290. Catalytic C(1), C(2)-Bond Cleavage of Long-Chain Aliphatic Alcohols and ω-Phenylalkyl Alcohols

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Summary

A catalytic one step procedure for the C(1), C(2)-bond cleavage of long-chain aliphatic alcohols and ω-phenyl alcohols has been investigated, using as examples decanol, dodecanol, hexadecanol, benzyl alcohol, 2-phenylethanol and 3-phenyl-propanol. The reactions, which were carried out in a continuous flow tubular reactor using a Ni/Cu catalyst, showed good activity and selectivity with respect to the cleavage products. On the basis of the experimental studies a reaction scheme for the heterogeneous catalytic C(1), C(2)-bond cleavage of the alcohols is suggested.

Introduction. – The present paper deals with the heterogeneous catalytic C(1), C(2)-bond cleavage of alcohols on a Ni/Cu catalyst. The dual step reaction (dehydrogenation, decarbonylation) is carried out as a one step procedure in a continuous flow tubular reactor and takes place according to the *Scheme 1.*

Scheme 1

$$RCH_2OH \xrightarrow[\text{catalyst}]{-H_2} RCHO \xrightarrow[\text{catalyst}]{-CO} RH + CO$$
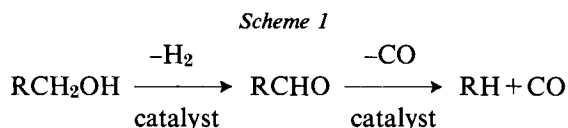
Generally the catalytic C(1), C(2)-bond cleavage of aldehydes (decarbonylation) is carried out homogeneously, using Ru- [1] [2] and Rh-complexes [3–8] as catalyst. Comparatively little work dealing with heterogeneous catalytic decarbonylation has been reported [9–12] and only the decarbonylation of aldehydes on a Pd-catalyst has been studied to any extent [9–11].

Experimental. – The experiments were run using a fixed bed reactor system which consisted essentially of the reactor tube (2.5 × 70 cm) and the metering system for the alcohol. The reactor tube temperature was controlled by an air-bath.

The catalyst used had the following properties: chemical composition (wt. %), NiO (60), CuO (6) on silica; apparent density, 1.85 g/cm³; specific surface (BET), 155 m²/g; geometrical shape, cylinders (diam. 4 mm, length 3 mm). A commercial catalyst which gave similar results is ICI 42.1. Before use the catalyst was reduced by a N₂/H₂ mixture, where the molar fraction of H₂ was continuously increased from zero to one in about 5 h. Simultaneously the catalyst was heated from RT. to 200°. These final conditions were then maintained for 4 h.

The reactants (*Fluka AG*) are listed in *Table*. The quantitative and qualitative analyses of the mixtures were carried out by means of a coupled GC./MS.-System (GC.: *Perkin-Elmer* Mod. 990 FID; MS.: *Hitachi-Perkin-Elmer* Mod. RM4-6L). The columns (4 mm × 2 m) used were: *Carbowax* 20M 4% on *Chromosorb G* AW/DMCS (80/100), FFAP 5% on *Chromosorb G* (80/100) and *Carbopack* C 0.1% Sp-1000. For the identification of the products, the IR., NMR. and mass spectra have been compared with those of reference samples.

Table. *Experimental results*

Temp.: 255°; feed of alcohol: 28 ml/h; catalyst load: aliphatic alcohols 50 g, ω-phenylalkyl alcohol 15 g

Alcohol	Conversion	Selectivity	Main product	Important by-product
$CH_3(CH_2)_9OH$	0.98	0.72	nonane	nonene isomers
$CH_3(CH_2)_{11}OH$	0.97	0.74	undecane	undecene isomers
$CH_3(CH_2)_{15}OH$	0.98	0.89	pentadecane	pentadecene isomers
$PhCH_2OH$	0.60	0.62	benzene	toluene
$Ph(CH_2)_2OH$	0.90	0.89	toluene	ethylbenzene
$Ph(CH_2)_3OH$	0.87	0.90	ethylbenzene	propylbenzene

