

Isomerization of Allyl Alcohol in the Presence of Raney Nickel

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Received June 1, 1981; revised November 20, 1981

Allyl alcohol was found to isomerize to propanal in the presence of Raney nickel. By means of deuterium labeling studies it was concluded that the reaction involves a 1,3-sigmatropic migration of hydrogen from C₁ to C₃ to form the enol of propanal.

INTRODUCTION

Allyl alcohol isomerizes to propanal in the presence of Raney nickel (1), alumina, zinc oxide (2), platinum group metals (3), copper (4), and complexes of nickel (5), iron (6), cobalt (7), rhodium, and ruthenium (8). The present study attempts to understand the mechanism of isomerization in the presence of Raney nickel.

EXPERIMENTAL

Proton nuclear magnetic resonance spectra (NMR) were recorded on a Varian XL 100 instrument. Mass spectra were recorded using a Varian MAT CH 7 instrument. Gas-liquid chromatography (GLC) analyses and separations were done on a Varian 1800 series chromatograph using hydrogen as carrier gas (thermal conductivity detector).

A. Catalyst Preparation

For each experiment a fresh catalyst was prepared using the following procedure:

Raney nickel. Ni-Al 50/50 alloy (5 g) was leached by adding the powder in small portions to sodium hydroxide solution (6.4 g of sodium hydroxide in 25 ml of water) during 1 hr, maintaining the temperature at 50°C by cooling in an ice bath. Then, the suspension was kept at 80°C in a hot water bath for another hour. After cooling to room temperature, the supernatant alkaline solution was decanted and the catalyst was

repeatedly washed with distilled water, until it was free from alkali. Then, the catalyst was washed three times with rectified spirit and twice with absolute alcohol and stored over absolute alcohol in the refrigerator.

Deuterated Raney nickel. Sodium (7.6 g) was dissolved in 56 ml of D₂O (isotopic purity 70%) placed in a roundbottom flask cooled in an ice bath. NaOD thus obtained was used to prepare the catalyst as above. The catalyst was washed with D₂O and stored over D₂O.

B. Preparation of Allyl Alcohol

(i) *Allyl alcohol (-OD).* It was prepared by the hydrolysis of sodium allyloxide using D₂O (70% isotopic purity) and the compound obtained was distilled (bp 97°C). The NMR (CDCl₃) showed the reduction in the intensity of the -OH signal and the mass spectrum showed a *d*₁ : *d*₀ ratio of 68 : 32.

(ii) *Allyl alcohol-1,1-d₂.* It was prepared by the method of Schuetz and Millard (9) by the reduction of acryloyl chloride with lithium aluminum deuteride (Fluka ≤ 99%) in 20% yield after microspinning band distillation. NMR (CDCl₃) showed 98% isotopic purity. The mass spectrum showed a *d*₂ : *d*₁ : *d*₀ ratio of 98 : 2 : 0.

C. Isomerization

The catalyst was placed in a round-bottom flask and was connected briefly to vacuum to remove the solvent and was kept

TABLE I
Effect of Catalyst-to-Substrate Ratio, Temperature, and Time

S. No.	Catalyst-to-substrate ratio (wt/wt)	Time (hr)	Temp. (°C)	Product distribution ^a (mole%)			
				Allyl alcohol	Propanal	<i>n</i> -Propanol	Acrolein
1	0.04	1	32	77	21	2	Traces
2	0.1	1	32	56	40	2	Traces
3	0.2	1	32	52	43	5	Traces
4	0.1	1	66	40	57	2	1
5	0.1	1	80	20	75	3	1
6	0.1	2	32	49	46	3	2
7	0.1	3	32	42	53	3	2
8	0.1	4	32	33	61	4	2

Note. Catalyst used: methanol-washed Raney nickel. Weight of allyl alcohol = 5 g.

^a Propene was also formed in traces (0.04 mole%).

under nitrogen. To this allyl alcohol was added and kept under magnetic stirring at the required temperature.

D. Analysis

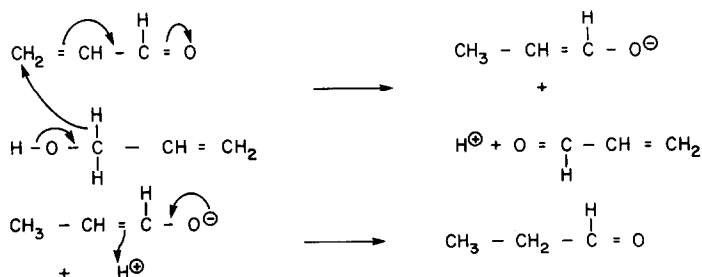
Reaction products were filtered off and the conversion was measured with GLC with 20% Carbowax 20M on Varaport 30, 80–100 mesh; 1.5-m column. The products were confirmed by comparing their retention times with authentic samples or by preparative gas chromatography and spectroscopic identification. The propanal from the reaction was separated as the 2,4-dinitrophenylhydrazone and recrystallized from ethanol. It was characterized by NMR (CDCl₃) and mass spectrum. It was established that during the 2,4-dinitrophenylhydrazone preparation there was no exchange of deuterium.

