♣ Chlorine-Containing Compounds as Copper Catalyst Poisons

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ABSTRACT

The effect of chlorine-containing substances on the rate of the copper chromite-catalyzed hydrogenation of soybean oil has been investigated. Using chlorinated soybean oil as a model substance, it was found that amounts corresponding to 25, 50 and 90 ppm Cl markedly decreased the rate of hydrogenation when added to a 0.5% Cu run at 170 C. Similar effects were found with various chlorinated alkanes. It was also found that the refined and bleached soybean oil contained noticeable amounts of an unknown catalyst poison. This made if difficult to calculate specific poisoning constants for chlorine (% Cu/ppm Cl). Attempts have been made to estimate minimal values for this constant.

INTRODUCTION

Fatty oils usually contain minor amounts of impurities that can act as hydrogenation catalyst poisons. This is especially true for fish oils which may sometimes contain substantial quantities (20-100 ppm) of sulfur or halogens (1), even after refining and bleaching. Although the effect of such poisons on the activity of nickel catalysts has been studied by a number of authors (2-7), similar studies with copper catalysts are few; A comprehensive investigation of the deactivating effect of a number of the minor components usually found in soybean oil was carried out by Koritala (8). Using a copper-on-silica catalyst, he found that most of the compounds studied reduced the rate of hydrogenation. Halogen-containing compounds were, however, not included in this work. In a recent study (9) of the reaction of alkyl chlorides over various copper catalysts, a dehydrohalogenation with the formation of adsorbed chlorine was found to take place. In this work, the effect of some chlorine-containing model compounds on the rate of the copper chromite-containing model compounds on the rate of the copper chromite-catalyzed hydrogenation of soybean oil is investigated.

Catalyst

The catalyst was a copper chromite (G-89) supplied by Girdler-Südchemie, containing about 39% Cu, 32% Cr and 2.5% Mn.

Materials

Refined and bleached soybean oil (IV=135) was delivered by A/S Denofa & Lilleborg Fabriker, Norway. Chlorinated soybean oil was prepared according to King (10). Mono- and dialkyl chlorides were supplied by Merck. 1,4-Dioxane (spectroscopic grade) was delivered by Kock-Light.

Hydrogenation

Hydrogenations were carried out at 170 C in an all-glass reactor charged with 30 g oil. Hydrogen was supplied through a glass sinter-ring situated at the bottom of the reactor at a rate of 2.8 L/min. The unreacted hydrogen was recirculated over an activated carbon column. A detailed description of the apparatus and the experimental procedure is given elsewhere (5).

Analytical Methods

Analysis of chlorine by combustion (E. Bladh, private communication) was carried out by injecting a dioxane-diluted oil sample into a combustion chamber where it burned in a pure oxygen atmosphere. The combustion gases were collected in a water trap and titrated with $Hg(NO_3)_2$ (1 mL equivalent to 50 μg chlorine) with diphenylcarbazone (0.5% in isopropanol) as indicator. The results were corrected for the chlorine content of dioxane (3-5 ppm). Reproducibility was generally better than ±10% for concentrations higher than 10 ppm Cl.

RESULTS

The effect of chlorine-containing substances on the activity of the copper chromite catalyst has been investigated by determining the rates of hydrogenation of soybean oil in the presence of small amounts of chlorinated soybean oil (Cl-SBO). This compound was chosen as a model substance due to its low vapor pressure. At the high temperature and the vigorous hydrogen flow through the reactor, lower molecular weight substances such as alkyl chlorides may easily give erroneous results due to stripping effects.

The hydrogenation reaction was followed by a semicontinuous recording of hydrogen consumption vs time. Figure 1 shows the effect of increasing amounts of Cl-SBO, expressed as ppm Cl, on the course of the hydrogenation of soybean oil. Each curve represents the average of three parallel runs. The standard deviation at various points is indicated.