Results and Discussion. – The results obtained for different alcohols are given in *Table*. Besides the products given in the table, all reactions yielded the corresponding aldehydes and minor compounds (see *Schemes 1* and *2*). The GC. analysis of the reaction mixture from benzyl alcohol showed a larger amount of the corresponding aldehyde (*ca.* 10% wt.) than that of the other alcohols examined (*ca.* 2% wt.). The long chain aliphatic alcohols indicated a definite increase in selectivity with increasing

Scheme 2. *C(1), C(2)-bond cleavage of dodecanol* (identified products are framed; conditions *cf. Table*)
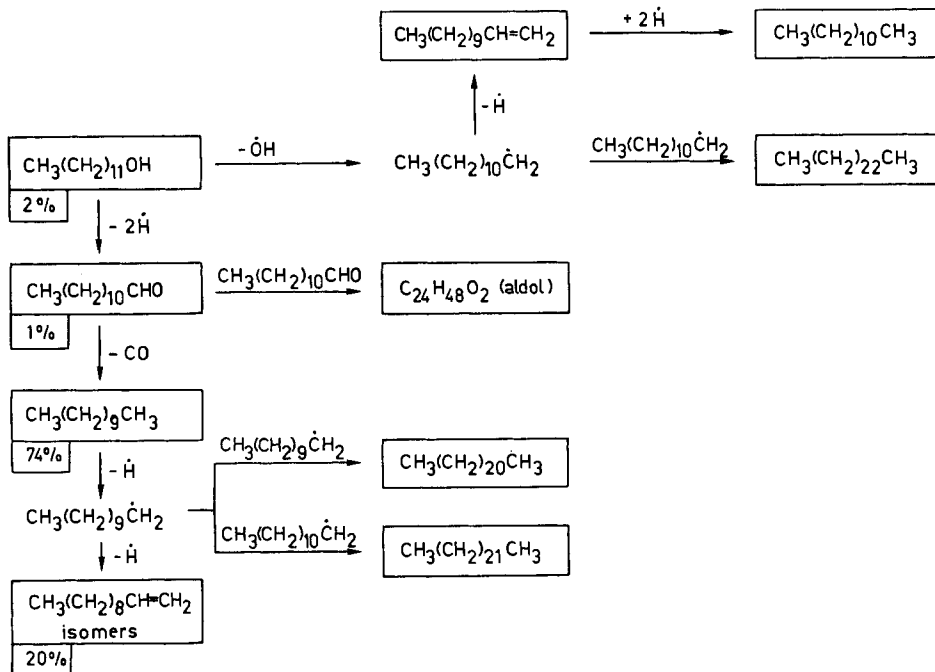
