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Dehydrohalogenation on Copper Catalysts

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The reactions of hexadecyl chloride on copper chromite, copper-on-silica, and Raney copper hydrogenation catalysts suspended in squalane have been studied in the temperature range 100–200°C. In the presence of hydrogen, dehydrohalogenation with the formation of hexadecene and adsorbed chlorine takes place. The total amount of hexadecene formed was found to increase with temperature. It is suggested that chemisorbed hydrogen takes part in the reaction mechanism. Similar results were obtained with hexadecyl bromide.

INTRODUCTION

The present paper reports some work carried out as part of an investigation of the poisoning effect of halogen-containing compounds on the copper-catalyzed hydrogenation of polyunsaturated fatty oils. Relatively few studies of the reactions of alkyl halogenides on metal surfaces have been published.

To our knowledge, the only one that includes copper metal is that of Anderson and McConkey (*1*). They studied the reactions of methyl chloride over a series of evaporated metal films and concluded that adsorption resulted in rupture of all carbon–chlorine bonds before any carbon–hydrogen bonds were broken. On several metals, including copper and nickel, methane was the only hydrocarbon product. Campbell and Kemball (*2*) have studied the catalytic hydrogenolysis of ethyl chloride and ethyl bromide on various evaporated metal films. The main reaction products were ethane and hydrogen halides, although ethylene was also formed on nickel and iron. It was shown that the hydrogen halides inhibited the reactions. The same authors (*3*) also showed that *tert*-butyl chloride reacts rapidly with hydrogen over nickel films at subzero temperatures to produce isobutene and isobutane. In a previous study of the poisoning effect of halogen-containing compounds on the nickel-catalyzed hydrogenation of polyunsaturated fatty oils (*4*), it was found that while vicinal dichlorides, 1,1-dichlorides, alkyl bromides, and alkyl iodides were powerful catalyst poisons, simple alkyl chlorides did not affect the catalyst activity. This was accounted for in terms of the competitive adsorption of the fatty acid double bonds and was recently verified by Heldal (*5*). In order to avoid such effects and also to simplify analysis, the present study was carried out with squalane as the liquid phase. Hexadecyl chloride was chosen as a model substance due to its low vapor pressure, thus minimizing losses due to stripping effects.

EXPERIMENTAL

The reactions were carried out in a 50-ml glass reactor equipped with a heating mantle and magnetic stirrer. The temperature was controlled by an Ether Mini temperature controller connected to a thermocouple inside the reactor. Hydrogen or nitrogen could be supplied through a capillary close to the bottom of the reactor. Injection of the reactant was performed through a septum at the top of the reactor. In a typical experiment, 20 g squalane and an amount of catalyst corresponding to 0.5% Cu (g Cu/100 g squalane) were charged into the reactor followed by evacuation and purging with ni-

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trogen. The temperature was raised to 170°C and the catalyst was reduced for 30 min in a slow (10 ml/min) stream of hydrogen. The temperature was then adjusted to the desired level followed by addition of the hexadecyl chloride. A water trap connected to the hydrogen gas outlet made it possible to determine whether hydrogen chloride was produced in the reactor and stripped off by the hydrogen gas. Filtered samples of the reaction mixture were analyzed by gas–liquid chromatography on a 1.75-m × 3-mm 3% Dexil 410 on 100/120-mesh Supelcoport column at 180°C. For separation of hexadecane and hexadecene, a column consisting of 12 cm 3% Dexil 410 on 100/120-mesh Supelcoport followed by 163 cm 10% SP-2340 on 100/120-mesh Chromosorb W AW operated at 120°C was used. Reagents: 1-hexadecyl chloride (zur syntese, 98%) and 1-hexadecyl bromide (zur syntese, 95%) were delivered by Merck. The copper chromite was Girdler G-89 containing about 39% Cu, 32% Cr, and 2.5% Mn. Raney copper (puriss) was obtained from Fluka AG. Copper-on-silica (15% Cu) was prepared according to Koritala (*6*). Silica gel, grade 951 with a specific surface area of 750 m^2/g, was obtained from W. R. Grace AB, Sweden. Squalane ($C_{30}H_{62}$) was supplied as pure grade by Koch-Light.

