-tungsten sulphide catalyst which had been obtained by wet precipitation; its composition is 2NiS.WS₃. This catalyst is already fully active at 200°C. and gave a practical conversion of 100%. Only at temperatures above 310 - 320°C. a small amount (2%) of hydrocarbons was formed. Its activity remained constant for several weeks. After removal from the reactor, not the slightest trace of a chemical or mechanical effect on the catalyst was found. On the basis of these extremely favorable properties, the experiments to convert aldehydes and ketones into amines were exclusively carried out with this catalyst. Only for the hydrogenating amination of isobutyraldehyde two other catalysts were tested.

Catalyst 68/2 This catalyst has the same composition as catalyst 118 but has been prepared in a different way (mixing of dry WcO₃ and NiCO₃ with subsequent sulphurization). This catalyst gave the same results as #118, except that at lower temperatures (220 - 240°C.) it gave somewhat lower yields.

Catalyst 1930 This catalyst is a copper-chromium-zinc catalyst of the composition 1 mole Cu:1 mole Cr:1 mole Zn. It is less active than the sulphurized nickel-tungsten catalyst. It only reacts at temperatures of 320 - 340°C. At these temperatures it converts aldehydes to amines only to 90%. It also has less mechanical strength and suffered a volume decrease of 40% in the experiment.

Experimental Part

At an operating pressure of 200 atm. (2,940 psig.) the conversion of isobutyraldehyde into isobutylamine was practically complete at temperatures above

200°C. (392°F.). The space velocity was 0.6. Provided that the temperature is kept below 320 - 340°C. (608 - 644°F.), only very small quantities of hydrocarbons are formed either by reduction or cracking.

The formation of primary amines in preference to secondary amines is controlled by temperature and ammonia concentration. At temperatures of 320 - 340°C. (608 - 644°F.), or in the presence of an excess of ammonia, the formation of primary amines is favored. Under these conditions 71 - 85% of primary amines are formed.

In a large-scale experiment a reactor of a length of about 5 feet was filled with 46 cubic inches of nickel-tungsten sulphide catalyst #118. With a space velocity varying from 0.6 - 1.2 and a molar ratio of aldehyde to ammonia of 1:28, 1:41 and 1:7 at temperatures ranging from 220 - 340°C. (428°F. - 644°F.), a conversion of 93 - 99% was reached yielding a product containing about 70% mono-isobutylamine, 25% diisobutylamine and 5% higher boiling substances.

From the heat of reaction which is 23.9 k cal. per mole, it has been calculated that at a ratio of 50 cc. formaldehyde : 1,000 liters of hydrogen and 1,000 liters of ammonia, the reaction can be carried out without the necessity of adding cold gas. When higher aldehydes or ketones are reacted the quantities of gas can be reduced corresponding to the higher molecular weight of these compounds, whereas the quantities of ammonia and hydrogen required for the reaction of lower molecular weight compounds, e. g., acetone, must be somewhat increased.

Isoamylamine

Isoamylamine was prepared analogous to isobutylamine at the following conditions: 80 cc. of nickel sulphide-tungsten sulphide catalyst #118, 50 cc. isoamylaldehyde, 300 cc. liquid ammonia, 300 liters fresh ammonia gas per hour, temperature 340°C. (644°F.). The pressure was the same as before. The amines obtained consisted of about 85% isoamylamine and 15% diisoamylamine.

Isohexylamine

The space velocity in these experiments was varied as compared to those previously established and it was found that up to a space velocity of 2 volumes of reaction gas per volume of catalyst per hour, the yield was still satisfactory. The yield in this case was 94% of amine calculated on the aldehyde charged. A further increase in the space velocity is not economical since it increases the quantity of heat of reaction to be dissipated. The throughput rate was found to be without effect on the ratio of primary to secondary amines which was solely controlled by the ammonia concentration. The temperature effect was similar to that found for isobutylamine, which means that with increasing temperatures the yield of primary amine increases. At 340°C. (644°F.) 78% primary and 16.4% secondary amines are formed, whereas at 260° (500°F.) 64.2% primary and 33.2% secondary amines were formed.

