Synthesis of 2-(dimethylamino)ethanol by the hydrogenolysis of tris(2-hydroxyethyl)amine

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A new reaction for the selective hydrogenolysis of tris(2-hydroxyethyl)amine into 2-(dimethylamino)ethanol by molecular hydrogen over metallic palladium catalyst is disclosed.

2-(Dimethylamino)ethanol **1** is currently produced by the reaction of ethylene oxide and dimethylamine,[1] and is used mainly as an intermediate, especially in the production of pharmaceuticals, crop protective agents and flocculents. The compound is also important in the preparation of chemicals for the paper and leather industries.[2]

In the course of studying the catalytic amination of aminoethanols, we unexpectedly found a new hydrogenolysis reaction of tris(2-hydroxyethyl)amine **2** to give 2-(dimethylamino)ethanol **1**, using molecular hydrogen over metallic palladium catalyst.

Supported palladium and platinum catalysts were used for the reaction. Experiments were performed in a continuous plug-flow reactor system at atmospheric pressure and 250–350 °C. The catalyst (4.0 g) was loaded into a borosilicate glass reactor (id 15 mm) equipped with a thermocouple.

The results of the experiments with different catalysts are presented in Table 1. It can be seen that under the reaction conditions, all catalysts based on palladium transform tris(2-hydroxyethyl)amine **2** into 2-(dimethylamino)ethanol **1** with a yield of up to 80%, despite the catalyst and the reactor operation not being optimized. After 20 to 30 h on-stream the palladium catalysts maintained their initial catalytic activities and no tar and coke deposition on the catalyst bed were observed.

Table 1 Hydrogenolysis[a] of tris(2-hydroxyethyl)amine **2** to give 2-(dimethylamino)ethanol **1** and *N,N*-bis(2-hydroxyethyl)methylamine **3**

Catalyst	T/°C	Time on-stream/ h	Conversion (%)	Selectivity (mol%) **1**	Selectivity (mol%) **3**
2% Pd/Al_2O_3	290	5	99	82	0
2% Pd/Al_2O_3	290	30	99	83	0
0.5% Pd/Al_2O_3	290	5	98	63	18
0.5% Pd/Al_2O_3	290	20	98	63	17
0.5% Pt/Al_2O_3	320	5	12	7	21

[a] Flow rate (mmol h^{-1} g_{cat}^{-1}): TEA, 3.5; H_2, 40.

In the case of 0.5% Pd/Al_2O_3 catalyst, the intermediate compound *N,N*-bis(2-hydroxyethyl)methylamine **3** was observed in the trapped product. The intermediate compound is subsequently hydrogenated to 2-(dimethylamino)ethanol **1**. In comparison with palladium, the platinum had only slight catalytic activity and selectivity for the reaction.

Taking into account the product compositions, a balanced equation for the selective hydrogenolysis of tris-(2-hydroxyethyl)amine under the studied condition can be proposed [eqn. (1)]. A small amount of methanol was found in the ice-cooled trap, and carbon monoxide and methane were detected in the gas effluent from the trap. Therefore, it can be suggested that a large proportion of the coproduced methanol was further decomposed into carbon monoxide, hydrogen and methane.

$$\underset{\mathbf{2}}{N(CH_2CH_2OH)_3} + 2H_2 = \underset{\mathbf{1}}{Me_2NCH_2CH_2OH} + 2MeOH \qquad (1)$$

In conventional aminoethanol production *via* ethylene oxide amination, the $R_2N(CH_2CH_2OH):RN(CH_2CH_2OH)_2:N(CH_2CH_2OH)_3$ ratio is approximately 40:35:25. Demand for $R_2N(CH_2CH_2OH)$ and $RN(CH_2CH_2OH)_2$ is relatively large, but that for the triethanol derivative is small under the present market conditions, and disposal of the surplus is expensive. The hydrogenolysis reported in this communication can be utilized to recycle the excess tris(2-hydroxyethyl)amine to give the more valuable products.

References

1 Carbides and Chemicals Corporation, USP 1,904,013 (1927).
2 Rhom and Haas, Co., GP 1,929,581 (1970).

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