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Selective Hydrogenation of 1,3-Cyclooctadiene and Diphenylacetylene on Copper Using the Water–Gas Shift Reaction as a Hydrogen Source

Selective catalytic hydrogenation of polyenes and acetylenes to monoolefins of a particular configuration is a matter of great interest in synthetic chemistry. Studies in this field have been principally devoted to the efficiency of catalytic systems and to the mechanism of the dihydrogen activation; many examples of stereo and regioselectivities have been discussed using either homogeneous or heterogeneous catalysts for the reduction of various compounds (substrates) with molecular hydrogen (*1*, *2*).

In the course of our studies on selective hydrogenation reactions catalyzed by transition metal derivatives, we found that water and carbon monoxide can be employed as reagents in place of the more expensive pure dihydrogen for the partial hydrogenation of 1,3-cyclooctadiene (C_8H_{12}) and of diphenylethyne ($C_{14}H_{10}$); these reactions are promoted by copper catalysts under relatively mild conditions. Experimental conditions and results are reported in Table 1.

A 6.5% copper on silica gel catalyst was prepared according to the procedure of Koritala (*3*) and it was used after a prereduction with H_2 at 200°C and 1 atm. Copper on alumina and "copper chromite" were also found to be active after reduction.

Preliminary kinetic studies and the analysis of gaseous products show that H_2, along with CO_2, is accumulated in the course of reactions suggesting that the water–gas shift reaction (1) takes place producing dihydrogen which is partially consumed by reaction (2) or (3).

$$H_2O + CO = H_2 + CO_2, \qquad (1)$$

$$\text{cyclo-1,3-}C_8H_{12} + H_2 \rightarrow \text{cyclo-}C_8H_{14}, \qquad (2)$$

$$C_6H_5C{\equiv}CC_6H_5 + H_2 \rightarrow C_6H_5CH{=}CHC_6H_5. \qquad (3)$$

Although the use of zinc oxide–copper oxide mixtures as catalyst for the water–gas shift reaction at higher temperatures (175–350°C) is well known (*4*) there are no reports on the use of copper or other different metal derivatives as catalysts for hydrogenations via the water–gas shift reaction. Therefore, our results seem interesting in connection also with the fact that carbon monoxide and carbon dioxide act often as poisons for many catalytic hydrogenations (*5*), and particularly water is an inhibitor for copper catalysts (*6*, *7*). The finding that only prereduced copper derivatives can be employed as catalysts for coupled reactions (1) + (2) or (1) + (3) indicates a strong inhibiting effect by using unreduced catalysts with divalent copper (on silica or as $CuO/CuCr_2O_4$): Reaction (1), and therefore the subsequent reaction (2) or (3), did not start at 140°C, whereas reactions (2) and (3) took place in the absence of CO and H_2O when pure H_2 was used. Moreover, the prereduction of Cu(II) to the active catalyst, by means of H_2, was also inhibited by water ($H_2O:Cu = 100$) at 200°C under hydrogen pressure (5 atm).

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TABLE 1

Hydrogenation of 1,3-Cyclooctadiene and Diphenylacetylene on Cu/SiO_2

Expt.	Substrate	t (h)	GLC analysis (mole%)
1[a,b]	1,3-C_8H_{12}	20	C_8H_{14} (ca. 100)
2[a,b]	1,3-C_8H_{12}	4	1,3-C_8H_{12}(81); C_8H_{14}(19)
3[a,b,c]	1,3-C_8H_{12}	4	1,3-C_8H_{12}(77); C_8H_{14}(23)
4[a,d]	$C_{14}H_{10}$	36	$C_{14}H_{10}$(4); Z-$C_{14}H_{12}$(93); E-$C_{14}H_{12}$(2)
5[e,f]	$C_{14}H_{10}$	8	$C_{14}H_{10}$(59); Z-$C_{14}H_{12}$(38); E-$C_{14}H_{12}$(2)
6[g,h]	1,3-C_8H_{12}	2	C_8H_{14} (ca. 100)
7[f,g]	$C_{14}H_{10}$	0.5	$C_{14}H_{10}$(4); Z-$C_{14}H_{12}$(85); E-$C_{14}H_{12}$(7); $C_{14}H_{16}$(4)

[a] Reaction carried out at 140°C in stainless-steel autoclave (40 ml), stirred magnetically.

[b] 1,3-C_8H_{12} (440 mg), H_2O (300 mg), Cu/SiO_2 (100 mg), tetrahydrofurane (THF) (5 ml), CO (5 atm).

[c] As *b* plus NaOH (1.5 mg).

[d] $C_{14}H_{10}$ (180 mg), H_2O (50 mg), Cu/SiO_2 (80 mg), THF (5 ml), CO (5 atm).

[e] In glass reactor (20 ml), stirred magnetically, at 140°C under a stream (3 ml min^{-1}) of CO (0.8 atm) and H_2O (0.2 atm).

[f] $C_{14}H_{10}$ (180 mg), Cu/SiO_2 (80 mg), Nujol (5 ml).

[g] In glass reactor (20 ml), stirred magnetically, at 140°C under pure H_2 at 1 atm.

[h] 1,3-C_8H_{12} (440 mg), Nujol (5 ml), Cu/SiO_2 (100 mg).

The selectivities found for the reactions here investigated are very high. Cycloocta-1,3-diene can be transformed into cyclooctene in ca. 100% yield (Expt 1). Unlike different homogeneous catalysts which require the presence of a strong alkali to promote reaction (1) (*8*), we found that Cu/SiO_2 is very little influenced by a small amount of NaOH (Expt 3). A higher hydrogenation rate has been observed by using pure H_2 (Expt 6).

The experiments with diphenylacetylene (Expts 4, 5, and 7) represent, to our knowledge, also the first example of the half-hydrogenation of alkynes catalyzed by copper derivatives. This reaction occurs at 140°C even at atmospheric pressure (Expt 5) by using a stream of CO and steam, and Z-stilbene ($C_{14}H_{12}$) is obtained in high yield. We have found a better yne : ene selectivity with H_2O and CO as reagents than in the case of pure dihydrogen as reagent (Expt 7), and this is probably due to the low hydrogen pressure available in the former experiment. In both cases, however, the selectivity is better or similar to that shown by palladium-modified catalysts and, particularly, the products of Expts 4 and 5 contained less than 0.3% of diphenylethane.

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