carbon chain length. ω-Phenylalkyl alcohols also gave good selectivity with the exception of benzyl alcohol. In the latter case considerable catalyst poisoning was observed during the reaction. In general the selectivities observed for the reaction on the Ni/Cu catalyst are comparable with those reported for Pd/C [9–11]. Conversion and selectivity of the heterogeneous catalytic C(1), C(2)-bond cleavage proved to be strongly temperature dependent (*Fig. 1* and *2*). For all alcohols tested, the optimum reaction temperature was 250–270°. On the basis of the observed product distribution, the *Schemes 2* and *3* are proposed for the reaction with dodecanol and 2-phenylethanol, respectively. The radicals indicated are not considered to be free radicals
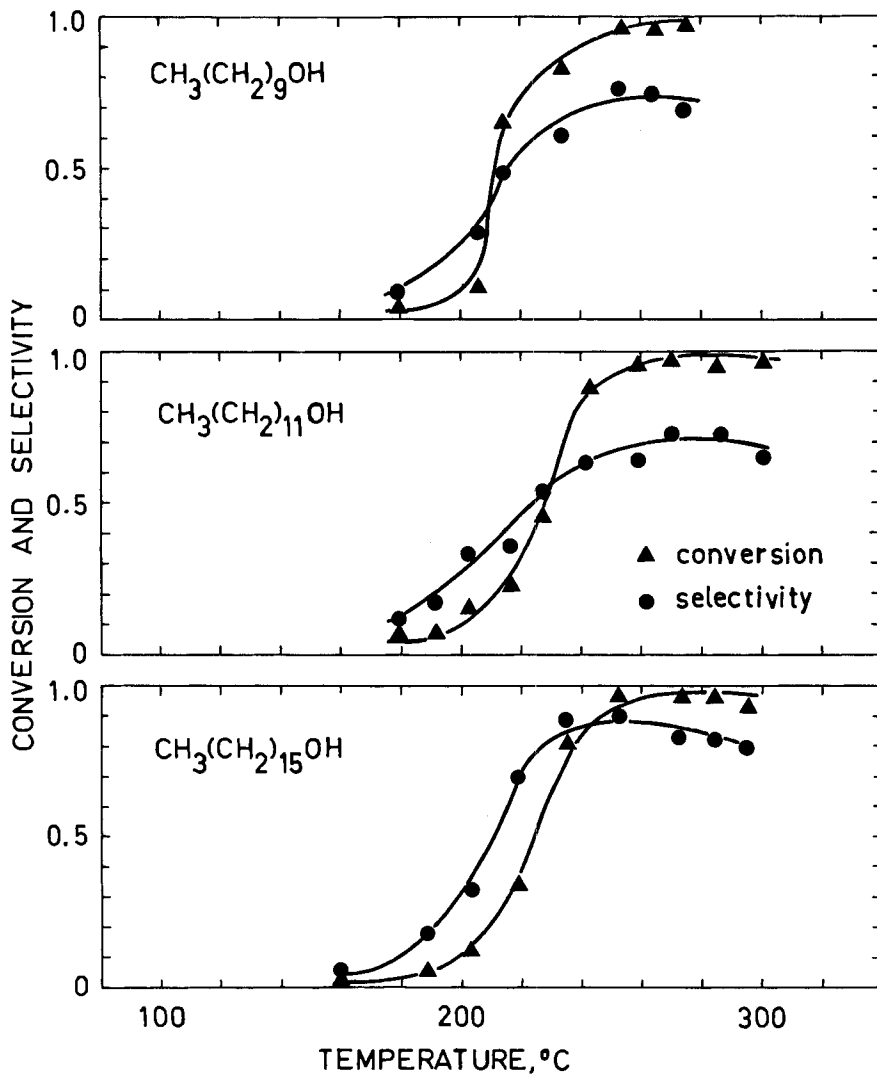