RESULTS

The reaction of hexadecyl chloride (HDCl) and hydrogen on various copper-based hydrogenation catalysts suspended in squalane was studied in the temperature range of 100–200°C at a hydrogen pressure of about 1 atm. GLC analysis of the liquid phase revealed that hexadecene (HDE) was the only hydrocarbon formed, i.e., a dehydrohalogenation was taking place.

The water in the water trap was analyzed for HCl by titration with $Hg(NO_3)_2$. In no case could HCl be detected. In some specially designed experiments the hydrogen flow was increased to 2.5 liters/min, passing into the liquid phase through a glass

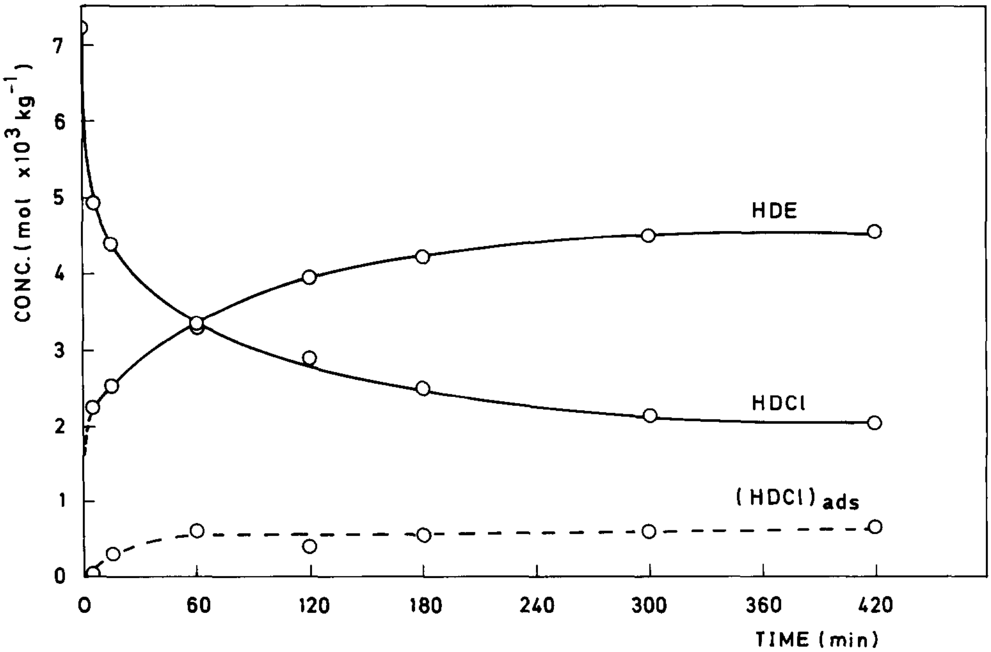


FIG. 1. Dehydrohalogenation of hexadecyl chloride (HDCl) on copper chromite at 100°C. Concentrations of HDCl and hexadecene (HDE) versus time. 0.5% Cu in 20 g squalane at 1 atm H_2. $C^0_{HDCl} = 7.5 \times 10^{-3}$ mole kg^{-1}. $(HDCl)_{ads} = C^0_{HDCl} - (C_{HDCl} + C_{HDE})$.

sinter filter in order to obtain finely dispersed gas. Even so, no HCl could be detected in the water trap. This result is in striking contrast to previous findings with Ni catalysts (*4, 5*) where the amount of HCl formed was proportional to the decrease in the concentration of the organic chloride.

Figure 1 illustrates the course of the reaction on a copper chromite catalyst at 100°C. The catalyst was reduced for 30 min at 170°C while suspended in the squalane phase prior to addition of HDCl. The broken curve represents the difference between the initial concentration of HDCl and the sum of the concentrations of HDCl and HDE versus time, and is assumed to indicate the amount of HDCl adsorbed on the catalyst. This material balance is based on the fact that no HCl was formed in the reaction and on separate experiments which showed that the modest stream of hydrogen through the reaction mixture did not cause any noticeable loss of HDCl in the course of 120 min at 170°C. Neither does it appear that HDE is lost, judging from the HDE curve of Fig. 1 and that at 200°C in Fig. 2.

