Hydrogenation of Unsaturated Fatty Acids to Unsaturated Fatty Alcohols: II. Kinetics and Mechanism of the Reaction Using Cu and Cd Oleates as Catalysts

J. D. RICHTER[1] and P. J. VAN DEN BERG, Laboratory for Chemical Engineering, Technological University Delft, The Netherlands

Abstract

The kinetics and mechanism of the Cu and Cd-soap-catalyzed hydrogenation of oleic acid have been studied. The reaction is first order in Cd and H_2, and also first order in Cu if the double bond is completely preserved during reduction of the carboxyl group to the hydroxyl group. It will deviate from this order if the selectivity is lower owing to an increased Cu concentration. The reaction rate-determining step is independent of the Cd concentration. Its activation energy, of 13.4 kcal/mole, corresponds to that of the chemisorption of hydrogen on Cu. Unsaturated and saturated fatty acids of the same chain length have the same reaction rate. A decrease of the chain length causes a decrease in the reaction rate and in the final degree of conversion. Water and low molecular weight acids have an inhibitory effect on the reaction. A reaction mechanism is proposed which is based on the assumption that cadmium oleate plays a double role: it stabilizes the copper sol and is intermediate for the hydrogenation.

Introduction

From the foregoing paper (1) it has been proved that metallic copper is the active part of the catalyst in a high-pressure hydrogenation of unsaturated fatty acids to unsaturated fatty alcohols, using Cu and Cd oleates as catalysts. In this paper a study of the kinetics of the reaction will be presented and a mechanism proposed for the catalyst and the reaction.

Experimental Procedures

The experiments were carried out batchwise in a rocking autoclave system of stainless steel (1). To eliminate the physical limitation of hydrogen diffusion in the solution and to ensure proper sampling at the beginning of the reaction, an inert solvent previously introduced into vessel C is saturated with hydrogen at the reaction temperature and at a hydrogen pressure which is about 50 atm. higher than the reaction pressure. From vessel B a certain amount of the reaction mixture is injected into vessel C.

The inert solvent used is a mixture of paraffins, consisting of 80% by weight of *n*-alkanes (from decane to tetradecane), and the rest includes branched and cyclic products. This saturated mixture is obtained by the hydrogenation of a urea adduct fraction of α-olefins. Its vapor pressure is low and does not hinder the chemical analysis.

The solution of hydrogen in the paraffin-acid mixture was determined at different acid concentrations at 250 C and 200 atm. The apparatus used was the same as that of the current experiments. The paraffin-acid ratio at point S of Figure 1 was selected. Then 100 ml of the paraffin mixture and 15 ml of oleic acid were heated to the specified temperature under

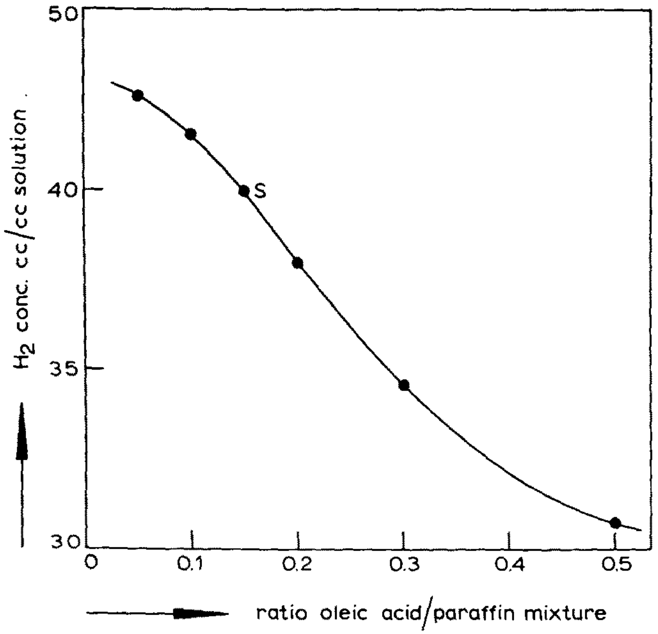

FIG. 1. Influence of the oleic acid/paraffin ratio on the hydrogen solubility. T: 250°C, P: 200 atm.

