Hydrogenation of Unsaturated Fatty Acids to Unsaturated Fatty Alcohols: III. Comparison of Different Soap Catalyst Systems

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Abstract

Copper oleate and cadmium oleate catalysts have been replaced by other metal compounds. Silver was the only metal which could be substituted for copper in the ratio range studied. Using nickel oleate, the degree of saturation of the double bond decreased with increasing cadmium oleate concentration. No comparable substitute was found for Cd. The composition of the final components is influenced by the use of a paraffinic solvent, which also has an effect on the saturation of the double bond. An explanation is given for the behavior of the catalyst when the reaction is not selective and is carried out in a paraffinic solvent. The catalytic system Ag/Cd soaps was also studied kinetically and analytically. The results show that the mechanism of the reaction using silver soap is identical with the one using copper soap.

Introduction

In the foregoing papers the main subject was a closer examination of the remarkable selective copper-cadmium system (1,2). It was expected that other metal soaps could be substituted for copper, cadmium or both cations. The substitution of Cd by Na, Zn, Ca, Mg and Ba resulted, however, in no reaction at all. If a small amount of Cd is added to the system (1 mole % Cd to 5 mole % Cu), there will be a selective hydrogenation. The reaction rate will increase proportionally with the amount of soap, except in the case of Zn oleate, for which a minimum was observed (3).

In the foregoing paper (2) it was shown that copper is the active part of the catalyst, and cadmium oleate reacts with the activated hydrogen through a double layer, hydrogenating the hydrophilic part of the molecule. An endeavour was made to account for this by substituting one of the metal-soaps.

Oleic acid was used as raw material for the hydrogenations which were carried out with or without a solvent. In both cases the apparatus described in the foregoing papers (1,2) was used. Experiments were also carried out in a gas-heated rolling autoclave with an inset vessel, although periodic sampling is not then possible. When no solvent is used the reaction mixture is introduced directly into vessel C and sampling is commenced as soon as the reaction mixture reaches the reaction conditions (250C and 250 atm.). When the rolling autoclave is used the reaction time is taken as the time during which the temperature remains between 250 and 300C; the initial pressure at 20C is 190 atm., and the reaction is carried out without a solvent.

Experimental Procedures

Table I gives a list of the different combinations, indicated by (+), when the paraffinic solvent is used, or by (−) in the absence of this solvent.

In the ratio range studied, only the system Ag/Cd can be employed as substitute for the Cu/Cd system, althought the conversion to alcohol is not so high (Fig. 1). Furthermore, Pb can be substituted for both cations if only the unsaturation of the double bond is taken into account, but the conversion to alcohol is too low. Hg precipitates as metal during the preparation of the soap, and its behavior during the reaction is questionable.

Hydrogenation in the presence of 5 mole % copper oleate, carried out in a solvent (Fig. 1), shows at first clearly a reactivity towards the double bond, but at a certain moment the carboxyl group is attacked and the degree of saturation of the double bond remains practically constant. The same mechanism is shown in Figure 2.

Some metal-soap systems as Ni/Cd, Cu/Zn and Co/Cd were also studied in other ratio ranges. The system Ni/Cd, with a constant Ni concentration of 5 mole % and variable cadmium concentrations of 5, 7.5, 10 and 12 mole % is shown in Figure 2. With increasing cadmium concentration a better selectivity will be obtained. The systems Cu/Zn and Co/Cd, with Cu and Co concentrations of 5 mole %, and Zn and Cd concentrations of 5, 7.5 and 10 mole %, showed no conversion of acid to alcohol, while a sat-

