Formation of 2-phenylethanol from styrene in the presence of zeolites and UV irradiation

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2-Phenylethanol is formed *via* an *in situ* multistep reaction by irradiation of styrene in the presence of silica–alumina compounds such as zeolites in aqueous and methanolic systems; the first step is presumably an oxidation.

The formation of anti-Markovnikov compounds by direct functionalization of olefins is of great interest for technical and synthetic applications. The Brown hydroboration–oxidation provides a useful tool to obtain the interesting products, but unfortunately this method is accompanied by disadvantages for its commercial application.[1–3] It is known that anti-Markovnikov addition can be achieved by the use of photosensitizers under photochemical reaction conditions, involving radical cations as intermediates.[4,5] It is also well known that zeolites are excellent hosts for photochemical reactions.[6–8] We tried to replace these photosensitizers by zeolites due to their known properties for the generation and stabilization of organic radicals adsorbed on their surface. Here we present some unexpected results pointing to an unusual combination of photochemical and thermal processes.

With regard to the work of Yates and Arnold we choose styrene as a model substance for our investigation.[9] By using EPR and UV spectroscopy we were able to show the formation of styrene radical cations on an H-ZSM-5 zeolite. The formation of this radical cation occurs, either in non-irradiated or in irradiated samples, equally as well in aqueous as in organic slurries of the zeolite with styrene. For the reaction we used the following reaction conditions: a 450 W mercury medium pressure lamp from Ace Glass, Inc., and quartz tube reactors with a magnetic stirrer placed beside the immersion lamp, while the reaction mixture is cooled by a centered cooling finger. In this reactor a mixture of typically 15 g water, 2 mmol styrene and 3 g of the zeolite was placed and irradiated for a period of 24 h at room temperature. After the reaction the mixture was centrifuged, the zeolite was separated and the fluid phase was extracted with Et_2O, then dried with Na_2SO_4 and, after evaporation of the solvent, analysed by gas chromatography. Instead of the zeolite a commercially available silica–alumina, Aldrich 34, 335–8 and CdS, ZnS and ZnO were used in other experiments. A 30 W D_2 lamp from Heraeus was also used as the irradiation source. In all cases the conversion was higher than 99%. In water the selectivity for 2-phenylethanol was 0.06% for H-ZSM-5 and 0.04% for SiO_2–Al_2O_3; for CdS, ZnS, ZnO or SiO_2 it was not detectable. But for H-ZSM-5 in MeOH the selectivity for 2-phenylethanol rises to 19.4%; methoxystyrene was not detected. Therefore we do not believe MeOH participates directly in this reaction and we regard this result as a proof for our proposed reaction mechanism (discussed below). Other by-products such as olefins, oligomers or alkylated styrene compounds were also not observed.

Although in the case of water as reaction medium the selectivity is negligible and more than 90% of the styrene reacts to form polymeric products, we tried to determine if direct addition of water in the anti-Markovnikov direction is the reason for the formation of 2-phenylethanol. By mass spectroscopy and cross checking experiments with the identified products, we identified the substances acting as intermediates in the reaction. Styrene is oxidized. This step is proved to be made possible by light below $\lambda \leqslant 290$ nm and we suspect the formation of superoxide radical anions and their reaction with styrene or the styrene radical cations. In the absence of the zeolite or silica–alumina under otherwise identical conditions no styrene oxide is found, but benzaldehyde is formed because of singlet oxygen formation. In the following step phenylacetaldehyde is formed *via* thermally or photochemically induced rearrangement of styrene oxide. The next steps are not clearly identified: possibly a decarbonylation and the formation of benzyl radicals take place, followed by a further reaction with formaldehyde or MeOH to give the corresponding alcohol. This could explain the drastically increased selectivity in the presence of MeOH. Nevertheless, the MeOH could act as an electron-donating reductant adsorbed on the surface. In this case the zeolite and the silica–alumina would show photo-semiconducting properties. A two-electron reduction of the phenylacetaldehyde would take place leading to 2-phenylethanol by *in situ* protonation. The assumed reaction steps are shown in Fig. 1.

The use of the deuterium lamp in our experiments increased the selectivity for 2-phenylethanol to 0.5% in aqueous systems. Due to the shorter reaction time of 6 h instead of 24 h in these experiments, the much lower overall irradiation energy, the specific spectra of both lamps and the absorption spectra of the organic and inorganic compounds, we assume the required wavelength to run the reaction to be *ca.* 210 nm. Although the spectra of styrene adsorbed on the zeolite shows a new broad absorption at $\lambda \approx 550$ nm, this absorption is not required for the reaction, as experiments with Pyrex reactors show. Other spectra with MeOH- or water-loaded zeolites showed no differences in the range $\lambda \leqslant 290$ nm that could be assigned to the creation of special electronic states too. Therefore we expect

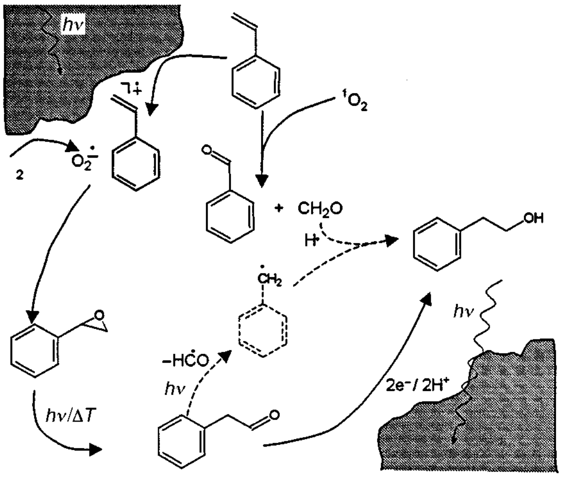

Fig. 1 Assumed reaction scheme for the formation of 2-phenylethanol from styrene.

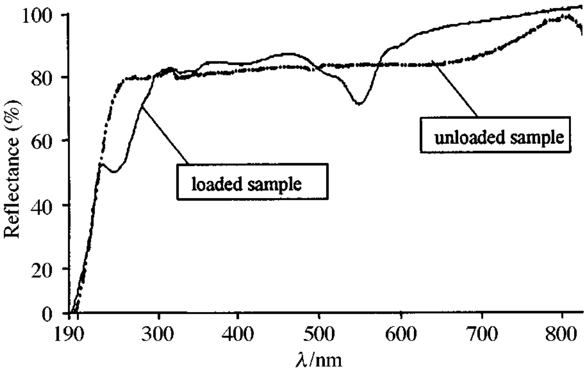

Fig. 2 UV–VIS reflectance spectra of the styrene loaded and unloaded zeolite H-ZSM-5.

the reaction to take place by direct excitation of the zeolite or the silica–alumina. Judging from the recorded spectra this is only possible by irradiation at $\lambda \leqslant 210$ nm. The spectra of preadsorbed styrene and without preadsorbtion of styrene are shown in Fig. 2. Experiments to obtain more reliable information and to run the reaction more selectively using UV lasers are planned. These would also enable us to carry out the kinetic studies which are currently lacking.

In conclusion, this is the first time, to the best of our knowledge, that the formation of 2-phenylethanol has occurred *via* the assumed reaction scheme, *i.e.* by a combination of the assumed thermal and photochemical steps *via* irradiation of styrene in the presence of silica–alumina and H-ZSM-5.

Furthermore, the substantial selectivity for the anti-Markovnikov product 2-phenylethanol under irradiation in the presence of H-ZSM-5 and MeOH is reported here for the first time.

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