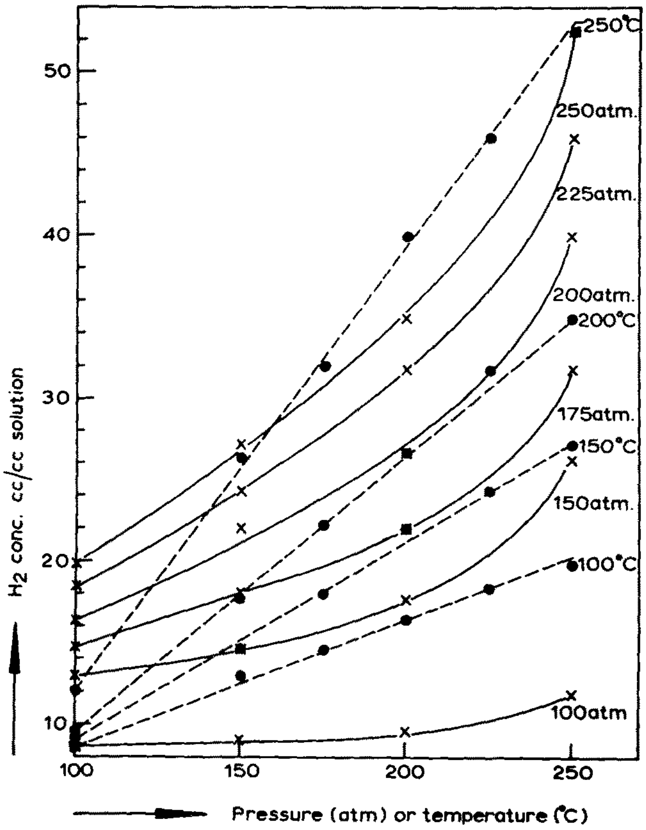

FIG. 2. Solubility of hydrogen in the oleic acid/paraffin mixture: 15/100cc.

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[1] Present address: Dutch State Mines, Geleen, The Netherlands.

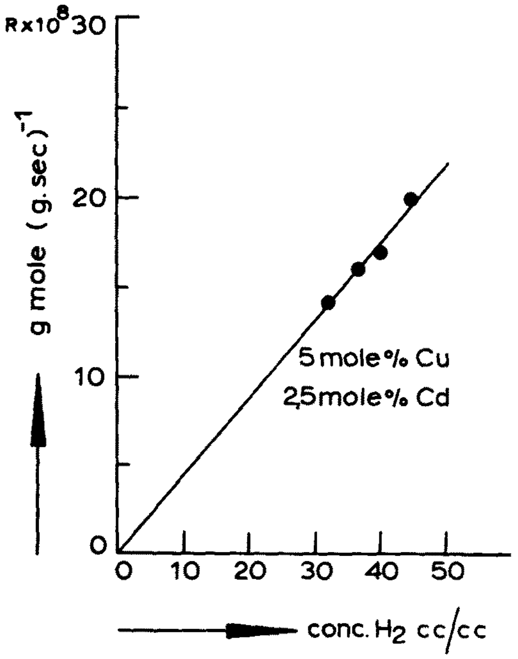


FIG. 3. Influence of the hydrogen concentration on the reaction rate.

different pressures and kept at these conditions for 2 hr. Sampling was effected through vessel F (1), which was kept at the reaction temperature. The dissolved gas was expanded, cooled and its volume measured in a gas burette. The hydrogen solubility in the paraffin-acid solution was plotted as a function of the pressure and temperature in Figure 2. At 250 C and 250 atm. the solubility is 40 ml H_2/ml solution, resulting in an amount equivalent to 1.8 times the amount necessary for the complete hydrogenation of acid to alcohol. The H_2 concentration remained constant throughout the experiment.

In all the experiments the solvent was saturated for 2 hr after reaching the desired pressure and temperature, whereupon the reaction mixture was injected.

Analysis

The samples taken during an experiment varied from 7 to 9 ml. First the metals were removed by agitation with a solution of 2N HCl, and the oil layer was then extracted by ether and washed with water. The etherous solution was dried on magnesium sulfate, filtered and evaporated in vacuum. From this solution the acid value, saponification value, hydroxyl value and iodine value were determined (2). As no hydrocarbons were detected in the experiments up to 300 C, the alcohol percentage could be obtained by substracting the amount of the ester plus acid from 100%.

