Catalyst-free Gas-phase Epoxidation of Alkenes

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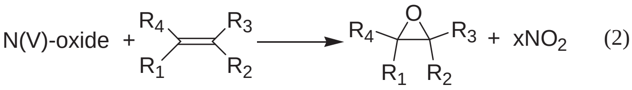
Butadiene, styrene, cyclohexene, allyl acetate, methyl methacrylate, and allyl alcohol were epoxidized in a gas-phase reaction in the absence of a catalyst. The applied oxidizing agent is ozone. With exception of allyl alcohol (selectivity to glycidol: 58%), the selectivity to the corresponding epoxide ranged from 88 to 97%. For acrylonitrile, there was no measureable conversion.

Epoxides are characterized by the highly reactive epoxy group caused by polarity and ring strain. This opens the possibility for a series of reactions frequently used in organic synthesis.[1] Generally, for the formation of epoxides several routes are applicable using percarboxylic acids,[2] hydroperoxides,[3] or hydrogen peroxide.[4] For the economically valuable ethylene oxide, a catalytic direct oxidation path exists with O_2 or air feed.[5] For propylene oxide, this approach does not work and at present complex multistep manufacturing processes are applied.[5]

In first communications from our laboratory, a novel route for the epoxidation of alkenes was presented proceeding in the homogeneous gas phase under low-pressure conditions.[6] 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 alkene forming finally the corresponding epoxide and NO_2. To date, it is not clear what the dominating N(V)-oxide is for the epoxidation process. In the course of the overall reaction, NO_2 is not consumed.

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



Using this synthesis route, ethylene, propylene, and butenes were epoxidized very efficiently with a selectivity to the epoxide of close to 100%.[6] Subject of this work is to find out whether this route is also useful for other alkenes (conjugated dienes, cyclic compounds, alkenes with polar groups) allowing a more generalized application for alkene's epoxidation in gas phase. In solution, a mixture of O_3 and NO_2 leads to a nitration of organics without epoxide formation.[7]

The experiments have been performed in a flow tube (length, 100 mm; inner diameter, 5 mm; quartz glass) at a total pressure of 10 mbar. O_3 and NO_2 were premixed and the resulting mixture was added to the alkene (diluted in He) at the entrance of the heated reaction zone (180–300 °C). NO_2 was chosen in a ≈5-fold excess over O_3 for preventing the reaction of O_3 with the alkene. The feed fraction of the alkenes was 1.3–1.6 vol % and the residence time of the gas mixture in the reaction zone was 8–16 ms. At the outlet of the flow tube a gas cell was attached for FT-IR analysis. Additionally, online GC–MS analysis of gas samples was carried out with special attention to the identification of by-products.

Table 1. Experimental findings for a temperature of 250 °C

Alkene	Alkene feed /vol %	Conversion /%	Selectivity to epoxide /%	By-products
Butadiene	1.4	28	97	Acrolein, furan
Styrene	1.3	22	91	Benzaldehyde
Cyclohexene	1.4	36	89	—
Allyl acetate	1.6	18	97	—
Methyl methacrylate	1.3	23	88	Methyl pyruvate
Allyl alcohol	1.4	15	58	Acrolein

In Table 1 a summary of the experimental finding is given.

For the epoxidation of butadiene, Figure 1 shows the conversion of the alkene and the selectivity to butadiene monoxide as a function of the reaction temperature for constant feed composition. Generally, a small temperature dependence of conversion and selectivity was observed in the investigated range of 180–300 °C. Butadiene monoxide was the only detected epoxide. There was no indication for the occurrence of the corresponding dioxide. The ratio of reacted butadiene/initial $O_3 = 1.0$ measured in the whole temperature range stands for an efficient utilization of O_3. Acrolein, furan (GC–MS), and traces of HNO_3 (FT-IR) were identified as by-products. The occurrence of acrolein indicates that in competition to pathway (2) carbonyl formation takes place after cleavage of the double bond. Carbonyl formation as a competing process with respect to epoxidation was already observed in former studies.[6] For the other by-product furan, from the mechanistic point of view, it can only be speculated how the ring closure occurs. In a few runs the feed composition was changed. The O_3/NO_2 feed was increased by a factor of 3.6 for a constant butadiene feed of 1.5 vol % resulting in an increase of the butadiene conversion from 28 to 76% at 250 °C. The selectivity to butadiene monoxide, however, dropped from 97 to 78% and the ratio of reacted butadiene/initial O_3 was ≈0.8. A further increase of the O_3/NO_2 feed by a factor of 1.7 (excess of O_3 over butadiene!) yielded a selectivity to butadiene monoxide of 67% for total conversion of butadiene. Obviously, under conditions of raised butadiene conversion, other reactions than the desired pathway (2) become more important. Probably, in a consecutive step the N(V)-oxide attacks butadiene monoxide resulting in a lowering of the selectivity to this product.

