# STUDY OF THE COMPETITIVE REACTIONS BETWEEN AN α-β-UNSATURATED ALDEHYDE AND ALLYLIC ALCOHOL ON A COPPER CHROMITE CATALYST

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It was previously shown that a copper chromium oxide catalyst (Cu/Cr=1) presents a good monohydrogenation selectivity towards conjugated dienes and a poor selectivity with α-unsaturated carbonyls. A study with a mixture citral-nerol at various hydrogen pressures allows to confirm that this is due to the reactivity of the intermediate allylic alcohol. At high pressure, the unsaturated alcohol competes with the initial reagent on the hydrogenation site; at low pressure, this competition decreases, but the allylic alcohol is isomerized on another active site.

Как уже ранее было установлено, катализатор окислов меди и хрома (Cu/Cr = 1) обладает хорошей моногидрирующей селективностью по отношению к сопряженным диенам и плохой селективностью по отношению к α-ненасыщенным карбонилам. На основе исследований со смесью Citral-Nerol при различных давлениях водорода выявили важную роль реактивности промежуточного аллильного спирта. При высоких давлениях ненасыщенный спирт конкурирует с исходным реагентом на центрах гидрирования; при низких давлениях эта конкуренция уменьшается, однако, аллильный спирт изомеризуется на других активных центрах.

INTRODUCTION

The selective hydrogenation of polyunsaturated organic compounds attracts great interest from both industrial and academic point of view. In fine chemicals industry, we often need a semi-hydrogenation, for example with industrial foodstuffs and partial hydrogenation of vegetable oils and fatty acids [1,2], or perfumery and synthesis of fragrances which require the selective formation of allylic alcohols [3]. The improvement of catalysts requires knowledge of their mode of operation. The mixed copper chromium oxides have been largely investigated in our laboratory [4-7]. Many mechanistic investigations have been performed on these solids with conjugated dienes [8], $\alpha$-$\beta$-ethylenic carbonyl compounds [9,10], allylic alcohols [11]. allylic ethers [12] and all the results have led us to propose $Cu^+$-$\bar{H}$ and $Cr^{3+}$-$\bar{H}$ associations as being, respectively, hydrogenation and isomerization active sites. These catalysts show an excellent monohydrogenation selectivity towards conjugated dienes [8], but unfortunately, a low selectivity to $\alpha$-$\beta$-ethylenic carbonyl compounds [9]. This discrepancy has been explained by the large difference between the nucleophilic character of each reagent and their primary products. In the case of conjugated dienes, the only primary products are the monoenes whose attraction for the electrophilic active sites is less strong than that of the initial reagent. So, we observe a perfect selectivity. No monoenes react before the total disappearance of dienes [8]. On the contrary, the allylic alcohols and the saturated carbonyls, the primary products of $\alpha$-$\beta$-ethylenic carbonyls hydrogenation, are able to compete on the active sites with the initial reagent. That gives rise to a poor selectivity, as opposed to some metals which lead to a surprising selectivity [13,14].

The aim of this work is to study the catalytic behavior of a mixture of an $\alpha$-$\beta$-unsaturated carbonyl and an allylic alcohol to confirm the competition and to try to find some working conditions leading to a best mono-hydrogenation selectivity.

EXPERIMENTAL

Copper chromium oxide (Cu/Cr=1) was obtained by coprecipitation of copper and chromium hydroxides with an ammonia solution followed by thermal decomposition at 370°C as previously described [15]. The catalyst was obtained by reduction in a flow of hydrogen at 150°C overnight.

The atmospheric and subatmospheric catalytic reactions were carried out in a thermostated all-glass reactor with a side entrance to remove the samples. The tests were performed with 300 mg of catalyst, 0.5 mL of organic substrate (Fluka purum grade) in 5 mL of decalin at 140 °C. The high pressure catalytic reactions were carried out in an Engineers autoclave equipped with a magnetic strirring system; all the amounts are then multiplied by ten. The products were analyzed by gas chomatography with a FID and a Carbowax 20 M capillary column.