Gas-chromatographic analysis were carried out in some cases, mainly to verify the distribution of the saturated and non-saturated compounds when the hydrogenation experiments included acids of lower molecular weight. In these cases a Becker gas chromatograph with a double flame ionization detector model 5003-2 and a flame convertor type 2032-E were used, with a copper column of 5 m length with an I.D. of 4 mm packed with 20% diethylene glycolsuccinate on 60–70 mesh chromosorb W (acid washed and DMCS treated). The conditions are as follows: carrier gas-nitrogen (28 ml/min); hydrogen (30 ml/min); air (300 ml/min); injection point temperature 190 C, initial temperature of the column 86 C during 6 min.; C_2 to C_{12} acids: programmation rate 4°/min; C_{12} to C_{14} acids: programmation rate 10°/min; final temperature: 200 C; velocity of the paper of the recorder 2 cm/min. The C_{12}, C_{14} and C_{18} acids had to be methylated and their high molecular weight esters transesterified, whilst the acids of lower molecular weight acids and their esters of high molecular weight were detected as such.

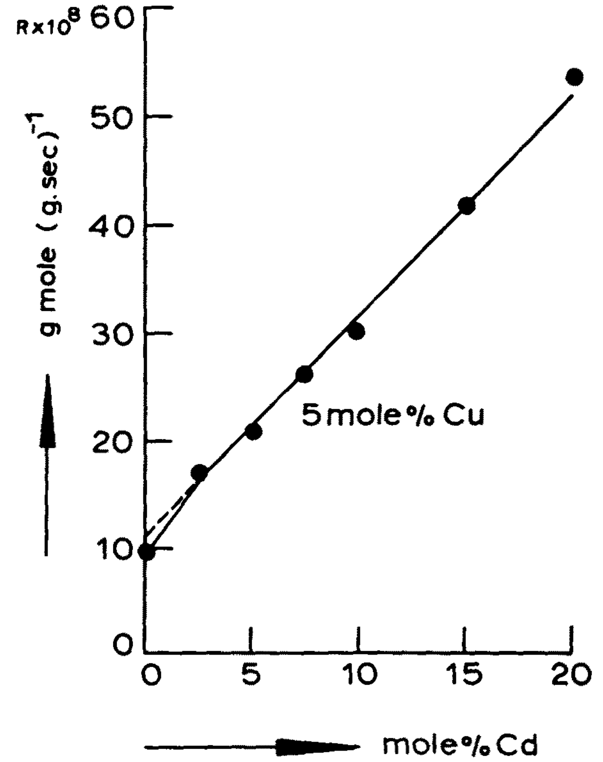


FIG. 4. Influence of the cadmium concentration on the reaction rate.

Raw Material

Oleic acid from different origins was used. However, no influence of the different purities was observed in the course of the hydrogenation reactions. The acid used in these series of experiments had the following values: Acid value (AV): 204; saponification value (SV): 206; iodine value (IV): 95, hydroxyl value (OHV): 0.

Preparation of the Metal-Soaps

Two methods were followed to prepare the metal-soaps. The first is the one already described in the preceding paper (1), the second was by treating the acid with a 10% alcoholic solution of NaOH on a water-bath. The Na salt was cooled on ice and an aqueous solution of the desired cation added (as salt solution) dropwise during vigorous stirring. The precipitate formed was filtered, washed with water and afterwards with small amounts of alcohol to eliminate the water, and was finally kept in vacuo to evaporate the alcohol residues.

It is very important that the metal-soap should be completely dry, otherwise no reproducible results will be obtained as the reaction may even be entirely inhibited.

Kinetics

The kinetic measurements were carried out with oleic acid, while Cu and Cd oleates were added as