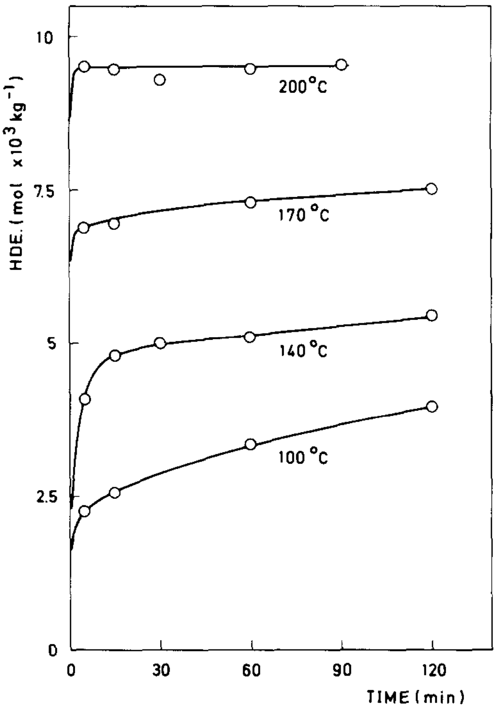


FIG. 2. Concentration of hexadecene (HDE) versus time at various temperatures. 0.5% Cu (copper chromite) in 20 g squalane at 1 atm H_2. $C^0_{HDCl} = 7.5 \times 10^{-3}$ mol kg^{-1} (100 and 140°C) and 12.5×10^{-3} mol kg^{-1} (170 and 200°C).

Increasing the initial concentration of HDCl by 50% had no visible effect on the amount of HDE produced. It thus appears that the catalyst sites responsible for dehydrohalogenation are completely poisoned by adsorbed chlorine.

Figure 2 shows the effect of temperature on the formation of HDE on the copper chromite catalyst.

Table 1 summarizes some experimental data at the various reaction temperatures. The total amount of chlorine (ΣCl) adsorbed (mmol/g CuCr) either as Cl atoms or as HDCl, when the rate of dehydrohalogenation was approximately zero, is given in the last column. ΣCl is set equal to the sum of HDE and $(HDCl)_{ads}$, as HDE and adsorbed chlorine atoms are formed in equimolar amounts.

Figures 3 and 4 illustrate the course of the reaction at 170°C on a copper-on-silica and a Raney Cu catalyst, respectively. It is seen that the copper-on-silica catalyst is by far the most efficient dehydrohalogenation catalyst in terms of the amount of HDE formed per unit weight of copper before the catalyst is completely poisoned.

TABLE 1

Final Concentration of HDE and $(HDCl)_{ads}$ and Corresponding Total Amount of Cl Adsorbed per Gram Catalyst at Various Temperatures

T (°C)	HDE[a]	$(HDCl)_{ads}$[a]	ΣCl[b]
100	4.5	0.6	0.40
140	5.5	0.8	0.49
170	7.6	1.1	0.68
200	9.5	1.8	0.88

[a] Concentrations in millimoles per kilogram.

[b] ΣCl = HDE + $(HDCl)_{ads}$ in millimoles per gram CuCr.

