Some aspects of the chlorination of benzene

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This thesis describes some aspects of the chlorination of benzene into monochlorobenzene. The greater part of all industrially produced monochlorobenzene is made by means of the chlorination of liquid benzene. In this process iron trichloride is used as a catalyst. This is formed in the reactor by reaction of chlorine with iron rings. The lower the chlorination rate is, the smaller the percentage of higher chlorinated benzenes will be.

It is a commonly accepted fact that the materials used in the industrial process have to be very carefully dried in order to ensure a satisfactory conversion rate. It has appeared from laboratory research, on the other hand, that small traces of water speed up this kind of reaction. We expected, therefore, that the best reaction rate might be obtained somewhere in the range of very low concentrations of water.

It was our main intention to try and determine quantitatively this influence of traces of water on the reaction rate. We also wanted to gain a better insight into the several process steps appearing in the absorption of chlorine from the gas into the liquid phase and in the desorption of hydrochloric acid the other way round.

In order to understand this complex reaction system it was absolutely essential to analyse the kinetics of the chlorination reaction carried out in a homogeneous liquid phase consisting of reaction components. We used iron trichloride and iodine as catalysts. Although not applied industrially, iodine has been analysed because we were looking for a catalyst the activity of which is not affected by traces of water.

The kinetic analysis made by other scientists have either produced contradictory results or are of little use to us because the mixture of benzene and monochlorobenzene was not employed as a solvent.

The kinetic relations described in chapter three have been determined either by measuring the decrease of the chlorine concentration with time, or by measuring the rise in temperature in a small, stirred reactor, well isolated and continuously fed. It is possible to keep the quality of the
catalyst constant using this reactor for the analysis of the catalytic activity of iron trichloride; more so, in fact, than in a (semi-) batchwise operated reactor. We determined for both catalysts to what extent the chlorination rates depend on the concentration of the components taking part in the reaction.

The reaction rates measured when using iron trichloride can be explained by assuming that a monocomplex of iron trichloride and water is the catalytically active compound. The part of iron trichloride present as the monocomplex is largest when the molecular ratio of water and iron trichloride is one. When this ratio increases the catalytic activity will go down rapidly because the monocomplex will be converted into higher hydrates.

This assertion is closely bound up with, and is supported by, the evidence found by determining part of the phase diagram B-FeCl₃-H₂O-HCl. It appeared that only the monocomplex is properly soluble in benzene. The higher hydrates, on the other hand, are almost completely insoluble, although their solubility is increased when hydrochloric acid is present. We see, therefore, that a small trace of water is essential for the preparation of a catalytically active solution of iron trichloride. Only too easily, however, so much water may be drawn from the air or otherwise that higher hydrates of iron trichloride will precipitate (the so-called "poisoning" of the catalyst).

We are now in a position as a result of the researches done, to prepare catalyst solutions of reproducible activity and to predict, fairly accurately, the chlorination rate when using iron trichloride as a catalyst.

We have not been able to demonstrate the mutual dependence of chlorination rates and the quantities of water in the reaction medium when iodine was used. A compound of iodine and chlorine, most probably ICl formed in an equilibrium reaction, is the active part of the catalyst. In mixtures of benzene and monochlorobenzene the chlorination rate of benzene is higher than in pure benzene.

Both kinds of catalyst have been employed when we carried out the chlorination reaction in a bubble column, cf. Chapter 4. Gaseous chlorine is added to this type of reactor and it has to dissolve into the liquid phase to get the reaction started. Hydrochloric acid formed during the reaction desorbs from the reaction medium.
When we add iron trichloride catalyst as a solution to the bubble column, the reactor can be manipulated in such a way (by drying the added benzene with the gaseous hydrochloric acid) that only the water combined with the iron trichloride remains in the reaction medium. Great catalytic activity is achieved in this way. The conversion rates measured seem to be higher than those predicted in the kinetic relations. The confidence intervals of the two measurements overlap however. When, in the bubble column, the catalyst is formed from iron rings in the reactor itself, as is the case in the industrial production, the phenomena then observed can almost completely be explained by means of the kinetic relations and the knowledge obtained by determining part of the phase diagram $\text{B-FeCl}_3-\text{H}_2\text{O-HCl}$.

As the reaction system in the bubble column is practically the same as the one used in industry, it is now possible to explain the catalyst formation and the dependence of the chlorination rate on traces of water in the latter. When iodine is used as a catalyst in the bubble column the actual reaction rates appear to be about five times as high as the ones predicted from the kinetic measurements. No simple explanation can be offered for this discrepancy. The solubility of chlorine in benzene saturated with hydrochloric acid appears to be at least twice the solubility, known from the literature on the subject, in benzene containing no hydrochloric acid.

When chlorine is absorbed the hydrochloric acid which desorbs and the evaporating benzene may very probably cause gas phase resistance. The cooperation of the mixing in the liquid phase and the chemical reaction is an unknown factor. It is impossible, because of these three factors, to determine from the measured quantities the mass transfer coefficients of absorption of chlorine into benzene.

More work has to be devoted to each of these three points.

Generally the reaction components are separated in one or more distillation columns in order to obtain pure monochlorobenzene. In the rectifying chlorination, as described in Chapter 5, reaction and distillation are concentrated in one apparatus. We checked the usefulness of this procedure in the chlorinations carried out in distillation columns. Over the chlorine supply, about halfway the column, the chlorination reaction takes place. Benzene and monochlorobenzene are separated in the bottom half of the column, the stripper.
Due to the fact that there is a minimum heteroazeotrope for benzene and water, the ever present traces of water gather at the top of the column. It is indispensable for satisfactory, reproducible catalyst formation that there are iron rings just beneath the top cooler.

Both when iron trichloride is added as a solution in benzene and when it is formed in the column from iron rings, decomposition reactions will take place in the stripper and a larger quantity of dichlorobenzene will consequently be formed. When iodine is added as a catalyst it reacts with the chlorine present giving iodochlorine. This component has a volatility somewhere between those of benzene and monochlorobenzene and accumulates therefore at a given height in the column. This is a suspended catalyst. Unfortunately, however, the application of iodine entails the formation of considerable quantities of by-products. The bottom product contained so much iodine that it doesn't seem feasible to maintain the chlorination reaction with iodine for a longer period with only one dose of catalyst.

To apply the rectifying chlorination with any success it is therefore necessary to find a catalyst having its boiling point near the one of benzene, giving no equilibrium reaction with chlorine and which is preferable not susceptible to traces of water.

In the final chapter considerations on the choice of a reactor for industrial use are elaborated into a design for a reactor; a limited number of boundary conditions were taken into account. This design, a bubble column, appears to agree reasonably well with the reactor developed empirically in industry.