Quantitatively, the poisoning effects are most easily seen by comparing rates of hydrogenation at constant iodine values, i.e., at approximately equal fatty acid compositions. Figure 2 gives the differential rates of hydrogenation, obtained graphically from Figure 1, as a function of the iodine value. The chlorine content of the oil was determined as a function of time for the various runs. Table I gives mean
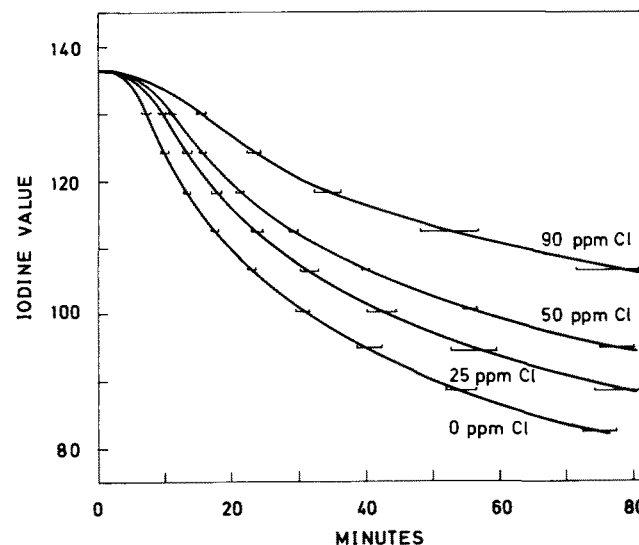

FIG. 1. Hydrogenation of soybean oil with copper chromite in the presence of various amounts of chlorinated soybean oil. 0.5% Cu, 170 C, 1 atm H_2.
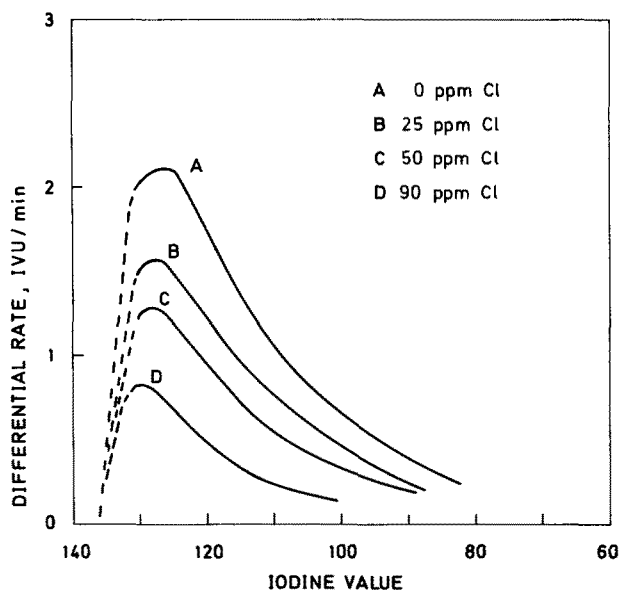
FIG. 2. Differential rates of hydrogenation vs iodine value with various amounts of chlorinated soybean oil added. 0.5% Cu, 170 C, 1 atm.
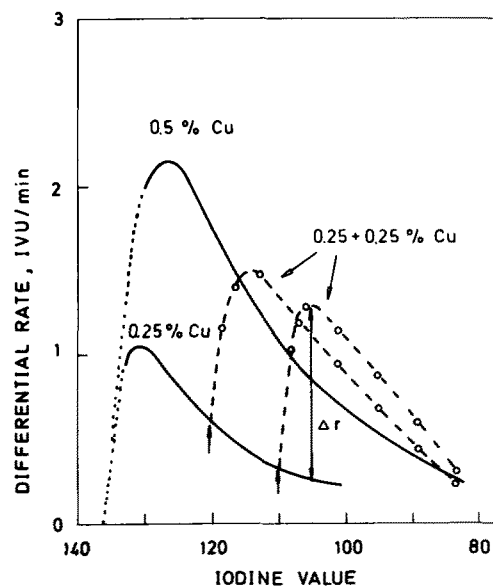

FIG. 3. Post-addition of 0.25% Cu to parent run with 0.25% Cu. In two separate runs, 0.25% Cu was added at IV = 120 and 110, respectively. The run with 0.5% Cu is included for comparison. Soybean oil, 170 C, 1 atm H_2.

