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The chlorination of cyclopentanone and cyclohexanone

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SUMMARY

Chlorinated ketones are useful intermediates in the synthesis of various organic products. Alicyclic five- and six-membered rings with a carbonyl group play an important role in the synthesis of compounds based on natural products. Chlorination of ketones are substitution reactions in which one, or more, hydrogen atom of the α -carbon atoms is replaced by chlorine. During the reaction hydrogen chloride is formed, which acts as a catalyst; therefore these reactions have an autocatalytic nature. Because there is more than one reactive hydrogen atom at the α -carbon atoms these reactions show a low selectivity to the monochloro product. Parallel with the chlorination reaction, an undesired acid catalyzed aldol condensation of the parent ketone takes place. Chlorinations on an industrial scale are mostly carried out in carbontetrachloride as solvent, its attractive properties being its inertness, the high solubility of starting material and product, and its relatively low atmospheric boiling point.

In this thesis the results of an investigation of the chlorination of cyclopentanone and cyclohexanone in the solvent carbontetrachloride and catalyzed by hydrogen chloride are described. Although the halogenation of aliphatic ketones in aqueous solvents is one of the most studied subjects of physical organic chemistry, no detailed information is available as to the chlorination in apolar aprotic solvents. In Chapter 2 the mechanism of the chlorination of ketones in polar solvent is described as presented in the literature.

Chapter 3 contains the results of an investigation of the kinetics of the chlorination of cyclopentanone and cyclohexanone and their monohalogenated products catalyzed by hydrogen chloride in carbontetrachloride. Some of the results are:

- the kinetic order in chlorine is zero,
- the kinetic order in hydrogen chloride is approximately one,
- the kinetic order in ketone and monochloro ketone depends on the ketone concentration, and varies from almost 2 at low to 1 at higher ketone concentrations.

Measurements of the kinetic isotope effects show that this variation cannot be explained by a change in the rate limiting step. The variation in the order of the ketone can excellently be explained by a self-association of the polar ketones in the apolar solvent. The value of the association constant could be determined by measuring the freezing point depression of solutions of cyclo-

pentanone in carbontetrachloride. The kinetic model as developed for the chlorination of the unsubstituted ketones can also be used for the chlorination of the monochloro ketones.

In the reaction mechanism the hydrogen chloride acts as an acid catalyst, and the ketone both as a base catalyst and as a substrate. This holds for the parent ketone as well as for the monochlorinated ketone. The unsubstituted ketone also reacts as a base catalyst in the consecutive chlorination of the monochloro compound. The contribution of this reaction determines to a large extent the selectivity of the chlorination to the monochloro ketone. Furthermore, it could be established that, even at low fractional conversions of the parent ketone, the three possible isomeric dichloro compounds are already formed. At fractional conversions as low as 5% of the ketone the selectivity to the monochloro compound does not exceed 86% in the chlorination of cyclopentanone and 81% in the chlorination of cyclohexanone. This is caused by a very rapid chlorination of the monochloro product by a hitherto still little understood mechanism.

Chapter 3 also contains the kinetics of the aldol condensation of the ketones catalyzed by hydrogen chloride. The order in hydrogen chloride is 2 and in ketone 1.5. Cyclohexanone appears to be much more reactive than cyclopentanone in the aldol condensation.

In an industrial reactor, the chlorine will be added as a gaseous component. The product hydrogen chloride usually is poorly soluble and will desorb. Before the chlorine can react in the liquid it has to be transferred from the gas to the liquid phase. The rate of absorption can be enhanced by a chemical reaction relative to the rate of purely physical absorption.

In Chapter 4 the influence of an autocatalytic reaction with simultaneous desorption of the catalyst on the absorption of a gaseous reactant is described. Calculations carried out using both the penetration and the film model showed that due to this type of reaction the absorption rate can be twice as high as due to the corresponding reaction without auto-catalysis. This is mainly caused by the locally high concentration of the catalyst in the reaction zone. Experiments carried out on the chlorination of cyclohexanone in a stirred cell confirm the calculated enhancement of the absorption rate.

In Chapter 5 the experimental results of the chlorination in some gas-liquid reactors are described. The chlorination is carried out in a trickle bed reactor, with gas and liquid in concurrent downward flow, both in the gas continuous and the pulsing flow regimes, and in a mechanically stirred gas-liquid contactor. Using the kinetic results as presented in Chapter 3, computer

calculations were carried out to compare the results of the calculations with the experimental ones. The results of the calculations are compared with the experimental ones in the trickle bed reactor and in the gas continuous flow regime. In the trickle bed reactor the results are 5-8% higher than predicted. In the gas continuous flow regime the choice of a suitable reactor is found to restrict the

calculations were carried out for these reactor types. The calculated values of the selectivity to the monochloro compound are in reasonable agreement with the experimental ones. It should be mentioned, however, that for the experiments in the trickle bed reactor, the calculated selectivities in the gas continuous flow regime are closer to the experimental values than in the pulsing flow regime. In the latter regime the experimental selectivities are 5-8% higher than predicted. Finally, some considerations are given concerning the choice of a suitable reactor system for the production of 2-chlorocyclopentanone on an industrial scale. The production of large quantities of heat is found to restrict the possibilities seriously.