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Note

Influence of atmosphere on the reactivity of nitro compounds[1]

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Abstract

Chloronitrobenzene can react with alkaline alcohol in two directions depending on the chemical conditions: substitution and reduction. The hazardous potential of the latter is caused by an autocatalysis. We investigated calorimetrically the reaction conditions under which the harmless substitution turns into reduction. The influence of the oxygen content of the atmosphere on the overturn to reduction demonstrated that it will be shifted back with increasing oxygen.

Keywords: *o*-Chloronitrobenzene; Substitution; Reduction; Atmosphere; Hazard

The interaction of *o*-chloronitrobenzene (*o*-CNB) with an alkaline solution of alcohol is complicated by two ways of reaction: substitution giving alkoxy compounds, i.e. ether and autocatalytic reduction of the nitro group with some intermediates. The decision for one of these reactions or for a combination of both depends on the choice of five parameters. The last reaction was the cause of a hazardous event in a chemical plant. Fig. 1 shows schematically the reaction mechanism [1–3]. In the case of substitution, one main product occurs. This is ethoxynitrobenzene, *i*-propoxynitrobenzene and *n*-propoxynitrobenzene, respectively, which are often introduced as adducts for further chemical processes. If one changes the parameters given below the substitution branch will be removed and transition to the reduction will be favoured. The reduction is a fast autocatalytic process accompanied by temperature jumps up to 30 K. The mechanism of this reaction is more complicated than that of substitution. Reduction and consecutive processes occur

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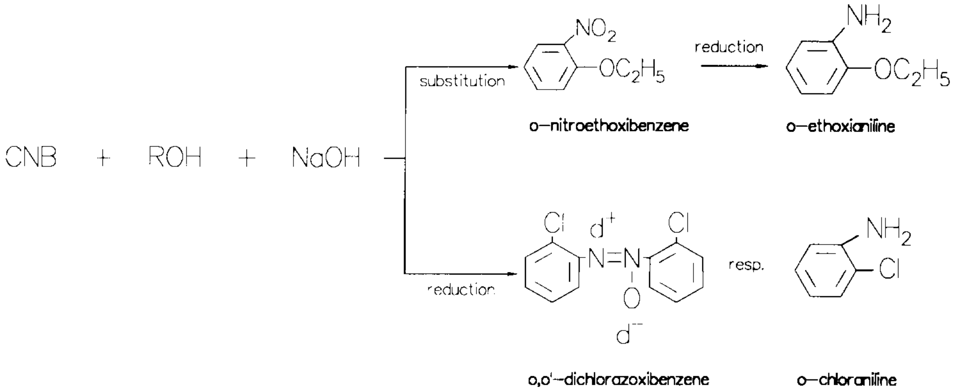

Fig. 1. Simplified scheme of the reaction of *o*-CNB with alkaline alcohol.

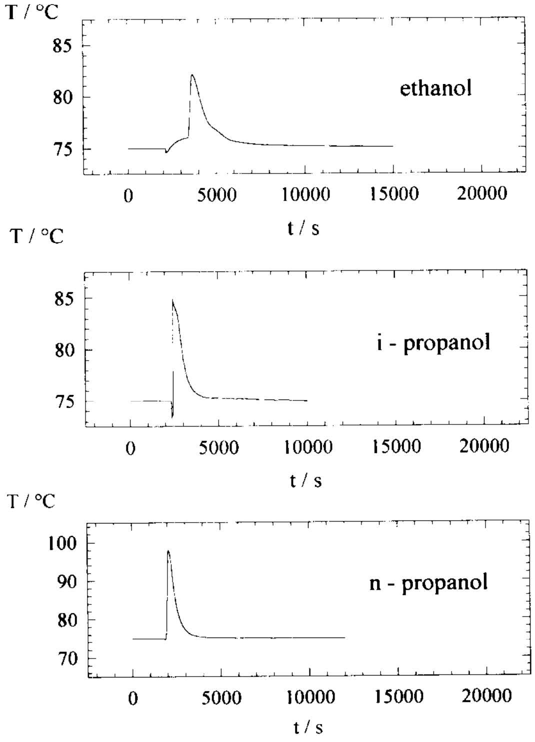

Fig. 2. Comparison of the influence of the alcohol on the reaction course of the experiment at 75°C in still air. $c_0(\text{NaOH}) = 0.980$ mol l^{-1}, $c_0(o\text{-CNB}) = 0.408$ mol l^{-1}.

simultaneously, leading to several products, for instance dichloroazoxybenzene and chloraniline.