TABLE I

Chlorine Content of the Oil as a Function of Time

time (min)	Cl (ppm)		
	25	50	90
0	25.7	49.1	92.9
3	25.4	43.4	85.6
6	7.0		53.7
10		9.3	23.7
20		7.1	7.1
60	4.9	3.3	5.90

values based on three parallels for each sample. The deviation from the mean value were generally within 3-18%, highest at the lowest concentrations of chlorine. The values for t = 0 represent samples taken after temperature equilibration in the reactor immediately prior to the addition of catalyst.

The rate of hydrogenation of the Cl-SBO poisoned oil to that of pure soybean oil, both rates taken at the same iodine value, is equal to the relative catalyst activity ($a_{r,Cl}$) at that iodine value. By comparing $a_{r,Cl}$ with the amount of chlorine adsorbed on the catalyst, the specific poisoning effect of chlorine (% Cu/ppm Cl) may be estimated. However, if the soybean oil contains some unknown catalyst poison, this calculation may be somewhat obscure, especially if the adsorption of the unknown poison is comparatively slow.

Koritala (8) has shown that refined and bleached soybean oil may contain substantial amounts of catalyst poisons. This finding has on several occasions been confirmed in our laboratory. Furthermore, large variations have occurred between various batches of oil.

The soybean oil used in our work was therefore checked for the presence of catalyst poisons by the catalyst "post-addition" technique (5). Figure 3 shows the results of two such experiments. To a run with 0.25% Cu was added another 0.25% Cu at an iodine value of 120. In a second

experiment, the 0.25% Cu was added at an iodine value of 110. The dashed lines in Figure 3 illustrate the increase in the rate of hydrogenation in the two cases. For comparison, the run with 0.5% Cu is included in the figure. It is seen that, in both cases, the maximal rates obtained after catalyst addition far exceed that of the run with 0.5% Cu added initially, or twice that of the parent run with 0.25% Cu. It is therefore evident that the refined and bleached soybean oil contains a considerable amount of catalyst poison.

Various low molecular weight chlorine containing compounds such as 1-chlorohexadecan, 1-chlorodecan, 1,8-dichloroctan, 1,6-dichlorohexan and 1,2-dichloroethane were also examined for their catalyst poisoning efficiency. Due to their comparatively high vapor pressures, quantitatively reliable results could not be obtained, as large amounts were shown to be stripped off the reaction vessel. However, the results of these experiments left no doubt about the ability of those compounds to poison the copper catalyst.

DISCUSSION

Figure 2 shows that the presence of ppm amounts of chlorinated soybean oil (Cl-SBO) markedly reduces the rate of the copper chromite-catalyzed hydrogenation of soybean oil. The results obtained with other chlorine-containing substances show that the poisoning effect is not specific for the Cl-SBO.

In a previous work (9), the reaction of 1-chlorohexadecan over various copper catalysts suspended in squalane was investigated in the presence of hydrogen. A dehydrohalogenation with the formation of hexadecene and adsorbed chlorine was found to take place. It may safely be assumed that the same reaction is taking place in the present hydrogenation experiments. The analytical results presented in Table I support this assumption. It is seen that the major part of the chlorine is removed from the liquid phase after about 20 min.