Isoheptylamine

The hydrogenating amination of isoheptylaldehyde proceeds analogous to the reactions previously described. At 340°C. (644°F.) 74.7% of primary isoheptylamine and 16.2% of secondary isoheptylamine are formed. At lower temperatures corresponding to the two previous experiments, the ratio shifts slightly toward the formation of secondary amines and at 220°C. (428°F.) 60.4% primary and 35.6% secondary amines are obtained.

Manufacture of Isopropylamine from Acetone

When acetone is passed at 300 - 320°C. (572 - 608°F.) at a pressure of 200 atm. (2,940 psig.) over the nickel sulphide-tungsten sulphide catalyst #118 in the presence of ammonia and hydrogen, and at a molar ratio of acetone, ammonia and hydrogen = 1 : 18 : 18, it appears as if 80 - 90% of monoisopropylamine had been formed.

If the analytical determination of monoisopropylamine is carried out by distillation instead of using the method of Briner and Goutillan, the yields are considerably smaller because condensation reactions of unknown nature occur with acetone in the method of B. and G. For the manufacture of monoisopropylamine on a somewhat larger scale the following method is best suited: 50 liters of acetone, 200 liters of liquid ammonia and 300 cubic meters of hydrogen are passed at 320°C. at 200 atm. over a nickel sulphide-tungsten sulphide catalyst with a space velocity of 1 calculated on liquid feed product. The reaction product is liquefied by cooling and the pressure reduced to 10 atm. At this pressure the excess ammonia is distilled off. After removal of the ammonia fractionation is continued at atmospheric pressure. The crude isopropylamine is further purified by distillation. In this way, yields of monoisopropylamine of about 50% based on the acetone reacted, are obtained. The remainder of the acetone is converted into higher boiling basic products of rather complex nature. Because of these side-reactions isopropylamine is comparatively expensive in spite of the easily available and cheap starting material.

2-Aminobutane from Methyl ethyl ketone

This amine has been made by passing 25 cc. of methyl ethyl ketone with 300 cc. of liquid ammonia and 300 liters of hydrogen per hour over the nickel sulphide-tungsten sulphide catalyst at 300°C.

Under these conditions 70% of the product were 2-aminobutane; the remaining 30% consisted to 50% of higher boiling products. Interference by side-reactions is less than in the case of acetone.

5-Methyl-2-aminooctane from 5-Methyloctanone-2

This amine was obtained by hydrogenating amination of the subject ketone under the following conditions: 80 cc. catalyst #118, 25 cc. of feed per hour, 300 cc. of ammonia, 300 liters of hydrogen at 300°C. The yield of distilled primary amine was 80%. The ketone serving as raw material is obtained by condensation of isohexylaldehyde with acetone, followed by hydrogenation of the olefine formed.

2,4-Dimethyl-3-aminopentane from isobutyronone

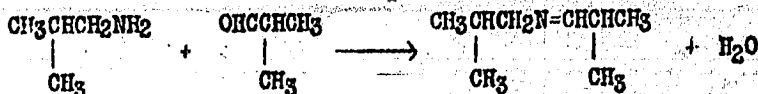
Isobutyronone (diisopropylketone) is obtained directly as one of the products of the isobutyl oil synthesis. If this ketone is passed over nickel sulphide-tungsten sulphide, together with ammonia and hydrogen at 320° and 200 atm. pressure, 2,4-dimethyl-3-aminopentane is obtained in a rather smooth reaction. The ratio of reagents used was 80 cc. of catalyst, 40 cc. isobutyronone, 400 liters hydrogen and 300 cc. of liquid ammonia.

Preparation of Secondary Amines

Since it is not possible to control the dehydrogenating amination of aldehydes and ketones in such a way that only secondary amines are obtained and

since the latter products are sometimes of commercial importance, a method for the manufacture of secondary amines was investigated.