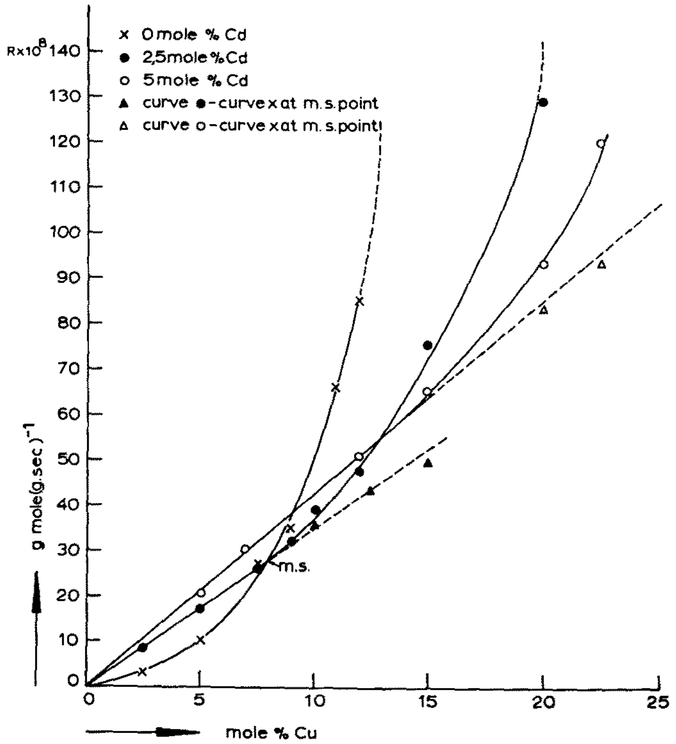


FIG. 5. Influence of the copper concentration on the reaction rate. M.s. maximum selectivity limit.

catalysts. The reaction rate is independent of the acid concentration in the studied range. The catalyst concentration is expressed in relation to the amount of oleic acid.

Analyzing the progression of the reaction, it was observed that in the beginning there is a sharp decrease in the acid concentration and increase in the ester concentration. The amount of alcohol increases slowly. When the ester concentration has achieved its maximum, the alcohol percentage increases sharply.

Influence of the hydrogen and cadmium concentration. Figures 3 and 4 show the influence of the H_2-concentration at 250 C and of the Cd concentration at 250 C and at 250 atm. Both show a first order character. The higher the Cd concentration the higher the ester content on completion of hydrogenation, which may be explained by the reaction:

$$A + CdOl_2 \rightleftarrows E + Cd(OH)_2$$

It may be mentioned that with the aid of x-ray diagrams $Cd(OH)_2$ was found in samples of the reaction product precipitated towards the end of the reaction, when more than 5 mole % of cadmium oleate was used.

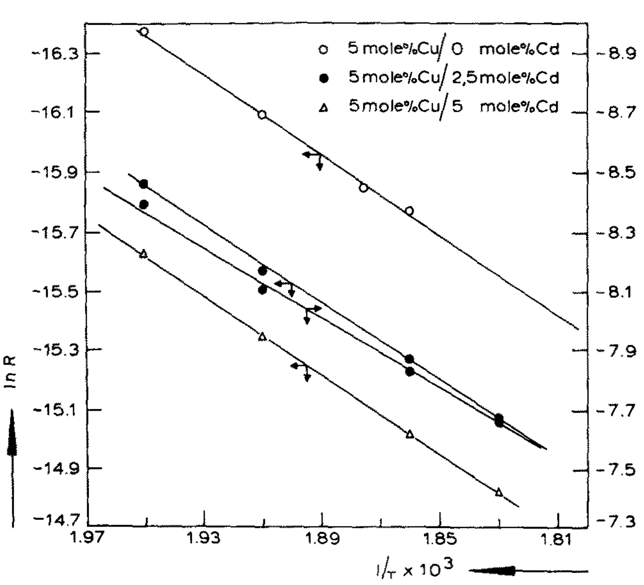


FIG. 6. Influence of the temperature on the reaction rate.

Influence of the copper concentration. Figure 5 shows two different aspects of the influence of the copper concentration at 250 C and 250 atm. In the absence of Cd this influence follows a parabolic curve, but in the presence of Cd it is directly proportional to the Cu concentration up to a certain value which roughly corresponds to the limit at which the reaction is still selective for the carboxyl group and bends then to a parabolic form.

Influence of temperature. In plotting the logarithm of the reaction rate against 1/T in the temperature range of 240 to 275 C, a straight line is obtained (Fig. 6). The slope is equivalent to an activation energy, E_a, of 13.4 kcal/mole and is independent of the cadmium concentration.

Influence of the chain length of the fatty acid. It is observed that saturated and unsaturated fatty acids have the same reaction rate when, for instance, erucic acid (C_{22}), oleic acid and 10-undecylenic acid are hydrogenated to their unsaturated alcohols in comparison with behenic (C_{22}), stearic and undecanoic acids. It seemed practical to study further the influence of the chain length by using the saturated acids and plotting the relative reaction rate or relative final degree of conversion as a function of the numbers of carbon atoms (Fig. 7). In every case 15 ml of the acid was injected into 100 ml of the solvent.

