

Autoxidation of Propene: The Effect of Surface

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The gas-phase autoxidation of propene is a promising route for the production of propene oxide,^{1,2} a key intermediate in the chemical industry. For this work, the system has been studied in detail in order to identify conditions for which the yield of propene oxide is maximised while still allowing a reasonable rate of reaction. To do this the reaction between propene and oxygen has been investigated over a range of temperatures, in reaction vessels of differing surface, and with varying proportions of propene and oxygen, to determine how these affect the rate of reaction and product yields.

It has previously been found that the temperature of the reaction has a large effect on the yield of propene oxide, with the selectivity increasing with decreasing temperature.³ However, reducing the temperature to increase epoxide yield has the obvious disadvantage of significantly reducing the rate of reaction. Therefore, if a lower reactor temperature were to be used to increase the yield of propene oxide, a method of increasing the overall rate of reaction needs to be found to allow a reasonable rate of epoxide production.

The effect on propene autoxidation of varying the surface of the reaction vessel was investigated in an attempt to obtain surface conditions which prevent the catalysed destruction of radical chain carriers, the loss of which slows the overall rate of reaction. Treating the surface with trimethoxymethane masks the silanol groups believed to be the catalytic sites on the surface of the glass reaction vessel, and indeed, this was found to increase significantly the rate of reaction without noticeably affecting the yield or type of products (Figure 1). This demonstrates that the dominant propagation reactions occur in the gas-phase and are not affected by the surface, while termination reactions on the wall can effectively be inhibited by removing or inactivating surface silanol groups.

Additionally, the reaction between propene and oxygen has been modelled by computer simulation, using an updated and improved reaction scheme that more accurately describes the formation of peroxides, which were monitored experimentally for this work. The reactions in this mechanism are fully reversible, and the effects of surface are simulated using first order reactions to represent either diffusion controlled or

convection controlled loss of radicals to the walls. These modifications extend the applicability of the previous model³ to ca. 600 K, and allow non-isothermal behaviour to be simulated.

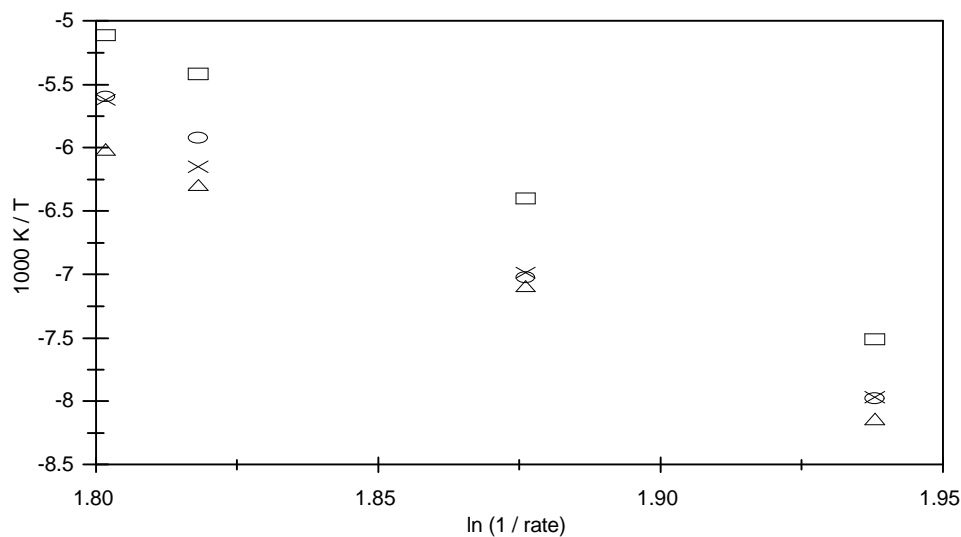


Figure 1. The effect of surface on the rate of reaction between propene and oxygen. □ = Pyrex protected with trimethoxymethane, × = Dehydrated Pyrex, ○ = Untreated Pyrex, △ = Pyrex coated with boric acid.

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- (2) Hayashi, T.; Han, L.-B.; Tsubota, S.; Haruta, M. *Ind. Eng. Chem. Res.* **1995**, *34*, 2298.
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