Fig. 1. *Dependence of conversion and selectivity on reaction temperature for the C(1), C(2)-bond cleavage of long chain aliphatic alcohols* (conditions *cf. Table*)

but are assumed to occur on the active sites of the catalyst surface. In order to give an idea of the importance of the different reactions the percentages (wt.%) of the main products are also given. The homologous alcohols examined showed the same types of reactions, so that the examples given can be considered to be representative for their homologues. The long chain aliphatic alcohols yielded the isomers of the dehydrogenated cleavage products as the most important by-products whereas in the case of the ω-phenylalkyl alcohols the corresponding ω-phenylalkanes were mainly obtained. One might think that the product distribution for higher molecular weight ω-phenylalkyl alcohols becomes similar to that of the long chain aliphatic alcohols.
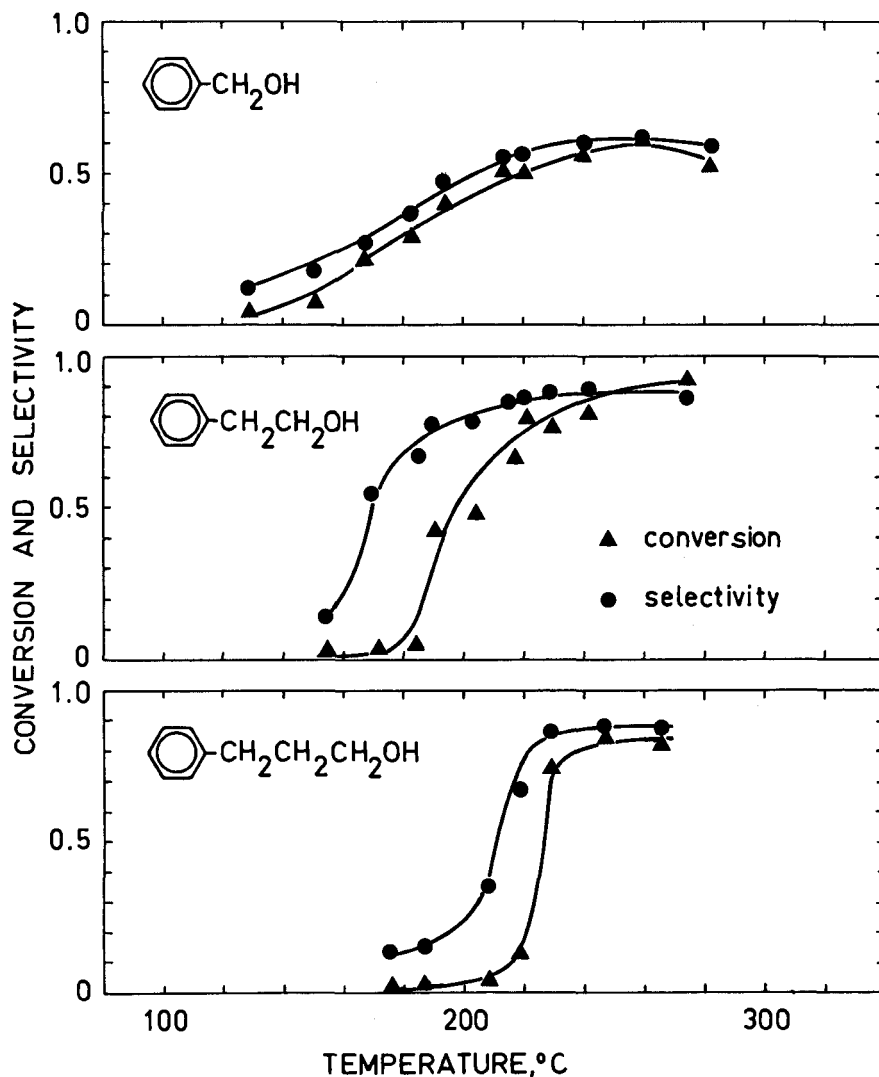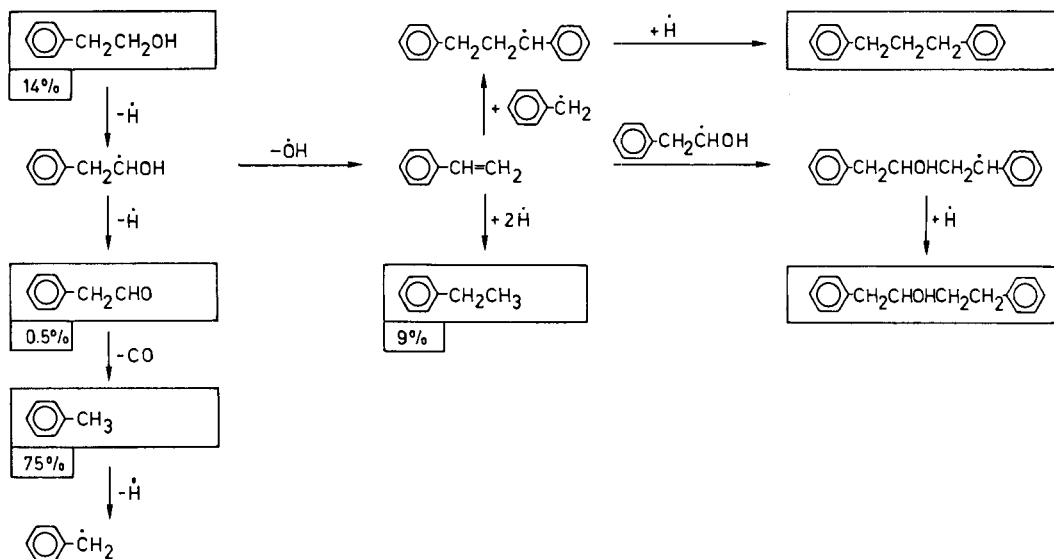