The addition of an aldehyde to a mixture of Cu and Cd soaps and their acid, did not show an inhibiting effect on the hydrogenation of the acid to the alcohol. The aldehyde will react to alcohol very slowly and the final conversion degree is low. It is probably partly dimerized at the commencement of hydrogenation. A versatic-9 acid (a mixture of highly

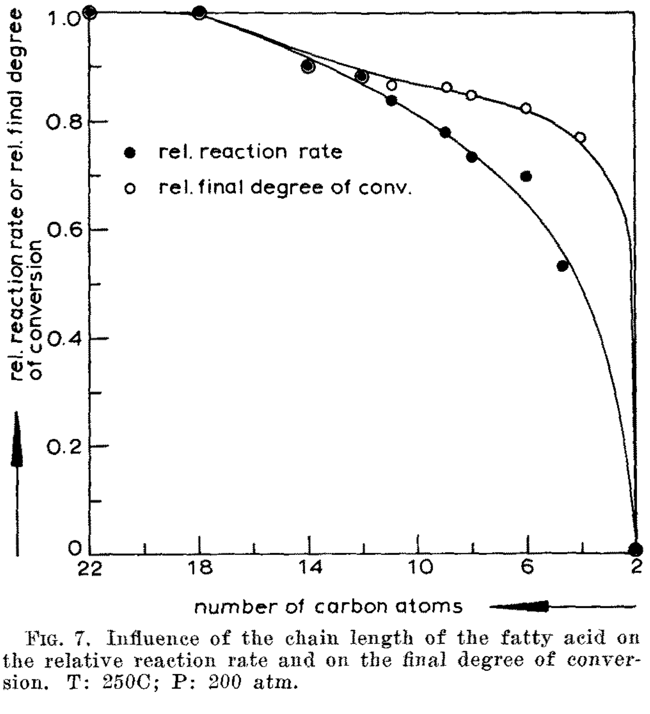


FIG. 7. Influence of the chain length of the fatty acid on the relative reaction rate and on the final degree of conversion. T: 250C; P: 200 atm.

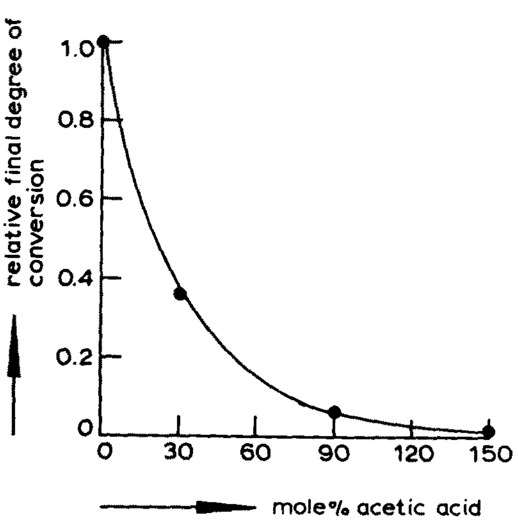


FIG. 8. Influence of the addition of acetic acid on the reaction rate, T: 250°C; P: 200 atm.

branched C_9 acids)[1] was likewise included in the experiments, but no reaction at all occurred.

Effect of adding a low-molecular acid and water. Acetic acid and water proved to have an inhibitive effect on the final degree of conversion (Fig. 8 and 9). The samples were reddish brown, but a turbidity was already observed after a few minutes in the reactor with 100 mole % H_2O. The percentage of added moles was based on the amount of oleic acid.

Discussion

The preceding paper (1) pointed out that a copper sol is the active part of the catalyst system and would therefore lend itself as an agent for the hydrogenation of acids to the corresponding alcohols. Although the presence of cadmium soap is indispensable for a selective reaction of the carboxyl group towards the double bond, the activation energy of the reaction is independent of the cadmium oleate concentration, which indicates that the adsorption or desorption of hydrogen on the copper catalyst is the most probable rate-determining step of the reaction.

The value of 13.4 kcal/mole found for the activation energy agrees well with values of 14.1 and 13 kcal/mole for the activated adsorption of hydrogen on reduced oxide powders of copper (3) and with the para-ortho hydrogen conversion on a copper film (4) respectively. This last-mentioned conversion indicates the chemisorption of hydrogen, not considering the mechanism which prevails (4,5). Other values for the activation energy of reactions on copper have been found, as for example, the hydrogen-deuterium reaction on foils (23.1 kcal/mole) (4), and on silica-supported metal (8 kcal/mole) (6). The ammonia-deuterium exchange reaction on evaporated films yielded values of 13.4 kcal/mole (7).

