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Controlling factors in the ruthenium-catalyzed oxidation of primary alcohols with sodium bromate

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Abstract

The homogeneous transition metal-catalyzed oxidation of alcohols via aldehydes to carboxylic acids has been investigated in detail. Special attention was focussed on the influence of the experimental conditions on the outcome of the reaction. In the oxidation of 1-octanol with sodium bromate and the catalyst rutheniumtrichloride even under mild reaction conditions (at 40 °C for 90 min) there is almost quantitative conversion. By directing the reaction by choice of the amount of the oxidizing agent, either 1-octanal or caprylic acid could be obtained in yields of 90%. Similar results were obtained with longer chain alcohols, demonstrating the general applicability of the approach.

Introduction

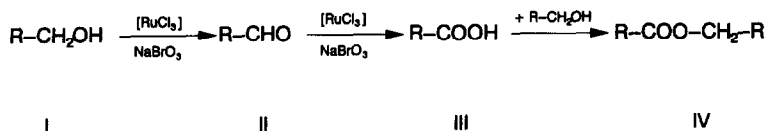
Catalytic oxidation is an important reaction in organic synthesis [1,2]. Homogeneous oxidation catalysts are used today even on the large industrial scale, for instance in the palladium/copper catalyzed Wacker oxidation of ethene to acetaldehyde.

Another oxidation reaction that is also of commercial importance is the homogeneously-catalyzed conversion of alcohols into aldehydes or carboxylic acids. This reaction can be performed under very mild conditions in the presence of ruthenium catalysts [3–10]. One effective oxidation agent is sodium bromate [6,11–12], which was used, for sample by Kanemoto et al. in the oxidation of primary alcohols to aldehydes and secondary alcohols to ketones.

We report here our systematic investigations of the ruthenium-catalyzed oxidation reaction of primary alcohols to aldehydes and of the latter to carboxylic acids. With 1-octanol as the model alcohol, we have examined the possibility of controlling the oxidation by varying the temperature, reaction time, amount of oxidation agent and the catalyst, and the pH of the mixture. The results are compared with those for the oxidation of 1-dodecanol, 1-hexadecanol and 2-hexyl-1-decanol.

Results and discussion

The ruthenium-catalyzed oxidation of primary alcohols yields aldehydes in the first step and carboxylic acids in the second step. In a subsequent reaction esters can be formed by reaction of the acid with unchanged alcohol (Scheme 1).



Scheme 1. Reaction scheme.

All our investigations involved a system in which the reaction took place in a two-phase system consisting of an aqueous $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ -buffer solution (pH 10) and an organic phase containing either methylene chloride or 1,2-dichloroethane depending on the reaction temperature required. To prepare the catalytic active species ruthenium trichloride trihydrate and the oxidizing agent sodium bromate were added to the reaction system, which was then stirred for some minutes at room temperature. After this catalyst preactivation the two-phase system was heated or cooled to the desired reaction temperature (0 to 70 °C), and 1-octanol was added, diluted with one of the solvents mentioned above. The kinetics of the oxidation were then monitored for up to 9 h.

a. Product control by variation of the reaction temperature

Figure 1 shows a plot of the extent of conversion of 1-octanol and of the yield of the various products octanal, caprylic acid, and octyl caprylate described in dependence of the reaction temperature.

Remarkably the oxidation was found to proceed even at a reaction temperature of 0 °C: the aldehyde was formed in 12% yield with high selectivity, and no caprylic acid was observed. When the temperature was raised the alcohol conversion and yield of aldehyde increased until the yield of octanal reached a maximum of 80% at a temperature of about 40 °C. Between 40 and 70 °C the alcohol conversion was