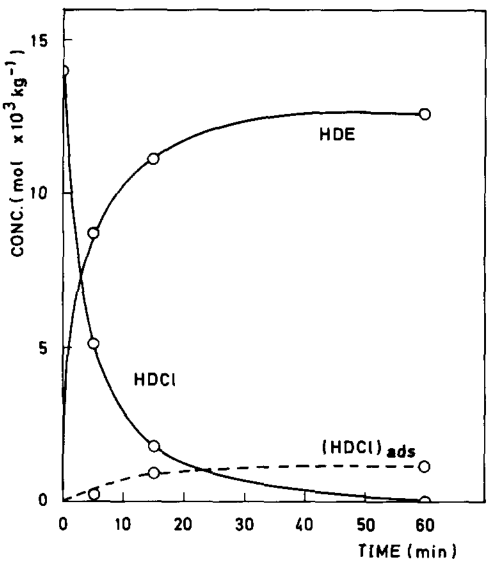


FIG. 3. Dehydrohalogenation of hexadecyl chloride (HDCl) on copper-on-silica at 170°C. Concentrations of HDCl and hexadecene (HDE) versus time. 0.5% Cu in 20 g squalane at 1 atm H_2. $C^0_{HDCl} = 14 \times 10^{-3}$ mol kg^{-1}. $(HDCl)_{ads} = C^0_{HDCl} - (C_{HDCl} + C_{HDE})$.

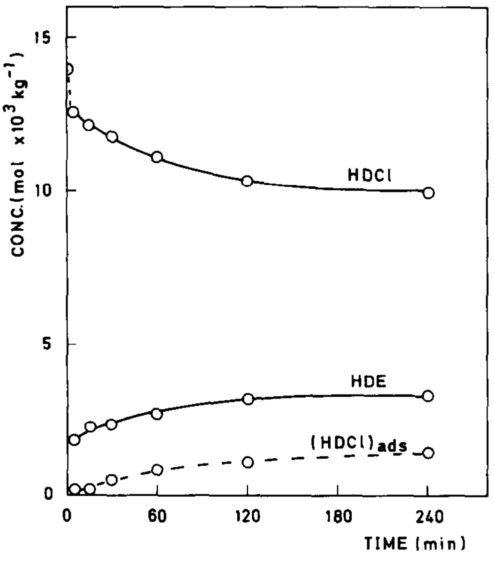


FIG. 4. Dehydrohalogenation of hexadecyl chloride (HDCl) on Raney Cu at 170°C. Concentrations of HDCl and hexadecene (HDE) versus time. 0.5% Cu in 20 g squalane at 1 atm H_2. $C^0_{HDCl} = 14 \times 10^{-3}$ mol kg^{-1}, $(HDCl)_{ads} = C^0_{HDCl} - (C_{HDCl} + C_{HDE})$.

A series of experiments carried out with hexadecyl bromide gave results which were qualitatively similar to those obtained with hexadecyl chloride.

The experimental procedure involves a reduction of CuO or $CuCr_2O_4$ to metallic Cu at 170°C and 1 atm H_2 for 30 min, as it seems fairly well established that metallic Cu is the active catalytic species in hydrogenation reactions (*7–10*). That this is the case also for the dehydrohalogenation reaction was verified in an experiment conducted in nitrogen atmosphere with unreduced copper chromite (0.5% Cu) and 2.7×10^{-4} mol HDCl in 20 g squalane at 170°C. In this case no HDE was formed. However, a slight decrease in the concentration of HDCl, corresponding to a loss of about 2×10^{-5} mol HDCl, was observed after 100 min. Apparently, even the unreduced copper chromite is able to adsorb some HDCl. A similar result was obtained with the copper-on-silica catalyst.

Although it may seem unlikely that the dehydrohalogenation reaction taking place on a reduced copper catalyst should require the presence of hydrogen, this was found to be the case. Figure 5 illustrates an experiment in which the copper chromite catalyst was prereduced for 3 hr at 170°C in a stream of H_2/N_2, followed by evacuation at 0.01 mm Hg for another 3 hr in order to remove adsorbed hydrogen. The pressure was restored with nitrogen and the catalyst was transferred to the reactor under a nitrogen blanket. It is seen that in this case only a small amount of hexadecene is formed. An almost identical result was obtained with the copper-on-silica catalyst.