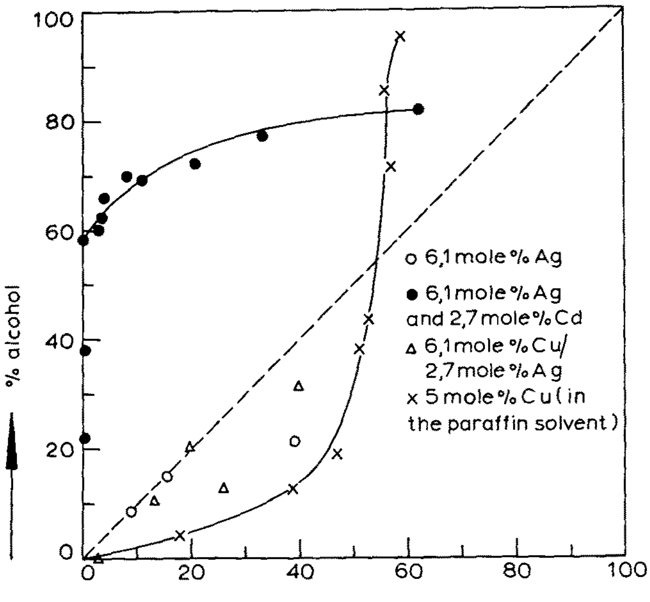

FIG. 1. Hydrogenation of oleic acid using metal-soaps as catalysts. For the reaction without the paraffin solvent. T: 300C initial P: 190 atm. Reaction-time: up to 4 hr. Reaction in the paraffin solvent T: 250C; P: 200 atm. Reaction-time 2 hr.

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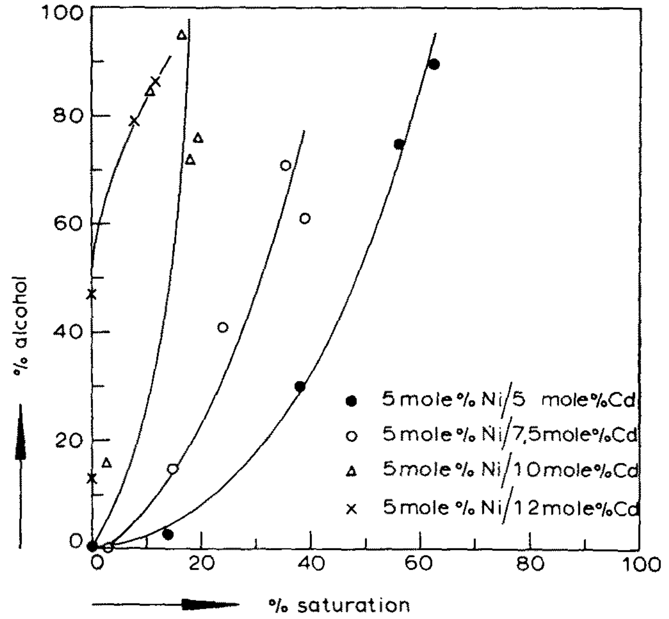

FIG. 2. Hydrogenation of oleic acid using Ni- and Cd-oleate as catalysts in the paraffin solvent T: 250C; P: 200 atm. Time: up to 90 min.

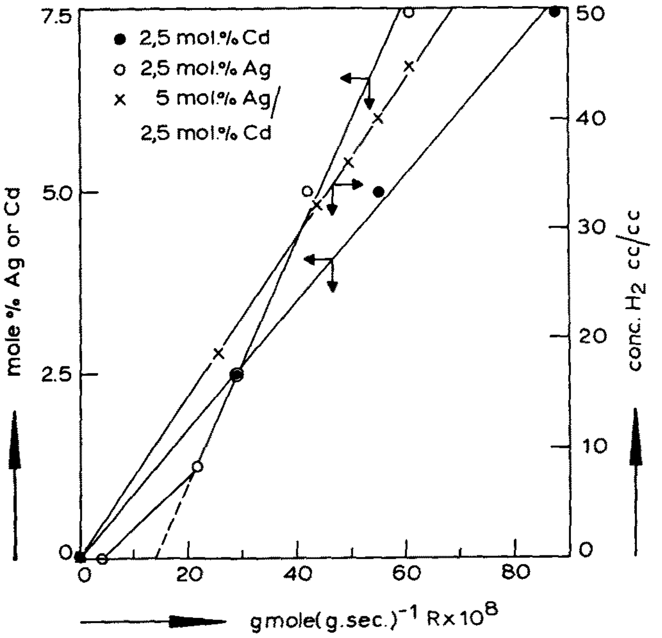

FIG. 3. Influence of the concentrations of hydrogen, cadmium and silver on the reaction rate T: 250C.

uration of about 20% occurs in the Cu/Zn system. These results are observed in the cases where a paraffinic solvent is present, as well as in its absence. An exception is observed when a Cu/Zn soap catalyst is used, at a ratio of 5:2.5 in the solvent (Table I).

Discussion

It is understood that the catalytic activity of metals in hydrogenation-type reactions depends upon geometric and electronic factors, the latter being of great relevance. For the necessary chemisorption to take place it is important that the metals shall possess vacant *d*-orbitals. If this is not the case, a small catalytic activity results, as shown by Group IB metals.