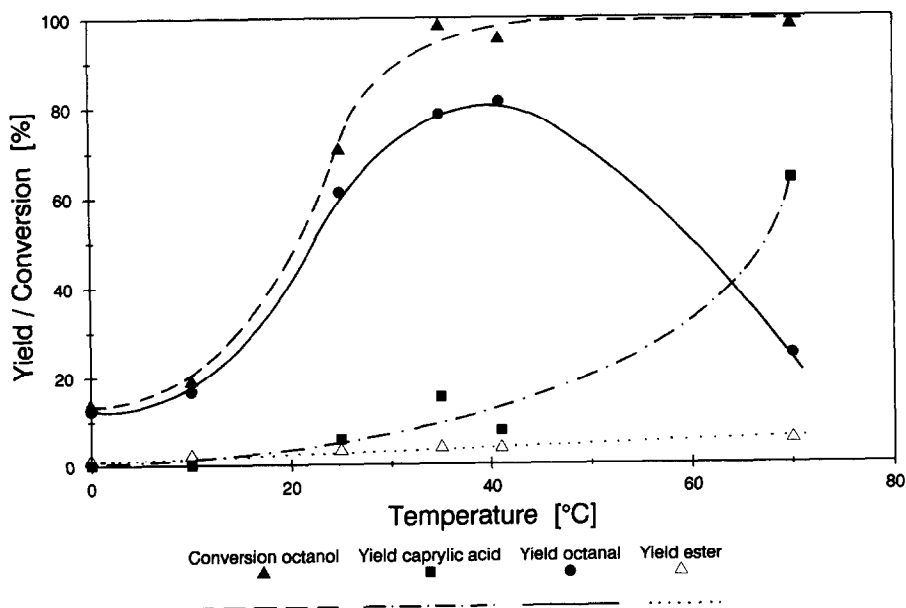


Fig. 1. Oxidation of 1-octanol: Influence of reaction temperature ($t = 90$ min; molar ratio octanol/ $\text{NaBrO}_3/\text{RuCl}_3 = 25/25/1$).

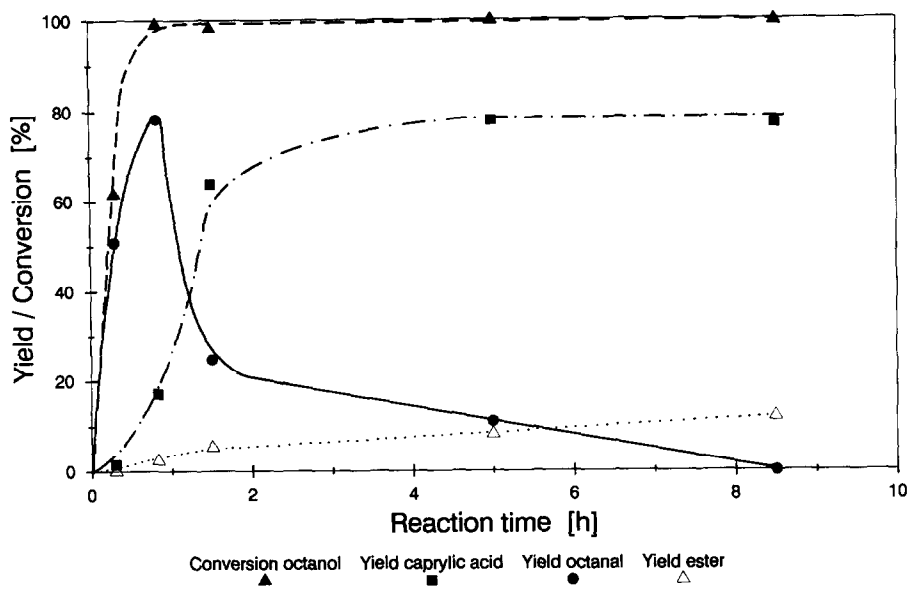


Fig. 2. Oxidation of 1-octanol: Influence of reaction time ($T = 70^{\circ}\text{C}$; molar ratio octanol/ $\text{NaBrO}_3/\text{RuCl}_3 = 25/25/1$).

quantitative, and the yield of aldehyde evidently decreases as that of caprylic acid correspondingly increases. Only a little of the ester is formed.

b. Product control by variation of the reaction time

Figure 2 presents the results of kinetic investigations of the oxidation reaction. As a typical example the course of the reaction at 70°C is shown.

