A GENERAL ROUTE FOR GAS-PHASE EPOXIDATION

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Introduction

Epoxides of interest on an industrial scale are especially propylene oxide (PO) and ethylene oxide (EO) with annual world-wide production capacities of approximately 5×10^6 tons each (1-3). In the future, an increasing market demand of these epoxides is expected. They are precursors for the production of polymers (polyesters, polyurethanes) or for solvents (glycols). For EO, there exists a well established direct formation route oxidizing ethylene by oxygen on a silver catalyst (1-3). For PO, however, this route does not work. Presently, PO is produced in complex processes either via the antiquated chlorohydrin route coupled with a large effluent load or via indirect oxidation routes (use of peracids or hydroperoxides) coupled with the formation of large amounts of co-products (2, 3). An attractive route seems to be the oxidation of propylene with H_2O_2 producing PO with high selectivity (> 90 %) and water in the presence of Titanium Silicalite (4). At present the H_2O_2 route is favored for the commercial process of the future (5). A further interesting route is the oxidation of propylene with O_2 / H_2 mixtures over supported nano-sized gold particles producing PO with high selectivity (> 99 %) but at very low propylene conversion (1 - 2 %) (6). Recently, results of an improved approach were reported describing a propylene conversion close to 10 % with a selectivity to PO better than 90 % (7).

In communications from this laboratory results of a novel route operating in the homogenous gas phase under low-pressure conditions are reported using O_3 as the oxidizing agent. Comprehensive investigations have been performed for propylene and ethylene epoxidation (8, 9). For a propylene conversion of 91.8 %, a selectivity to PO of 93.3 % was found. An optimal O_3 utilization of approximately 95 % (reacted propylene / initial O_3 = 0.95) was achieved by limiting the propylene conversion to 20 – 30 %. The epoxidation of ethylene yielded a selectivity to EO of 90 % and better in a wide range of conditions. The maximum formation rates of PO and EO measured were 3640 and 2870 g per hour and per liter of reaction volume, respectively. The usability of this approach was also shown for 1-butene, *iso*-butene, *trans*-butene, 1,3-butadiene, styrene, cyclohexene, allyl acetate, and methyl methacrylate (8, 10). In this paper results from the epoxidation of tetramethylethylene are presented.

Experimental

The experiments have been performed in a flow tube (length, 100 mm; inner diameter, 5 mm; quartz glass) at reduced pressure. O_3 and NO_2 were premixed in O_2 and the resulting mixture was added to the olefin at the entrance of a heated reaction zone (200 – 400 °C). NO_2 was chosen in a ~3-fold excess over O_3 for preventing the reaction of O_3 with the olefin. The residence time of the gas mixture in the reaction zone was in the order of 1 – 10 ms. At the outlet of the flow tube a gas cell was attached for FT-IR analysis of the olefin, the corresponding epoxide, carbonylic substances, CO_2, and nitrogen oxide containing species. Additionally, online GC-MS analysis of gas samples was carried out with special attention to the identification of byproducts.

Reaction Mechanism

The overall process can be described by the following sequence of reaction pathways. First, NO_2 is oxidized by O_3 producing nitrogen(V)-oxides via pathway (1). An excess of

$$NO_2 + O_3 \xrightarrow{(NO_2)} N(V)\text{-oxide} + O_2 \qquad (1)$$

NO_2 over O_3 was chosen (NO_2 / O_3 = 3 on a molar basis) for suppressing the reaction of residual O_3 with the olefin. The formed nitrogen(V)-oxides (NO_3, N_2O_5, N_2O_6 the dimer of NO_3) attack the olefin and transmit an O-atom producing the corresponding epoxide.
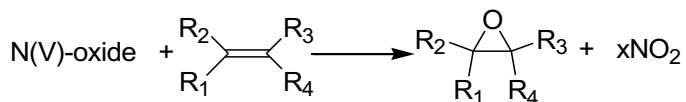
Up to now it is not clear what nitrogen(V)-species is most important for the epoxidation step. Furthermore, it is noteworthy that in the overall reaction no NO_2 is consumed.

Results and Discussion

Figure 1 shows experimental findings from the epoxidation of tetramethylethylene at a total pressure of 100 mbar. The feed consisted of 0.92 vol% of tetramethylethylene and 0.85 vol% O_3. The pressure gas was O_2 and the residence time of the gas mixture in the heated reaction zone was in the range 7.0 – 9.2 ms. The measured conversion of tetramethylethylene of > 99.9 % (200 – 275 °C) exceeded the expected value of 92 % according to the reaction mechanism given above. This behavior was already observed for 1,3-butadiene. Obviously, in the case of electron-rich olefins also other reactants than nitrogen(V)-oxides can attack the olefin leading to epoxides, at least partly. It can be speculated that this unknown reactant is a RO_2-type species.