For styrene, cyclohexene, allyl acetate, and methyl methacrylate, temperature dependent measurements were carried out with an alkene conversion of 18–36%. The corresponding epoxides represented the main products with selectivities close to 100% under these conditions, cf. examples given in Table 1. By-products, if any detected, arose from the cleavage of the former double bond, i.e. benzaldehyde from styrene and methyl

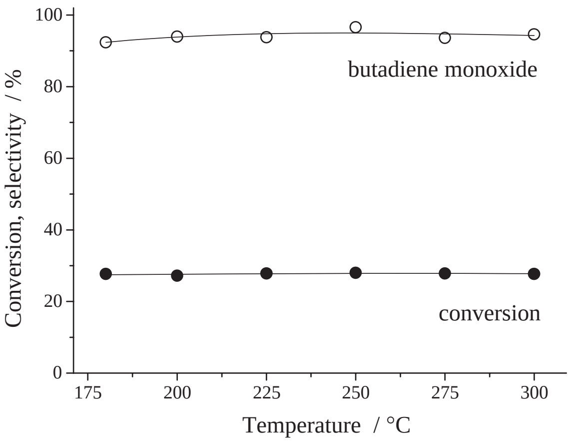


Figure 1. Temperature dependent data for butadiene conversion and selectivity to butadiene monoxide for constant feed composition.

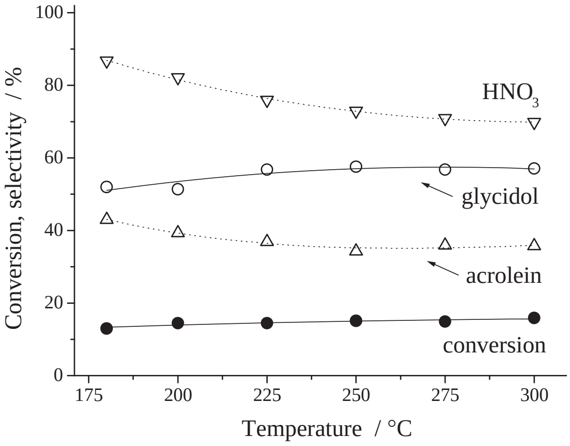


Figure 2. Temperature dependent data for the conversion of allyl alcohol and the selectivity to glycidol, acrolein, and HNO_3 for constant feed composition.

pyruvate from methyl methacrylate.

In the case of the epoxidation of allyl alcohol, acrolein and HNO_3 were detected in large amounts beside the main product glycidol, cf. Figure 2. It is noteworthy, that HNO_3 was twice as much as acrolein. Glycidol is a less stable product that tends to polymerize at higher temperatures or it decomposes.[8] Thermal decomposition of glycidol can be assumed for describing the formation of acrolein together with water. In a subsequent step, water can react with N_2O_5 (a possible N(V)-oxide) via $H_2O + N_2O_5 \rightarrow 2\ HNO_3$. On the other hand, the production of acrolein and water is also possible directly from the reaction of the N(V)-oxides with allyl alcohol in competition to the desired glycidol formation. The temperature dependence measurement, given in Figure 2, shows an increase of the selectivity to glycidol with increasing temperature. For acrolein, an inverse behavior was measured. If thermal decomposition of glycidol is responsible for the formation of acrolein, with increasing temperature a decrease of glycidol is expected contrary to the observation. That makes the direct pathway (in competition to glycidol formation) more likely than the consecutive reaction (thermal decomposition) of glycidol formed. The ratio of reacted allyl alcohol/initial O_3 was ≈ 0.55 pointing at N(V)-oxide consuming steps other than the epoxidation such as the reaction with water producing HNO_3.

In experiments with acrylonitrile, the amount of reacted alkene was too low for a reasonable determination of the conversion even for an increased acrylonitrile feed of 2.9 vol %. As a result of GC–MS analysis, two trace products were obtained. No endeavors have been made for identification.

In summary, the formation of epoxides from a series of alkenes was studied in the gas phase in the absence of a catalyst. A N(V)-oxide, produced in the reaction of O_3 with NO_2, served as the real oxidizing agent. For butadiene, styrene, cyclohexene, allyl acetate, and methyl methacrylate, the selectivity to the corresponding epoxide was 88–97% with an alkene conversion of 18–36%. Detected by-products were mainly carbonyls derived from the cleavage of the double bond attacked. For allyl alcohol, the selectivity to glycidol was distinctively lower (58%) caused by a competing/consecutive path leading to acrolein. The reactivity of acrylonitrile was found to be insufficient for a measurable reactant conversion.

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