From Table I it can be seen that only metals of Group IB are actually able to hydrogenate the unsaturated fatty acids selectively to their unsaturated alcohols in the presence of cadmium oleate—in the ratio range studied. This indicates that only metals with poor catalytic activity will be inhibited to hydrogenate the double bond in the presence of smaller amounts of cadmium soap, while metals of the transition series, which are known as active hydrogenation catalysts, will mainly hydrogenate the double bond. Their activity can be directed, however, to the carboxyl group by lowering the ratio of active-metal catalyst to cadmium oleate (Fig. 2).

In cases where hydrogenations are not selective and are carried out with the paraffin solvent, another aspect becomes apparent, namely, that the double bond is partly hydrogenated in the first place, during which the carboxyl group remains practically unreacted. At a certain stage of the reaction the saturation remains practically constant and the carboxyl group is reduced. This might account for the initiation period of the selective hydrogenation, during which there is no reaction because the catalyst has to be activated. The activation energy needed for the saturation of the double bond is much lower and will thus occur first. The catalyst particles which are responsible for the hydrogenation of the double bond are not stabilized, and will agglomerate. These particles, if in the paraffinic solvent, will partly sink to the bottom of the vessel, but without a solvent they will remain in solution owing to the higher acid and cadmium soap concentrations, which prevents them from forming large agglomerates, in which case a partial stabilization is still possible.

Copper powder (average size 50 μ), when reduced in a very diluted H_2 stream (1% in N_2) at 200 C, is not able to reduce oleic acid to oleyl alcohol in the presence of cadmium oleate. The reaction product has a yellow to slightly reddish color, and the copper is found in the bottom of the vessel.

The results obtained now lead to the following rules for the choice of an active-metal catalyst: it should be a metal which is able to activate hydrogen; it should be a metal in a state of oxidation which can easily be reduced to its metallic form under reaction conditions; it should be a metal which is able to form a sol and be stabilized by other metal-soaps.

Regarding the second part of the catalytic system, the following rules apply: it must be able to exist in the form of a soap soluble in the acid; it should not be reduced to its metallic state under reaction conditions; it must be able to stabilize the colloidal particles of the activated metal; as a solution in the acid, it must not be able to hydrogenate the double bond; the cation-carboxyl group when adsorbed should be readily hydrogenated under reaction conditions.

Not all combinations will be effective, as there is still a chance that the two components will be incompatible and so inhibit the reaction.

Further Considerations Regarding the Ag and Cd Oleate Catalyst System

Considering the results obtained with the catalytic system Ag/Cd oleate (Fig. 1), a more detailed study, such as an analysis of the catalyst system leaving the reactor as well as kinetic measurements will be carried out. This should afford a better insight into the mechanism of the reaction.

Kinetics

All the experiments and the preparation of the

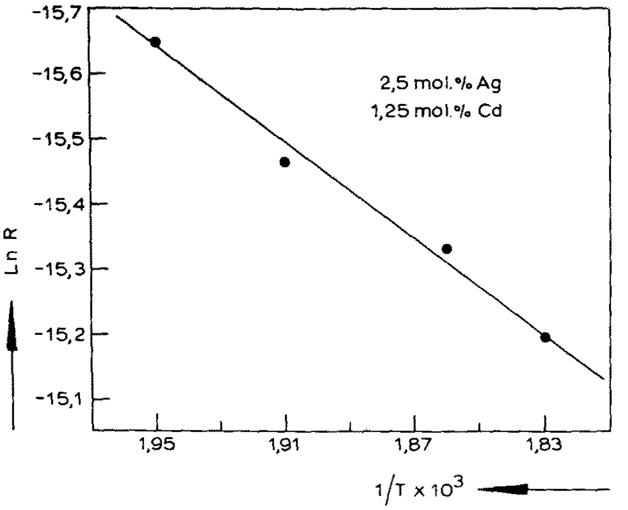

FIG. 4. Influence of the temperature on the reaction rate.

soap were carried out as described in the foregoing papers (1, 2).

Influence of the concentrations of silver, cadmium, hydrogen and of the temperature. From the experiments shown in Figure 3 it may be concluded that the reaction is first order in Ag, Cd and H_2 in the range studied, that is, 0 to 7.5 mole % Ag, in the presence of 2.5 mole % Cd. As in the Cu/Cd system, the higher the cadmium concentration the lower the final degree of conversion.

