The chlorination of cyclopentanone and cyclohexanone

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Publication date:
1980

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Maatman, H. (1980). *The chlorination of cyclopentanone and cyclohexanone* s.n.

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 apolair 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 apolair 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 mono-
chloro 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 cyclopenta-
none in the aldol condensation.

In an industrial reactor, the chlorine will be added as a gaseous compo-
nent. 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 carrie
of the selectivity to th
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5-8% higher than predict
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is found to restrict the

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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-chlorocyclo-
pentanone on an industrial scale. The production of large quantities of heat
is found to restrict the possibilities seriously.