The question was to find the conditions under which substitution changes into reduction, from the following varying parameters:

(1) initial concentration of *o*-CNB;
(2) kind (sodium/potassium hydroxide) and initial concentration of alkalihydroxide;
(3) kind of alcohol (ethanol, *i*-propanol, *n*-propanol);
(4) initial temperature;
(5) composition of atmosphere and its flow conditions.

During the calorimetric measurements, some regularities were recognizable. An increase of the initial concentration strengthens reduction and lowers the portion of the substitution.

Comparing the effect of potassium/sodium hydroxide, in the presence of sodium hydroxide, CNB is more reactive.

The difference in the behaviour of the reaction depending on the kind of alcohol is shown clearly in Fig. 2. In the same reaction mixture, only the alcohol was changed from ethanol to *i*-propanol. The latter gave a growing reduction rate and temperature, while substitution could only be observed for a few seconds. This time is shorter for *n*-propanol and the temperature jump for reduction increased to the highest level.

At temperatures below 75°C only substitution could be observed. For temperature increases up to 92°C the reduction can still take place with low initial concentrations of CNB and alkaline hydroxide.

The last parameter we investigated was the composition of the atmosphere and its flow conditions and its effect on the reaction mechanism. Therefore we studied two reac-

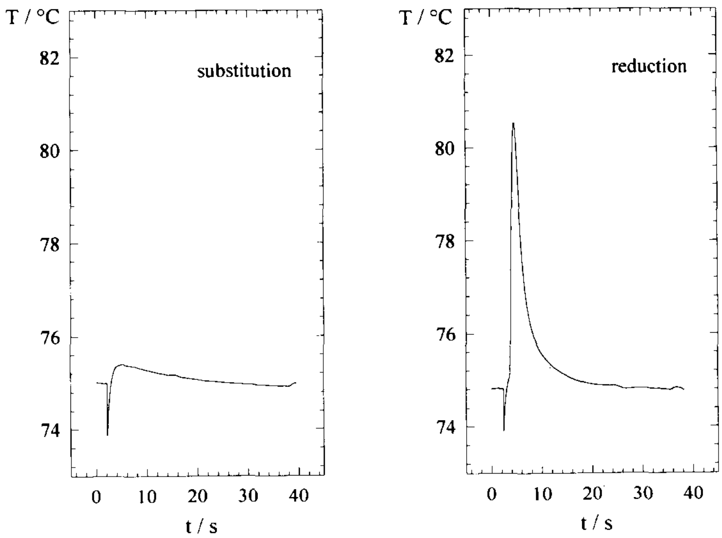

Fig. 3. Typical temperature–time courses of reaction mixtures for substitution and reduction at 75°C in *n*-propanol and still air. c_0(*o*-CNB) = 0.408 mol l^{-1}; c_0(NaOH) = 0.519 mol l^{-1}; c_0(NaOH) = 0.538 mol l^{-1}.

tion mixtures under the following conditions in *n*-propanol at 75°C in still air:

(1) $c(o\text{-CNB}) = 0.408\ \text{mol l}^{-1}$;

(2) $c(\text{sodium hydroxide}) = 0.519$ mol/l (substitution), = 0.538 mol/l (reduction).

The results are shown in Fig. 3, which unequivocally demonstrates the influence of the initial concentration of sodium hydroxide on the course of the reaction. An artificial atmosphere was prepared by stepwise increase of oxygen in pure argon. This gas mixture flowed through the reaction chamber at a rate of 0.6 ml min^{-1}.

The calorimeter we used was built up of a thermostated double wall glass reactor for the first component, i.e. solution of sodium hydroxide in alcohol. It was equipped with a platin sensor, one gas tube inlet for the atmosphere and one connection tube to the vessel, in which the second component was thermostated. The temperature–time course was measured using an electronic device of the automatic calorimeter ACTRON 4.3 [4] and the data accumulated on a personal computer.

