The oxychlorination of acetone

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SUMMARY

In the introduction of chapter 1 a brief outline is given of the applications of monochloroacetone in chemical industry. A number of preparative methods, all using chlorine as a raw material, is discussed. The main drawback of these processes is that apart from monochloroacetone equimolar amounts of hydrogen chloride are produced as a byproduct.
In the past this formation of HCl in chlorination processes has stimulated the development of the so-called oxychlorination processes for the production of chlorinated hydrocarbons. A well-known example of the processes is the oxychlorination of ethylene as a step in the manufacturing process of polyvinylchloride. Instead of chlorine HCl and O_2 are used as raw materials.
Chapter 2 gives a survey of the literature on the oxychlorination of acetone with $CuCl_2$ as a catalyst. For this reaction both a liquid phase and a heterogeneous gas phase process might be used.
The results of the kinetic investigation of the liquid phase oxychlorination are given in chapter 3. A rate equation is derived which gives a quantitative description of the influence of the HCl and the $CuCl_2$ concentrations on the rate of the reaction between acetone and $CuCl_2$. With this reaction model an apparent contradiction in literature regarding the effect of HCl on the reaction rate could be explained. For the influences of the concentrations of CuCl, LiCl, acetone and water qualitative explanations are given which are in agreement with the information from literature.

A fully quantitative description of the liquid phase oxychlorination of acetone only seems possible after the determination of the concentrations of the various copper complexes which are believed to exist in the reaction medium.

Chapter 4 gives a description of a number of preliminary experiments on the heterogeneous gas phase oxychlorination, which led to the choice of a catalyst and to the specifications for the design of a reactor for the kinetic investigation.

In chapter 5 a detailed description is given of the reactor design. Special attention is devoted to the effect of the dimensions of the reactor and of the catalyst particles on the temperature and concentration gradients occurring in the catalyst bed. Finally a so-called continuous stirred gas solid reactor is chosen for the systematic kinetic investigation. The catalyst bed in the reactor is situated in the annular space between two concentric tubes. This geometry enables the use of a small wall-to-wall distance at a freely chosen cross sectional area.

Chapter 6 gives the results of the systematic kinetic investigation. A kinetic model is derived for a catalyst, whose composition changes with changing gas phase conditions. It proves that water plays a crucial role in the oxychlorination process. At relatively low water partial pressures hysteresis occurs, for which a qualitative explanation is given. At water partial pressures of about 0.4 atm. the reaction rate becomes zero order in p_{H_2O}. At high HCl conversions its rate of conversion is limited by the rate of diffusion in the pores of the catalyst.

Based on the kinetic model for a catalyst of changing composition a rate equation is derived which quantitatively describes the effect of the acetone and the oxygen partial pressures on the oxychlorination rate.
Finally it is concluded that the gas phase oxychlorination of acetone offers an attractive alternative for the processes mentioned in chapter 1.