RESULTS AND DISCUSSION

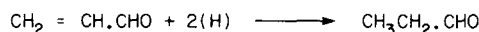
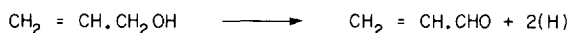
Allyl alcohol when brought into contact with Raney nickel at room temperature underwent a vigorous exothermic reaction. The main product was propanal with traces of *n*-propanol, acrolein, and propene. Conversion to propanal was 20–80% depending on amount and type of the catalyst, reaction time, and temperature (Table 1). Increase in catalyst: substrate ratio (Nos. 1–3, Table 1), increase in temperature (Nos. 2, 4, and 5, Table 1), and increase in reaction time (Nos. 2, 6, 7, and 8, Table 1), all tended to increase the yield of propanal.

The following mechanisms may be considered for the reaction:

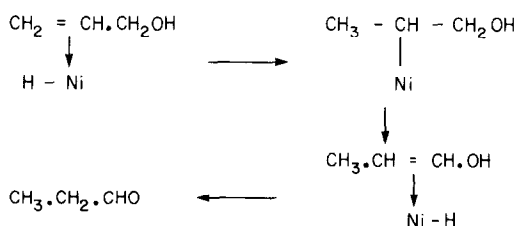
A. Dehydrogenation followed by the hydrogen transfer from allyl alcohol to acrolein as proposed for the gas-phase reaction over zinc oxide (2):



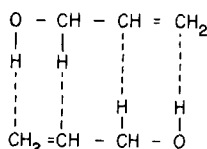
B. Dehydrogenation-hydrogenation mechanism:



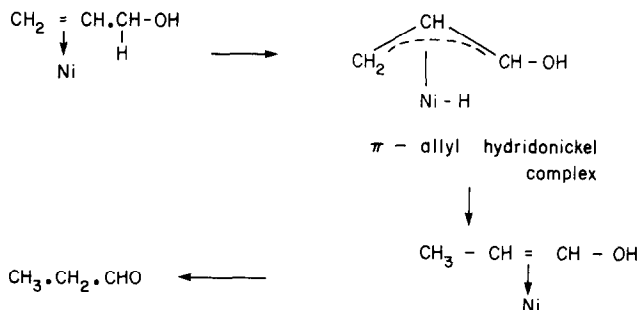
C. Isomerization through the half-hydrogenated state similar to the isomerization of olefins during catalytic hydrogenation (10):



D. Direct transfer of hydrogen between two molecules. A model for such a process is represented below:



E. Hydrogen abstraction by metal to form a π -allyl species followed by reversal to form the enol of propanal (π -allylic mechanism) as proposed for the homogeneous reaction with iron pentacarbonyl (6):



F. Olefin-metal interaction following by 1,3-sigmatropic hydrogen shift without actually involving metal-hydride species:

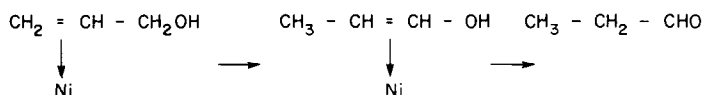


TABLE 2
Effect of Hydrogen Acceptor and Donor in the Reaction Medium

S. No.	Reactants ^a (mole ratio)	Product distribution (mole%)				Hydrogen acceptor and donor (mole%)	
		Allyl alcohol	Propanal	<i>n</i> -Propanol	Acrolein		
1	Allyl alcohol: Isopropyl alcohol (1:1)	72	24	3	Traces	<i>Isopropyl alcohol</i> 98	<i>Acetone</i> 2
2	Allyl alcohol: acetone (1:1)	72	24	3	—	2	98
3	Allyl alcohol: Butanal (1:1)	73	24	2	—	<i>n</i> -Butanol 1	<i>Butanal</i> 99
4	Allyl alcohol: Acrolein (1:1)	73	24	2	—		
5	Acrolein: Isopropyl alcohol (1:1)	—	15	Traces	84	<i>Isopropyl alcohol</i> 84	<i>Acetone</i> 16

Note. Catalyst-to-substrate ratio (wt/wt): 0.04. Temperature of the reaction: 32°C. Reaction time: 1 hr.