The chemical nature of "R" as well as the source of this species is unknown. For temperatures above 275 °C there was a small decrease of tetramethylethylene conversion with

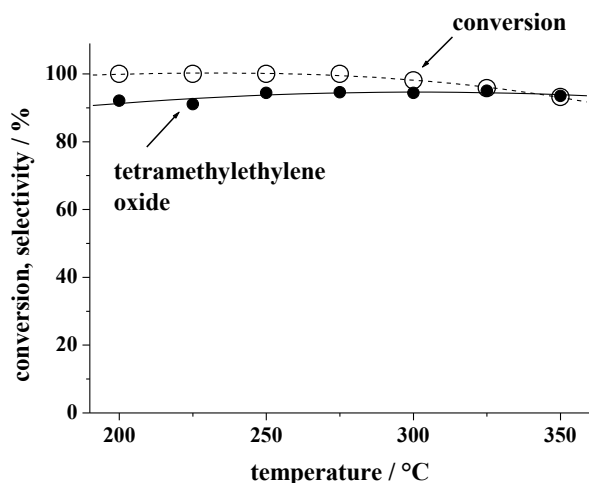increasing temperature yielding the expected conversion of 92 % at 350 °C.

Figure 1. Epoxidation of tetramethylethylene to tetramethylethylene oxide at 100 mbar. Feed: 0.92 vol% tetramethylethylene, 0.85 vol% O_3.

In the whole temperature range the selectivity to tetramethylethylene oxide was better than 90 % with a maximum value of ~ 95 % between 250 and 325 °C. Other products detected were acetone and pinacolone, cf. Figure 2. Acetone represents the oxidation product after cleavage of olefin's double bond. Pinacolone can arise from a competition step during oxidation or from the rearrangement of formed tetramethylethylene oxide. Organic products containing NO- or NO2-groups were not detected. The FT-IR signal for CO_2 was below the detection limit, i.e. the selectivity to CO_2 was < 0.2 %.
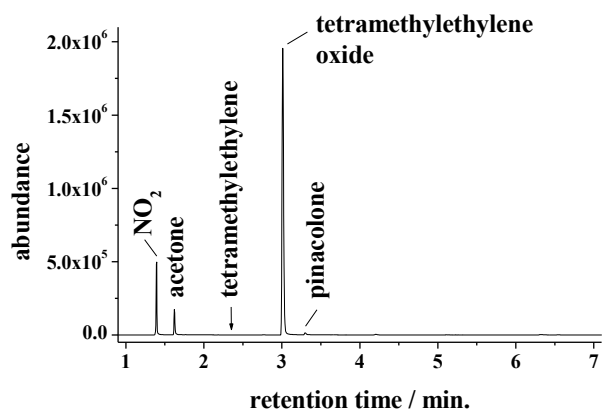

Figure 2. Result of the GC-MS analysis (35 – 200 amu) for the experiment at 200 °C are depicted in Figure 1.
For a selectivity to tetramethylethylene oxide of 95 % (total tetramethylethylene conversion) at 275 °C and a residence time of 7.6 ms a formation rate of tetramethylethylene oxide of 870 g per hour and per liter reaction volume follows. Especially shortening of the residence time as well as an

increase of the reactants in the feed can lead to an increase of the formation rate of the epoxide up to a factor of 10 without noticeable epoxide damage. Under conditions of a total pressure around 1000 mbar the selectivity to tetramethylethylene oxide is below 95 %.

Conclusions

A novel route for the epoxidation of olefins is presented proceeding in the homogeneous gas phase under low-pressure conditions. In this method, O_3 reacts with NO_2 and the resulting N(V)-oxides (NO_3, N_2O_5, N_2O_6) epoxidize the olefin forming finally the corresponding epoxide and NO_2. A selectivity up to 100 % as well as total conversion of the olefin are possible. This approach was tested in detail for the epoxidation of propylene and ethylene so far. For a series of other olefins the usability was shown.

In this paper experimental results for the epoxidation of tetramethylethylene are given. At a total pressure of 100 mbar (0.92 vol% tetramethylethylene, 0.85 vol% O_3) the selectivity to tetramethylethylene oxide was ~ 95 % between 250 and 325 °C. In the temperature range 200 – 275 °C the conversion of tetramethylethylene was > 99.9 %. Acetone and pinacolone were detected as the byproducts.

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