We found for the substitution experiment with $c = 0.519\ \text{mol l}^{-1}$ that the reduction only takes place in an argon atmosphere with two or less percent oxygen (Fig. 4). Examining the second reaction mixture, substitution was observed exclusively if an argon atmosphere with four or more percent oxygen was applied.

In further tests, it could be shown that an increase of oxygen in an argon atmosphere increases the portion of substitution and decreases that of unwanted reduction.

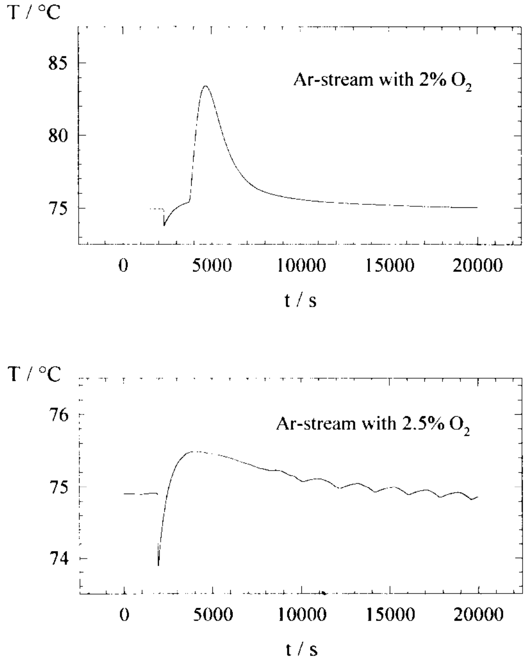

Fig. 4. Comparison of the influence of two different atmospheres on the reaction course of the substitution experiment at 75°C in *n*-propanol. $c_0(\text{NaOH}) = 0.519\ \text{mol l}^{-1}$; $c_0(o\text{-CNB}) = 0.408\ \text{mol l}^{-1}$.

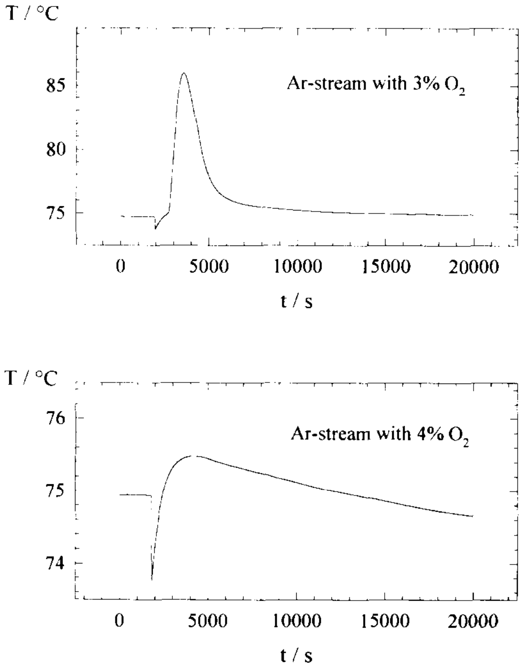

Fig. 5. Comparison of the influence of two different atmospheres on the reaction course of the reduction experiment at 75°C in *n*-propanol. $c_0(\mathrm{NaOH}) = 0.538$ mol l^{-1}; $c_0(o\text{-CNB}) = 0.408$ mol l^{-1}.

For the kinetic evaluation it is desirable to know the concentration–time course for CNB and the reaction products: in the case of substitution, alkoxynitrobenzene and in the case of reduction, dichloroalkoxybenzene and chloronitroaniline. HPLC enabled us to confirm the presence of two reaction mechanisms: substitution and reduction. It could be shown that the turnover of CNB in the substitution reaction is less than that in the reduction reaction. Thus, substitution leads only to one main product in contrast to reduction.

Quantitative results of the kinetic evaluation will be published soon. They were obtained by application of our method of non-linear optimization [5].

The calorimeter has proved to be a useful instrument for the investigation of chemical reactions.

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