The primarily-formed primary amine is condensed with aldehyde or ketons to a Schiff base according to the following equation:



The reaction product is then hydrogenated and subsequently converted into the secondary base. These reactions can be carried out either separately or simultaneously.

Secondary Amines by the 2-Stage Process

The following amines were prepared by this method: Diisobutylamine, di-n-propylamine, diisopropylamine, n-propylisobutylamine.

Diisobutylamine

The condensation of isobutyraldehyde with isobutylamine to the Schiff base takes place by simple mixing of equi-molecular amounts of the two components. Since the reaction takes place spontaneously with strong heat formation, it is advantageous to drop the aldehyde into the stirred amine and control the dropping speed so that the temperature of the reaction mass does not exceed 60 - 70°C. The same results are obtained when amine is dropped into aldehydes.

The water formed in the course of the reaction separates out as a lower layer. In order to keep the solubility of water in the reaction mass small, it is desirable to work with the lowest possible excess of aldehyde or amine. The Schiff base can be directly hydrogenated to diisobutylamine without further purification. The nickel tungsten-sulphide catalyst #118 is used for the hydrogenation of the Schiff base. Hydrogenation is carried out continuously at temperatures between 220 - 240°C. The hydrogenation of the base can be carried out with wide variations of the reaction conditions without affecting the conversion. At temperatures varying between 220° and 240°C. and pressures varying from 20 to 200 atm. always almost complete hydrogenation was obtained.

The heat of reaction for the hydrogenation was found to be 10.8 k cal. per mole. It was calculated that the temperature rises 21.7°C. when 500 liters of hydrogen are reacted with 38 grams of Schiff base so that this ratio probably can be used in commercial practice without the necessity of adding cold gas.

Di-n-propylamine

It was found that the reaction conditions which were used in the previous experiments could not be simply applied to the synthesis of di-n-propylamine.

It was found that when propylamine is reacted with the corresponding aldehyde, not only the expected Schiff base is formed, but further reaction of the isohexenylaldehyde with n-propylamine takes

place which decreases the yield of the desired product. It was found recently that the side reaction is suppressed if the propylamine used is completely free of secondary amines.

Diisopropylamine

Isopropylamine was reacted with acetone in an autoclave at 160°C. and the condensation product was subsequently hydrogenated at 200 atm. with catalyst #118 at 240°C. The reaction of acetone with n-propylamine can be carried out at room temperature very easily in contrast to the reaction of isopropylamine, which probably can be explained by the decreased reactivity of isopropylamine because of the neighboring methyl group.

n-Propylisobutylamine

This mixed secondary amine could be easily synthesized by preparing the Schiff base from n-propylamine and isobutyraldehyde and hydrogenating it at 220°C.

Secondary Amines by the 1-Stage Process

The experiments were carried out in such a way that the condensation to the Schiff base and hydrogenation were not carried out separately but that the reaction was carried out in the presence of hydrogen.

As an example, e. g., 20 cc. of aldehyde were passed over the nickel sulphide-tungsten sulphide catalyst together with 60 cc. of methylamine at a temperature of 180°C. and a pressure of 200 atm. using 200 liters of ammonia gas. The yield of secondary amine was, on the average, 95%. The entire water formed during the reaction is carried through the reactor and is separated by subsequent dehydration of the distillate.

Condensation of ketones with methylamine in the presence of hydrogen can be carried out in the same way.

Tertiary Amines

For the manufacture of tertiary amines the following possibilities are available:

1. The reaction of alcohols with dimethylamine,
2. The reaction of primary amines with dimethylether,
3. The reaction of chlorinated hydrocarbons with dimethylamine.

The yields obtained by reactions 1 and 2 are unsatisfactory because of the high temperatures required which result in the disproportionation of amine and ether and always give primary and secondary amines as by-products.

The third method is difficult because of the non-availability of pure chlorinated hydrocarbons with more than 3 carbon atoms.

A new method for the synthesis of tertiary amines was, however, found in the course of these investigations.