RESULTS AND DISCUSSION
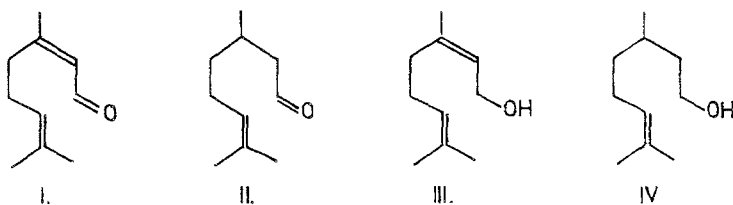


During citral(I) hydrogenation at atmospheric pressure, citronellal(II) nerol(III) appear simultaneously at the initial stage of the reaction (Fig. 1). The ratio of the amounts of these two primary products is about 5 in favor of the saturated aldehyde(II). Citronellol(IV), the saturated alcohol* appears before complete consumption of the starting material

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*The isolated $C_6-H_7$ double bond, never hydrogenated in our working conditions, will not be considered.
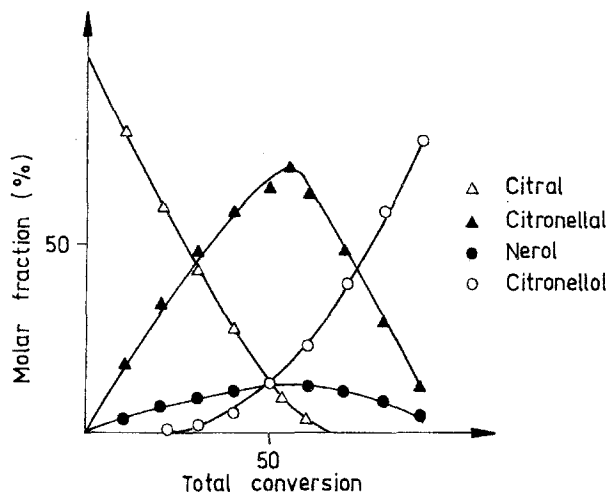
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Fig. 1. Hydrogenation of citral on copper chromite
catalyst. Liquid phase, atmospheric pressure,
140°C

but remains a secondary product [10]. The higher amounts of
both primary products (II) and (III) are reached for the same
conversion value which roughly corresponds almost to the total
disappearance of citral. Clearly, citronellal and nerol react
at the same time as citral but it seems that the adsorption of
the unsaturated alcohol and the saturated aldehyde on the cata-
lyst surface is weaker than that of the unsaturated aldehyde.
Figure 2 shows a typical time course of the reaction of the
allylic alcohol, nerol(III), alone. Two main primary products
are observed: citronellol(IV) from the direct hydrogenation,
and citronellal(II) from the double bond isomerization and
rapid keto-enol equilibrium. The initial formation rate of the
latter product (II) is faster that that of the former (IV), but
citronellal itself undergoes hydrogenation and the trends are
soon reversed. We have to note that in our working conditions,
only citronellol is obtained from direct citronellal hydrogena-
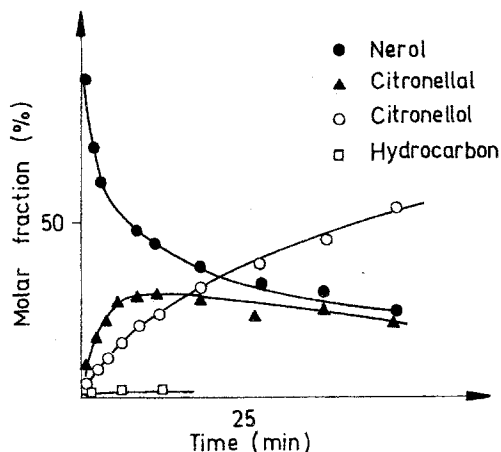tion.

Fig. 2. Hydrogenation of nerol on copper chromite cata-
lyst. Liquid phase, atmospheric pressure, 140°C