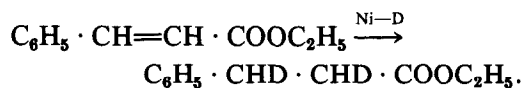
^a About 0.1 mole of each reactant was used.

The present studies were designed mainly to differentiate between the above mechanisms.

Results presented in Table 2 showed that the formation of propanal was unaffected by the presence of a hydrogen acceptor and a hydrogen donor. An experiment with allyl alcohol, acrolein, and Raney nickel gave the same yield of propanal as without acrolein. If mechanism A is operative on Raney nickel, the yield of propanal should be increased. In fact this was found to be so by Weston and Adkins in their studies over zinc oxide. Our observation suggests that the mechanism on Raney nickel is not the same as that on zinc oxide. Hence mechanism A may be disregarded. Intermediacy of acrolein was felt unlikely since it was found that acrolein alone when stirred with Raney nickel for a short time at room temperature underwent nearly complete polymerization.

Raney nickel retains a large quantity of hydrogen released during its preparation

from Ni-Al alloy and alkali. To understand the role, if any, of this hydrogen in the isomerization process the catalyst was prepared by using D₂O/NaOD so that only deuterium was present on the catalyst. This catalyst was designated as Ni-D. It was shown that this deuterium can take part in reducing double bonds, by stirring the catalyst with ethyl cinnamate under nitrogen. Ethyl dideutero cinnamate was obtained.

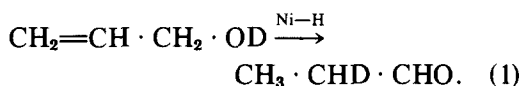


It was found that this deuterium was not taken up by the allyl alcohol or propanal during the isomerization.

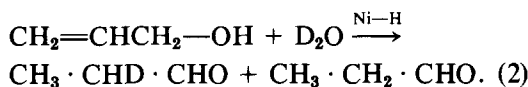
The nature of the hydrogen present in Raney nickel is not fully understood. While the earlier workers (11) had assumed NiH₂ to be present, recent studies (12) have disproved the existence of bulk NiH₂. The hydrogen seems to be present as surface hydride (13) or chemisorbed hydrogen (14). In

the light of these facts, our observation with Ni-D cited above can be taken as strong evidence against mechanisms B and C.

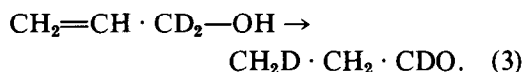
The isomerized product, propanal, from Raney nickel and allyl alcohol (—OD, isotopic purity 68%) showed the incorporation of deuterium (60–70%) at the C₂ position as evidenced from the NMR and mass spectra of the 2,4-dinitrophenylhydrazone.



Similarly, propanal from allyl alcohol/D₂O (0.7:1.0) and Raney nickel also showed the incorporation of deuterium at the C₂ position.



Allyl alcohol -1,1-*d*₂ gave propanal with the deuterium at the C₁ and C₃ positions (NMR integration ratio of CH₃:CH₂:CH was 2.3:2.0:0.3) with Raney nickel.



These observations help to rule out mechanism D as well as B. Further, these observations clearly showed that a hydrogen from C₁ migrated to C₃ without losing its identity by exchanging with hydrogen present on Raney nickel and the enol so formed tautomerized with the hydrogen of the —OH migrating to C₂ without losing its identity. The intermediacy of the enol was confirmed by observations (1) and (2). That the incorporation of deuterium in the propanal in (2) did not take place after the formation of propanal was proved by an independent experiment where undeuterated propanal was stirred with Raney nickel in D₂O under the experimental conditions. The recovered propanal was free of deuterium.

The 1,3-hydrogen shift (C₁ to C₃) may be as in mechanism E or F. The former is similar to the mechanism proposed by

Smith and co-workers (15) for the deuterium exchange during the hydrogenation of olefins. In this case, it will have to be assumed that the π-allyl hydridonickel complex rearranged with the H of Ni-H migrating to C₃ without losing its identity by admixture with the "surface nickel hydride" present in Raney nickel. Since this is unlikely, on the balance one is led to believe that the reaction proceeds by mechanism F involving a 1,3-sigmatropic migration of hydrogen without the intermediate formation of Ni-H complex.

While, 1,3-sigmatropic rearrangement of hydrogen is symmetry forbidden, it has been shown to be facile in an olefin coordinated to a transition metal, by a suprafacial pathway, since the back-donation of metal *d* electron to the olefin could result in a molecular orbital of proper symmetry (16).

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