Poisoning effects may, in some cases, be quantified by so-called specific poisoning constants. In the present case, such a constant, expressed as % Cu poisoned/ppm Cl adsorbed, could be calculated from the curves in Figure 2 pro-

vided that (a) the reduction in catalyst activity per molecule of Cl adsorbed is independent of surface coverage and (b) other catalyst poisons are not present. Neither condition seems to be fulfilled in the present experiments. The surface of the copper-chromite has previously (9) been found to be distinctly heterogeneous with respect to its activity toward dehydrohalogenation. The same may well be the case for the hydrogenation reaction.

Furthermore, as is evident from Figure 3, a significant amount of unknown catalyst poisons seems to be present in the refined and bleached soybean oil. A few simple calculations may serve to illustrate this. With reference to Figure 3, it may be assumed that the increase in rate (Δr) caused by addition of 0.25% Cu to the parent run with 0.25% Cu approximately represents the rate that can be obtained at that iodine value with an amount of fresh, unpoisoned catalyst corresponding to 0.25% Cu. The activity of the parent run catalyst relative to that of fresh, unpoisoned catalyst is then $a_r = r_{0.25}/\Delta r$. According to this definition, a_r is a measure of the deactivating effect of the unknown poison present in the refined and bleached soybean oil. The value of a_r may depend on both the quality of the oil, the amount of catalyst present and the time of contact between catalyst and oil.

The two post-addition experiments in Figure 3 give values of a_r equal to 0.33 and 0.26 at IV=115 and 105, respectively. It appears that at an IV=115, corresponding to a hydrogenation time of about 30 min, the unknown poison is still being adsorbed. For the 0.5% Cu run, the relative catalyst activity at IV=105 may similarly be estimated to be $a_r = r_{0.5}/2\Delta r = 0.4$. The higher value as compared to the 0.25% Cu run may be due to the shorter time of contact between catalyst and poison (larger hydrogenation rate) or it may be related to the total amount of catalyst poison present in the soybean oil. Although both conditions a and b above appear to be violated in the present system, the curves in Figure 2 may be used to estimate the order of magnitude of the specific poisoning constant (K_{Cl}) for chlorine on the copper chromite catalyst. In order to do this, one has to apply the undoubtedly erroneous assumption that the catalyst surface is uniform with respect to the activity of the catalytic sites, independent of the coverage of the unknown poison. At an IV=105, the total catalyst activity of the 0.5% parent run ($a_r = 0.4$) should correspond to 40% of 0.5% unpoisoned copper, i.e., to 0.2% Cu. Values of K_{Cl} may then be calculated from the equation:

$$K_{Cl} = 0.2(1 - a_{r,Cl})/\Delta(\text{ppm Cl}),$$

where $a_{r,Cl}$ is the relative activity of a chlorine-poisoned run, equal to the ratio of the rate of the chlorine-poisoned run to that of the parent run, both rates taken at an iodine

TABLE II

Specific poisoning Constant for Chlorine on Copper Chromite at 170 C

Cl (ppm)	Δ(ppm Cl)	$a_{r,Cl}$[a]	K_{Cl} (% Cu/ppm Cl) at IV = 105
25	20.8	0.69	0.0030
50	45.8	0.48	0.0023
90	87	0.18	0.0019

[a]Relative catalyst activity in chlorine-poisoned soybean oil, obtained from differential rates of hydrogenation at IV = 105.

value of 105. Δ(ppm Cl) is the amount of chlorine adsorbed according to Table I.

Table II gives the values of K_{Cl} calculated from the above equation for the runs with 25, 50 and 90 ppm Cl, respectively. It is seen that the values for K_{Cl} decrease with increasing amount of chlorine, i.e., the poisoning is selective. As already stated, the assumption of a uniform catalyst surface is apparently not a good one. The values of K_{Cl} must therefore be considered as absolute minimal values for the given amounts of chlorine adsorbed. The deviation from the true values, i.e., the values that would have been obtained in the absence of the unknown poison ($a_r = 1$), obviously depends on the relative magnitude of the activity of the catalytic sites covered with the unknown poison, and may also be influenced by a competitive adsorption between the two types of poison.

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