Experiments on desorption of hydrogen from copper powders, showed that sites equivalent to an adsorption energy up to 14 kcal/mole were desorbed at 150 C (8), which is in accordance with experiments carried out by heating the precipitate obtained by adding ethyl alcohol to the reaction product (9).

The enthalpy of activation ΔH* may be calculated by:

$$\Delta H^* = E_a\text{-}RT \qquad (10)$$

$$\Delta H^* = 12.4 \text{ kcal/mole.}$$

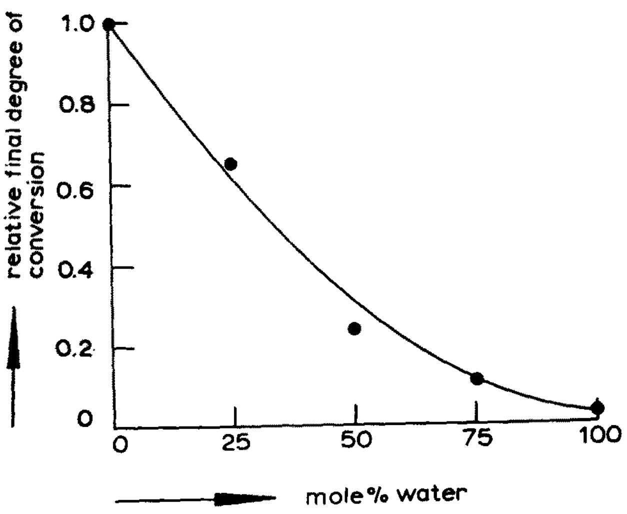
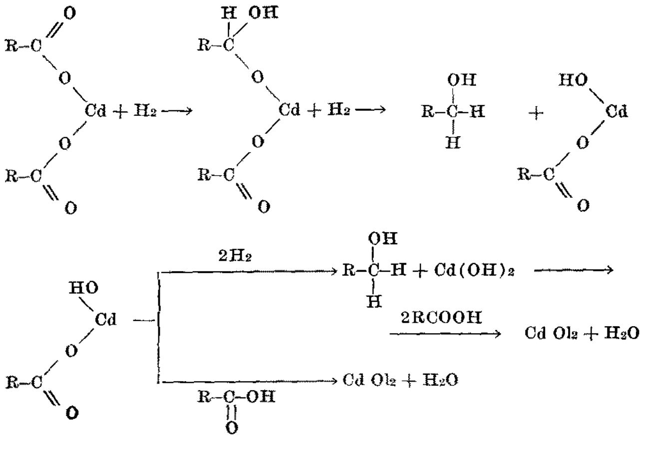


FIG. 9. Influence of the addition of water on the reaction rate, T: 250°C; P: 200 atm.

This value for the activation enthalpy is higher than the one found for the adsorption heat of the para-ortho hydrogen conversion (8 kcal/mole). It may also be compared to the values found by calorimetry techniques in the case of the activated adsorption of hydrogen on reduced copper oxides (9 kcal/mole) and copper powders (10 kcal/mole) (11). The small discrepancy may be due to a lower coverage of the catalyst surface.

From Figure 5 the following aspects become apparent: the reaction without cadmium at a certain concentration of copper is faster than in the presence of Cd; secondly, the reaction follows a first order rate in the presence of Cd, increasing in order rate only after reaching the maximum selectivity limit. Substracting the rates of the reaction with Cu only from those with Cu and Cd, starting from the maximum selectivity limit, a straight line is obtained which will follow the first order path (dotted line in the figure). This indicates an inhibitive character of the Cd soap, preventing the hydrogenation of the -COO group. But it was also verified that the reaction is first order in Cd. This might mean that selective hydrogenation would not be achieved by reaction with the acid directly, but via the Cd oleate. The smaller polar ion will be preferentially adsorbed to the polar surface, and the larger apolar oleate chain remains in the solution. Atoms or molecules when adsorbed on surfaces are much more accessible to the other molecules and hence far more reactive than in their original state. Termolecular reactions being ruled out in adsorbed films, the following mechanism is now proposed:



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[1] 56% of 2,2-diisopropylpropanoic acid, 29% of 2,3,4,4-tetramethylpentanoic acid and 15% of several highly branched C_9 acids.