Fig. 2. *Dependence of conversion and selectivity on reaction temperature for the C(1), C(2)-bond cleavage of ω-phenylalkyl alcohols* (conditions cf. Table)

Scheme 3. *C(1), C(2)-bond cleavage of 2-phenylethanol* (identified products are framed; conditions *cf. Table*)

C_6H_5-CH_2CH_2OH

14%

| -Ḣ

C_6H_5-$CH_2\dot{C}HOH$ —$-\dot{O}H$→ C_6H_5-$CH=CH_2$

| -Ḣ | +2Ḣ

C_6H_5-CH_2CHO C_6H_5-CH_2CH_3

0.5%   9%

| -CO

C_6H_5-CH_3

75%

| -Ḣ

C_6H_5-$\dot{C}H_2$

C_6H_5-$CH_2CH_2\dot{C}H$-C_6H_5 —+Ḣ→ C_6H_5-$CH_2CH_2CH_2$-C_6H_5

↑ +C_6H_5-$\dot{C}H_2$

C_6H_5-$CH_2\dot{C}HOH$

→ C_6H_5-$CH_2CHOHCH_2\dot{C}H$-C_6H_5

| +Ḣ

C_6H_5-$CH_2CHOHCH_2CH_2$-C_6H_5

However, in the homologous series examined this tendency has not yet been observed. Contrary to the experiments described above, tests carried out with a Cu/silica catalyst gave only very small amounts (*ca.* 1 wt. %) of the cleavage product and the product mixture consisted mainly of the corresponding aldehydes together with small amounts of aldol condensation products. Experiments carried out with Cu/Ni catalysts of different composition showed that there is a remarkable decrease of (C, C)-bond attack with increasing Cu content, whereas it seems that the (C, H)-bond attack is not strongly influenced by the Cu content. Similar observations have been reported in other reactions [14] [15].

During the reaction of benzyl alcohol considerable catalyst poisoning was observed. To investigate the reason for this decay, different physical methods were applied such as N_2-adsorption, Hg-penetration and X-ray diffraction. Samples of the unused (reduced) and the deactivated catalyst were compared. The N_2-adsorption measurements showed that the observed deactivation was unlikely to have been caused by a decrease of specific surface since the measured values were: active sample 155 m^2/g; deactivated sample 153 m^2/g. The integral pore size distribution determined by the Hg-penetration method showed no significant difference between the two samples. Furthermore no significant change in the Ni-crystallite size of the samples was detected by X-ray diffraction line broadening. From the measurements described so far, we conclude that the deactivation was not caused by macro-structural changes. The decay seemed to be caused merely by irreversibly adsorbed aldol and dimerization products on the catalyst surface, as desorption experiments showed. This conclusion is supported by the observation that, contrary to the other alcohols examined, the decay during the reaction of benzyl alcohol is very fast (decrease in conversion within 20 h of more than 15% of the initial value).

The aldol product formation depends strongly on the aldehyde concentration and this concentration was much higher (ca. 10 wt. %) in the reaction with benzyl alcohol.

The experiments described above show the possibility of carrying out C(1), C(2)-bond cleavage on a Ni/Cu-catalyst. Furthermore, the following generalisation can be made for a wider range of reactions than that investigated:

- C(1), C(2)-bonds of aldehydes are not strongly attacked by pure Cu-catalysts, whereas Ni shows a strong activity in C(1), C(2)-bond cleavage;
- The use of Ni-catalysts in multiple step reactions involving aldehydes as intermediates can lead to considerable decrease in selectivity because of the occurence of decarbonylation. An example of such a type of reaction is found in the amination of long chain aliphatic alcohols, where the intermediate aldehyde can undergo decarbonylation instead of the desired condensation [16].

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