Once again the outcome of the oxidation can be substantially controlled. The alcohol is converted quantitatively within ca. 60 min. The yield of the aldehyde reaches a maximum of 80% after 50 min and then decreases rapidly. Between 50 and 90 min larger amounts of the aldehyde formed are converted into the carboxylic acid and the reaction subsequently proceeds much slower, and seven hours more are needed to oxidize the remaining octanal into caprylic acid or the ester. Noteworthy is the short reaction time during which the aldehyde predominates; i.e. the peak in the kinetic diagram is very sharp.

Similar variation of the product yields was observed for oxidations at lower temperatures, but as expected, in such cases the maximum yield of aldehyde is somewhat higher, and the aldehyde peak in the kinetic diagram appears at longer reaction times and shows a broader distribution.

c. Product control by variation of the amount of oxidizing agent

Figure 3 shows the influence of the ratio of sodium bromate to octanol for a reaction at 70°C for a time of 50 min, i.e. under the conditions corresponding maximum aldehyde formation in Fig. 2.

The conversion of octanol is quantitative at a ratio of 0.5 mol sodium bromate to 1 mol octanol. The yield of the aldehyde increases to a maximum of 90%. Higher

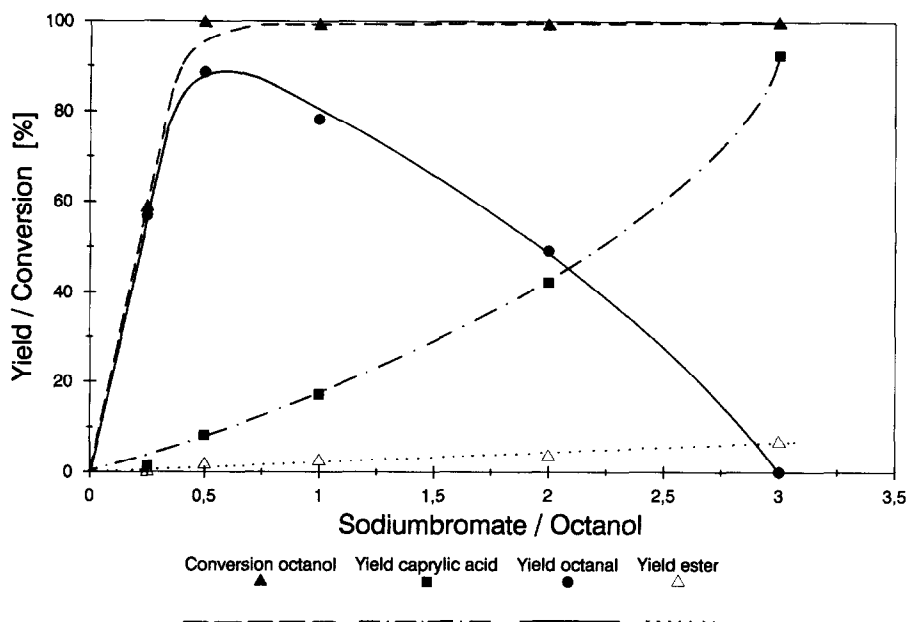


Fig. 3. Oxidation of 1-octanol: Influence of the amount of oxidizing agent ($T = 70^\circ \text{C}$; $t = 50 \text{ min}$; molar ratio octanol/ $\text{RuCl}_3 = 25/1$).

ratios lead to higher percentages of caprylic acid. At a molar ratio of 3:1 aldehyde is no longer formed and complete conversion of the octanol into caprylic acid (92%) and caprylic ester (8%) occurs.