The plot of the logarithm of the reaction rate against 1/T, is a straight line (Fig. 4). In the selected temperature range of 240 to 275 C it is found that the activation energy is 7.1 kcal/mole.

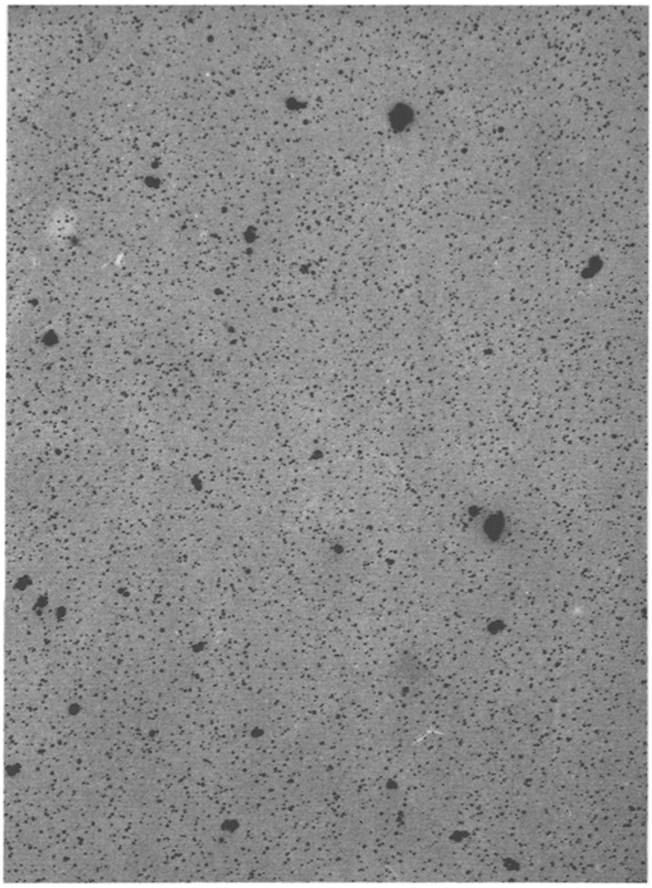

FIG. 5. Electron micrograph of the precipitated product. Enlargement: X117.600, reduced approximately 50%.

Analysis of the reaction product concerning the catalyst system. The reaction product obtained by the hydrogenation of oleic acid with silver oleate and cadmium oleate at 250 C and 250 atm. is a dark brown solution. On adding oxygen-free alcohol a black precipitation is observed, which, when dried, assumes a bluish metallic aspect. This precipitate dissolves readily in benzene, ether and paraffins. Except for the x-ray analysis, all other experiments were carried out with 5 mole % Ag and 2.5 mole % Cd.

X-ray analysis. An x-ray diffraction pattern of the reaction product solution shows a diagram of metallic silver (see Table II) with a broad silver line at $\Theta = 18.5 - 20.0°$.

Polarographic analysis. The product precipitated by alcohol and dried as well as the alcoholic filtrate were analyzed by polarography. The dried product contained mostly Ag and about 4.5% of Cd. No Ag was found in the filtrate.

Spectroscopy. Infrared analysis of the dried product, pressed to KBr to a pellet, showed a spectrum corresponding to an oleate.

TABLE I

Influence of Different Catalysts Systems on the Conversion and Selectivity of the Hydrogenation of Oleic Acid to Oleyl Alcohol