DISCUSSION

The main reaction products resulting from the copper-catalyzed dehydrohalogenation of hexadecyl chloride (HDCl) appear to be hexadecene (HDE) and equimolar amounts of chlorine, as no noticeable amounts of HCl could be detected. It is furthermore well established (*11, 13*) that

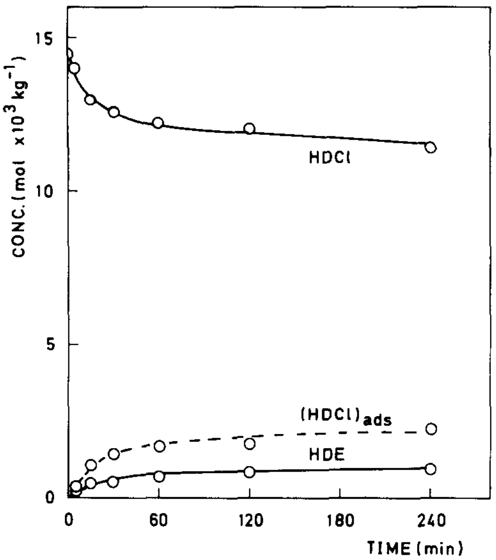


FIG. 5. Dehydrohalogenation of hexadecyl chloride (HDCl) on reduced copper chromite at 170°C in nitrogen atmosphere. Concentrations of HDCl and hexadecene (HDE) versus time. 0.5% Cu in 20 g squalane. $C^0_{HDCl} = 14.5 \times 10^{-3}$ mol kg^{-1}. $(HDCl)_{ads} = C^0_{HDCl} - (C_{HDCl} + C_{HDE})$.

the chlorine formed remains adsorbed on the catalyst surface at the temperatures in question.

From Fig. 1 it is seen that the rate of formation of HDE is approximately zero after a reaction time of 420 min at 100°C. Apparently, the catalyst is at this point almost completely poisoned towards further dehydrohalogenation.

It is furthermore seen that after a short period of very rapid reaction, in which about 40% of the final amount of HDE is formed, the rate decreases quite abruptly to a substantially lower value. This effect is even more pronounced at higher temperatures, as is evident from Fig. 2. Thereafter the rate proceeds to decrease in a manner to be expected from the fact that the poisoned fraction of the catalyst surface increases proportionally to the amount of HDE formed. This reaction pattern may perhaps be ascribed to the presence of various types of catalytic sites, the activities of which are widely different. In the first stage of the reaction, dehydrohalogenation mainly takes place on the most active "Type 1" sites. When the point is reached where the rapid decrease in rate is evident, the major part of the Type 1 sites is poisoned by adsorbed chlorine and the reaction proceeds on the less active "Type 2" sites. Due to the high rate of reaction in the first stage, the decrease in rate due to the increasing poisoning of Type 1 sites is not easily observed.

From Fig. 2 it is seen that both the rate and the amount of HDE formed in the first stage increase with increasing temperature, whereas the opposite is true for the second stage. At 200°C the contribution from the second stage is almost negligible. While the increase in rate may be ascribed to the apparent activation energy of the reaction, the increase in the amount of HDE formed during the first stage implies that the number of Type 1 sites increases with temperature. This follows from the fact that HDE and adsorbed chlorine are formed in equimolar amounts and it appears unlikely that adsorbed chlorine is subject to a rapid surface migration from Type 1 to Type 2 sites. The decrease in HDE formed in the second stage at higher temperatures similarly indicates that the number of Type 2 sites decreases with increasing temperature.

For the same reasons, the increase with temperature in the total amount of HDE formed (Table 1) indicates that the total number of catalytic sites available for dehydrohalogenation also increases. It thus appears that the distribution of the catalytic sites between various levels of activity depends on temperature.

From Table 1 it is seen that the amount of HDCl adsorbed on the catalyst increases with temperature, contrary to what would be expected for an adsorption. Within the time scale of the experiments, this HDCl appears to remain adsorbed on the surface without further reaction. It seems that even a third type of catalyst site is present. Regarding the possibility of a positive heat of adsorption as unlikely, it appears that the number of these sites increases with temperature. Although the Cr_2O_3 known to be present (*8*) in the copper chromite catalyst may play a role, it cannot be entirely responsible, as some "permanently" adsorbed HDCl is also found with the copper-on-silica and the Raney Cu catalysts.