Obviously the bromate/alcohol-ratio offers the easiest possibility to force the oxidation either to the aldehyde or to the acid. Under the reaction conditions given in Figure 3 both products can be obtained in maximum yield and selectivity.

d. Effects of other changes in the reaction conditions

The results in Figure 3 were obtained at an octanol/ruthenium-catalyst ratio of 25/1. Higher proportions of alcohol are less favourable. For instance, increase in the octanol/catalyst-ratio from 25/1 to 75/1 lowers the yield of aldehyde from 90 to 38% and lower the extent of conversion of the alcohol from 100 to only 42%.

As expected, the nature of the transition metal catalyst also has an important influence. The complex tris(triphenylphosphine)ruthenium dichloride $\text{RuCl}_2(\text{PPh}_3)_3$ has only a low activity compared with that of ruthenium trichloride: the maximum conversion of alcohols is only 30% and the yield of aldehyde is limited to 18%. Use of the analogous rhodium compounds rhodium trichloride and Wilkinson's catalyst $\text{RhCl}(\text{PPh}_3)_3$ leads to conversions of $< 10\%$ and yields of aldehyde of $< 1\%$. Summarizing, ruthenium trichloride proved to be the best oxidation catalyst.

Under the standard conditions described above the pH value was always kept at 10. Lowering the pH to 7 by use of a phosphate buffer solution also had a major influence. At high conversions of 96%, the amount of aldehyde was decreased from 90 to 1%, and high yields of caprylic acid and ester were obtained. When a buffer solution was not used there was no conversion of the alcohol.

Table 1

Oxidation of long chain alcohols with sodium bromate ^a

Alcohol	Reaction time (h)	Temperature (°C)	Sodium bromate/alcohol ratio	Conversion (%)	Yield aldehyde (%)
1-Dodecanol	1.5	35	2/1	72	69
1-Hexadecanol	0.8	70	1/1	100	87
2-Hexyl-1-decanol	1.5	35	2/1	96	92

^a Cat.: RuCl₃; molar ratio alcohol/catalyst = 25/1.*e. Reactions involving long chain alcohols*

It seemed of interest to see whether results similar to these obtained with 1-octanol would also be observed with longer chain fatty alcohols, which in two phase reactions often behave differently from their short-chain analogues. Because sterically hindered substrates often show a lower reactivity in homogeneous catalytic reactions linear as well as branched long chain alcohols were investigated. Some results with 1-dodecanol, 1-hexadecanol and 2-hexyl-1-decanol are shown in Table 1.

The data in Table 1 show that long chain alcohols are also highly reactive. Under non-optimized conditions yields of aldehydes of about 70–90% were obtained, and no significant difference between linear and branched alcohols were observed.

Concluding remarks

These results show that the ruthenium-catalyzed two phase oxidation of alcohols with sodium bromate provides a general route to aldehydes or carboxylic acids. Reaction conditions can be chosen to direct the reaction either towards the aldehydes, or towards the acids and esters.

Experimental

The reactions were carried out in 500 ml-glass vessels fitted with a reflux condenser. The samples were analyzed by GLC with a Hewlett Packard GC 5890A fitted with an OV 101 column (25 m · 0.32 mm).

A typical reaction was carried out as follows: 1 g of RuCl₃ · 3H₂O (3.8 mmol) was dissolved in 150 ml of a buffer solution of NaHCO₃ and Na₂CO₃ (pH 10). Then 75 ml of 1,2-dichloroethane and 11.5 g sodium bromate (76 mmol) were added and the mixture was stirred for 30 min at ambient temperature. This preactivated mixture was warmed to 70 °C and then a solution of 12 ml of 1-octanol (76 mmol) in 80 ml of 1,2-dichloroethane was added, and the mixture stirred for a further 60 min then allowed to cool to 0 °C. The two phases were separated, and the organic phase was centrifuged and dried over sodium sulfate. After evaporation of the solvent the sample was analyzed by GLC.

Acknowledgements

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