Cat-alsyst	Cat-alsyst	Ratio cat. mole %	% conversion acid to alcohol	% saturation of the d. bond	Solvent	Reaction time min.
Cu	....	5:0	96, 5	59	+	120
	Cd	5:2, 5	91, 5	0	+	120
	Cd	6, 1:2, 7	90	0	—	?
	Zn	5:2, 5	28	19	—	20
	Zn	5:2, 5	60	60	+	180
	Zn	5:5	73	70	—	60
	Ag	5:2, 5	65	55	+	120
	Hg	5:2, 5	0	0	+	240
	Co	6, 1:2, 7	71	97	—	21[1]
	Pb	5:2, 5	20	0	+	180
	Ce	5:2, 5	0	0	+	240
	Cr	5:2, 5	0	0	+	210
	Sn	5:2, 5	0	0	+	120
Ag	....	6, 1:0[1]	Fig. 1			
	Cd	6, 1:2, 7[1]	Fig. 1			
	Cd	5:2, 5	80	0	+	90
	Hg	6, 1:2, 7	37	45	—	?[1]
	Hg	5:2, 5	0	0	+	150
	Zn	5:2, 5	0	0	+	240
Zn	....	10:0	7, 5	5	—	60
	Cd	5:2, 5	7, 5	0	—	20
	Cd	5:2, 5	12, 5	0	+	240
	Hg	5:2, 5	10	0	+	240
Hg	Cd	6, 1:2, 7	Results randomly distributed[1]			
	Cd	5:2, 5	22	0	+	240
Co	....	6, 1:0	2, 5	10	—	20[1]
	Cd	6, 1:2, 7	2, 5	10	—	30[1]
Pb	Cd	5:2, 5	14, 6	0	+	180
Ni	....	5:0	0	65	—	240
	Cd	5:2, 5	2, 5	65	—	240
Ce	....	5:0	5	85	—	240
	Cd	5:2, 5	25	80	—	180
	Cd	5:2, 5	20	65	+	120
Cr	Cd	5:2, 5	15	0	+	240
Cd	....	100:0	58	0	—	20

[1] Experiments carried out on a rolling autoclave.

TABLE II

X-ray Diffraction Patterns of Silver (Θ_{Ag}) and Reaction Product Solution (Θ_{exp}), Using 11.2 and 5.6 Mole % of Ag and Cd Oleate Respectively in Oleic Acid. Debye-Scherrer Diagram. Straumanis Photograph. Exposure time: 4 hr With Al Folio. a = 4.086 Å

hkl	Θ_{Ag}	I	Θ_{exp}	I
111	19°06′	m	18°30′ 20°00′	m
200	22°12′	w	22°24′	w
220	32°18′	m	32°18′	w
311	38°42′	s	38°30′	w
222	40°54′	m	40°48′	w
400	49°03′	w		
331	55°12′	s		
420	67°36′	s		

Electron microscopy. The photograph obtained with an electron microscope (1) shows particles corresponding to an average diameter of 54 A (Fig. 5). This medium size may be taken as being the average primary particle size. The particles are found to be very well dispersed. The few dark patches in the photograph show agglomerates.

Hydrogenation reaction, using the precipitated reaction product. On adding the reaction product precipitated by alcohol to a mixture of oleic acid and cadmium oleate at the ratio Ag/Cd of 5/2.5 and reducing the whole in the paraffin solvent at 250 C and 200 atm. of hydrogen, a selective reaction takes place as in the case of copper. This precipitate retains its bluish metallic aspect and its hydrogenation capacities even if kept in the atmosphere.

Discussion. In the kinetic measurements, silver shows the same behavior as copper. The hydrogenation is not selective in the absence of cadmium.

Activation energy measurements by the chemisorption of H_2 on a silver film, determined by para-ortho hydrogen conversion, resulted in 2.68 kcal/mole in the range between 90 and 140 C (4). Other workers in the field, however, found 7.2 to 8.6 kcal/mole at 90 to 200 C (5), this being defined by the authors as the "apparent" activation energy due to partial sintering. The value of 14.1 kcal/mole for the activation energy on the ammonia-deuterium exchange reaction on a silver film at 271 C is another available figure (6). From this variety of results it is not possible to come to any direct conclusions concerning the reaction mechanism of the rate-determining step.

The heat of adsorption for the para-ortho hydrogen conversion (4), corresponded to half of the value found here (6.1 kcal/mole).

Although all the results are of about the same order of magnitude as those for the chemisorption of hydrogen, it is not unlikely that owing to the much smaller particles, which seem to be better dispersed, and to the larger amount of sites per unit surface area, a higher activation energy and activation enthalpy may be expected.

Water and acetic acid show an inhibitive effect on the reaction rate and on the final conversion, as in the case of copper.

From the analysis of the catalyst component of the reaction product it may be concluded that metallic silver is the active part of the catalyst for the hydrogenation. Fully comparable to the copper system, cadmium oleate will stabilize the silver sol.

It is a fairly satisfactory conclusion that silver gives rise to the same hydrogenating mechanism as copper, because: metallic silver as copper belongs to the Group IB metals; its work function is similar to that of copper (102.9 kcal/mole for Cu and 103.7 kcal/mole for Ag (6)); the percentage *d*-character (36%) is identical with copper (7); its crystal structure is identical with copper.

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