The competitive reactions between citral and nerol have
been performed with an equimolecular mixture at various hydro-
gen pressures  (Figs 3a-3e). At atmospheric pressure we notice
a simultaneous disappearance of both reagents. Comparison of
the initial rates confirms that the unsaturated aldehyde is
more reactive than the allylic alcohol, even if it is partly
regenerated from the citral. As a matter of fact, if we assume
that the citronellal to citronellol ratio is still 5 (Fig. 1),
we can deduce from Fig. 3c that 50% of the initial amount of
citral is transformed into 8% of nerol ("Nerol product") and
42% of citronellal, respectively, after 20 min of reaction; now,
there is 80% of the initial nerol remaining at this time, which
is more even without the "Nerol product" than the remaining
citral. This situation increases with the $H_2$ pressure. For ex-
ample, at 2 atm the amount of nerol which disappears, is just
replaced by the "Nerol product"; at 10 atm the production of
nerol becomes more important than its disappearance. Obviously,
high pressure favors unsaturated aldehyde hydrogenation rela-
tive to the hydrogenation of the allylic alcohol. However, the

monohydrogenation selectivity is not improved because high pressure also favors citronellal hydrogenation. Hence, even if the saturated alcohol is always a secondary product, the higher the pressure, the sooner citronellol appears. Nevertheless, whatever the hydrogenation reaction considered, the one that takes place on a cuprous site [9] depends on the hydrogen pressure. When this pressure is very low (Fig. 3e), hydrogenation is very weak and the unsaturated aldehyde does not react. The allylic alcohol is no more hydrogenated but can undergo isomerization, which takes place on a chromium site [11] and gives rise to citronellal.
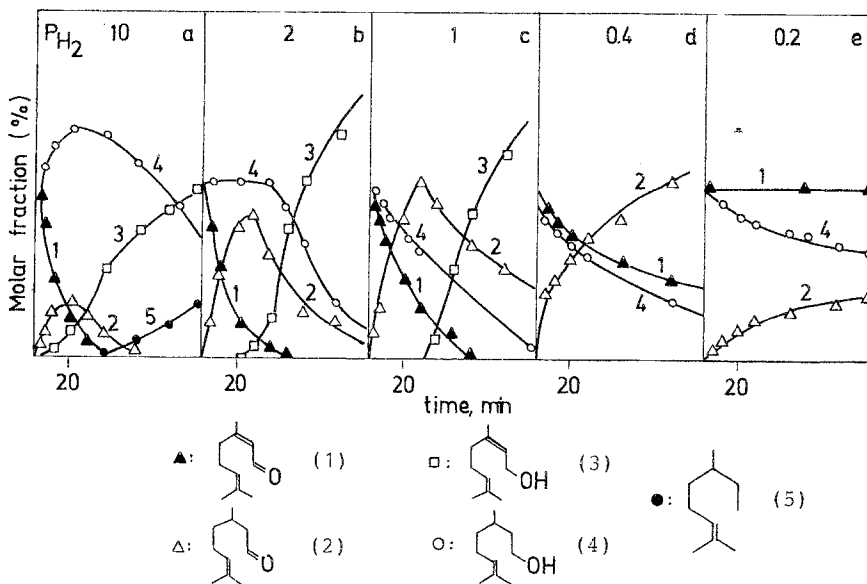


Fig. 3. Competitive hydrogenation citral-nerol at various hydrogen pressures (atm). Liquid phase, 140°C

At a medium pressure (Fig. 3d), the unsaturated aldehyde can be monohydrogenated, unlike the saturated carbonyl or the allylic alcohol, and the saturated alcohol does not appear. Unfortun-

ately, the allylic alcohol is isomerized and in this case the only primary product from citral seems to be citronellal. So, the hydrogenation is a function of the hydrogen pressure. The allylic alcohols can undergo various changes depending on the pressure: isomerization (ISOM) predominates at low pressure, whereas hydrogenation (HYT) becomes important at high pressure. Moreover, we can see (Fig. 3a) the hydrogenolysis (HYL) of the C—O bond to appear beyond 10 atm. The relative rates of ISOM and HYT are reversed at about 0.5 atm.

CONCLUSION

The poor monohydrogenation selectivity from α-ß-unsaturated carbonyls obtained on a mixed copper chromium oxide is assumed to be due to the reactivity of one of the primary products, namely the allylic alcohol. The study of the pressure effect shows that at low hydrogen pressure the unsaturated carbonyl does not react but the allylic alcohol slowly disappears through an isomerization reaction. At higher pressure, the α-ß-ethylenic carbonyl is hydrogenated but, unfortunately, if the isomerization of the allylic alcohol decreases, this product competes with the starting carbonyl to undergo a hydrogenation reaction.

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