SYNTHESES OF NITROGEN CONTAINING HETEROCYCLES
OVER COPPER CHROMITE

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The reactions of 1,2-diaminopropane, 1-amino-2-propanol, 1-amino-2-ethanol and N-(β-aminoethyl)-1,2-diaminoethane in the gas phase over copper chromite have been investigated with the objective of synthesising nitrogen containing heterocycles. At 240-360°C 1,2-diaminopropane gave principally methyl- and 2,5-dimethylpyrazine, whereas the basic reaction for 1-amino-2-propanol was dehydration to give 1-aminoethyl-2-methylaziridine (with a selectivity of up to 78%). The main cyclic product from the dehydration of 1-amino-2-ethanol was pyrazine, while piperazine was formed together with pyrazine from N-(β-aminoethyl)-1,2-diaminoethane.

Catalytic dehydration of aminoalcohols and deamination of polyamines is a suitable method for the synthesis of nitrogen containing heterocycles, in particular pyrazine bases and other 1,4-diazines [1]. For example, dehydration of 1-amino-2-propanol in a stream of hydrogen over calcium promoted copper chromite led to the selective formation of 2,5-dimethylpyrazine [2]. A considerable amount of 2,5-dimethylpiperazine was also obtained in the initial stages of the process in a reducing atmosphere. The objective of the present work was to study the conversions of 1-amino-2-propanol and, for comparison, some other polyfunctional amines — 1,2-aminopropane, 1-amino-2-ethanol, and diethylenetriamine (N-(β-aminoethyl)-1,2-diaminoethane) — with the same catalyst but not under reducing conditions.

![Graph](image-url)

Fig. 1. Dependence of product yields from passing 1-amino-2-propanol over Cu(CrO₂)₂ on the reaction temperature: 1) 1-aminoethyl-2-methylaziridine, 2) 1-amino-2-propanol, 3) ethanol, 4) methyamine, 5) 2,3,5-trimethylpyrazine, 6) methanol, 7) 2,5-dimethylypyrazine, 8) 2,5-dimethyl-3-ethylpyrazine, 9) methylypyrazine. Contact time 2 sec.
The variation with temperature of the composition of the reaction products from 1-amino-2-propanol passed over a calcium promoted copper chromite catalyst in a stream of air is shown in Fig. 1. The course of the reaction is very different from that carried out in the presence of hydrogen [2]. Unexpectedly pyrazine bases are formed in considerably smaller amounts, piperazine is not formed at all, and the yield of low molecular products is increased (methanol, methylamine, ethanol, isopropanol).

The principal reaction product is the compound C$_5$H$_{12}$N$_2$, molecular mass 100, which, according to the mass spectrum, most closely corresponds to 1-aminoethyl-2-methylaziridine. The following possible fragmentation is proposed on the established m/z for the fragments:

![Fragmentation Diagram]

This compound is unstable and underwent further reactions during isolation. Its synthesis has not been described in the literature although the preparation of aziridine and its derivatives by unimolecular cyclodehydration of aminoalcohols is well known (for references on the synthesis of aziridine from 1-amino-2-ethanol over oxide catalysts see [3]).