Figures 3 and 4 illustrate that the dehydrohalogenation reaction is not specific for the copper chromite catalyst. From Fig. 3 it is seen that the copper-on-silica catalyst distinguishes itself from the other catalysts on two accounts. For one thing, the abrupt change in the rate of formation of HDE at low reaction times appears to be absent. A possible explanation may be that the Type 2 sites, if present at all, are converted to Type 1 sites at this temperature. Experiments carried out at lower temperatures might resolve this question. Secondly, the concentration of HDCl is seen to be negligible after about 60 min. Thus when compared on a weight basis, the copper-on-silica catalyst is by far the most effective dehydrohalogenation catalyst. It is interesting to note that this catalyst was also found to be more active than the copper chromite in the hydrogenation of fatty oils (*5*).

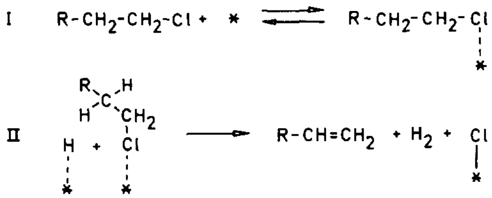
From Fig. 4 it is seen that a relatively modest amount of HDE is formed on the Raney Cu catalyst. This is not unexpected in view of the relatively low surface areas of such catalysts.

Earlier studies of the reaction of alkyl chlorides with hydrogen on nickel surfaces (*2, 3, 5*) have revealed that alkenes as well as alkanes are formed. In contrast to the present results with copper catalysts, it was also shown that on nickel, HCl is produced in an amount that is almost proportional to the decrease in the concentration of the organic chloride. Assuming that alkanes result from hydrogenation of alkenes produced by dehydrohalogenation, the absence of alkane formation over copper catalysts is understandable as it is a well-established fact that copper catalysts do not hydrogenate olefinic double bonds.

In Figs. 1, 3, 4, and 5 the curves denoted $(HDCl)_{ads}$ are obtained from a material balance in which the possible adsorption of hexadecene was neglected. Recently Lidefelt (*12*) showed that olefins do adsorb on copper catalysts, although no hydrogenation takes place. In spite of this, it seems unlikely that hexadecene is able to compete successfully with hexadecyl chloride for the active sites on the catalyst. This is supported by the results obtained in a recent study of the effect of chlorinated compounds on the copper chromite-catalyzed hydrogenation of soybean oil (*13*). Here it was shown that chlorinated compounds in amounts corresponding to about 3×10^{-3} mol Cl/kg oil adsorbed rapidly and quantitatively on copper chromite (0.5%) in spite of the large concentration of polyunsaturated acyl groups. It was also shown that the reduction in catalyst activity per molecule Cl adsorbed decreased with increasing coverage. Although other explanations may be possible, such selective poisoning seems to support the view that the copper surface is distinctly heterogeneous with respect to the activity of the various catalytic sites.

From a mechanistic point of view it is interesting to note that the dehydrohalogenation mechanism apparently involves participation of chemisorbed hydrogen. Figure 5 shows that when a prereduced copper chromite catalyst is reacted with hexadecyl chloride in a nitrogen atmosphere, the amount of hexadecene formed is only about 15% of that obtained in the presence of hydrogen. This dehydrohalogenation may either be due to some "irreversibly" adsorbed hydrogen (*14*) remaining on the catalyst after evacuation or to the presence of some catalytic sites that are able to promote dehydrohalogenation without the participation of hydrogen. As expected, a noticeable amount of HDCl remains adsorbed on the catalyst, as indicated by the broken curve in Fig. 5.

Although the experimental results indicate that chemisorbed hydrogen participates in the reaction mechanism, no information as to the specific role of hydrogen has been obtained. The following mechanism may, however, be one possibility:



It is entirely possible that Reaction II includes intermediate steps as, for instance, a rupture of the carbon–hydrogen bond. Campbell and Kemball (*2*) suggested alternative mechanisms for the formation of ethylene from gaseous ethyl chloride on nickel films in the presence of hydrogen at 184–343°C. These mechanisms were based on a reversible adsorption of ethyl chloride as the first step, but did not include participation of chemisorbed hydrogen in the surface reactions. In view of the present results on alkene formation over copper catalysts, however, the possibility that a similar mechanism is operating over nickel cannot be entirely excluded.

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