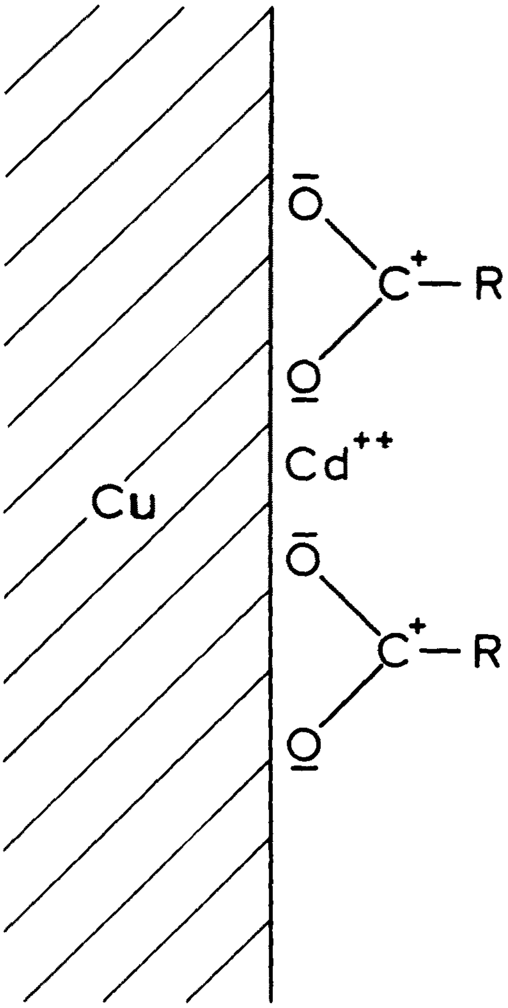

FIG. 10. The proposed mechanism for the Cu-Cd double layer.

The double layer would be formed as represented in Fig. 10.

As the reaction is independent of the acid concentration, it would seem quite reasonable to suppose that the ester (E) formed by the reaction between alcohol (A) and acid (Z), will not be hydrogenated. The equilibrium of the reaction:

$$Z + A \rightleftarrows E + H_2O$$

is established very quickly. At a certain stage of the reaction, when the acid concentration is very low and is needed to react with the Cd oleate intermediate or $Cd(OH)_2$, the equilibrium will shift to the left, achieving the final conversion at an ester content which depends upon the Cd oleate concentration.

The reaction rate of the selective reduction, being first order in Cu, Cd and H_2 is expressed as:

$$R = k(Cu)(Cd)(H_2)\ [1 + C/(k_1(Cd))]$$
$$R_{Cd} = k_1(Cd) + C \quad \text{(for cadmium only)}$$

Where C is the extrapolated reaction rate when the Cd concentration is nil, and R_{Cd} the reaction rate depending only upon the Cd concentration.

$$k = 5.3 \cdot 10^4\ (\text{g mole/g})^{-2}\ \text{sec}^{-1}$$
$$\left.\begin{aligned} k_1 &= 3.7 \cdot 10^{-3}\ \text{sec}^{-1} \\ C &= 1.2 \cdot 10^{-7}\ \text{g mole}(\text{g sec})^{-1} \end{aligned}\right\}\ \text{for 5 mole \% Cu}$$

For other values of the Cu-percentage the ratio C/k_1 is constant.

Figure 7 shows that the reaction rate and the final degree of conversion decreases with the chain length of the fatty acid. The same dependence on chain length holds good for the stabilization of sols (12). For example, oleic acid and stearic acid have the same stabilization effect on graphite suspensions in benzene but lower-molecular acids have a lesser effect. It may be concluded that cadmium soap of lower-molecular fatty acids would not stabilize the copper particles as well as it homologues longer chain compounds. Alcohols do not stabilize sols as well as acids of the same chain length (13). Water would inhibit the reaction by hindering the adsorption of the surface-active agent, in this case the Cd soap. Experiments pointed out that 5% of water added to an organosol could destroy it within 12 hr (14).

In the case where the reaction is not selective the double-bond saturation occurs in the first phase of the reaction. This is due to the reaction of adsorbed hydrogen of the non-stabilized particles with the double bond, followed by agglomeration. The coarser particles will settle and cease to be active owing to the fact that their surface is too small and the amount of adsorbed hydrogen negligible. It is known that the equilibrium coverage of hydrogen measured on a copper film is low (5).

No geometrical or positional isomerization takes place during selective hydrogenation, with or without the use of the paraffinic solvent (15).

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