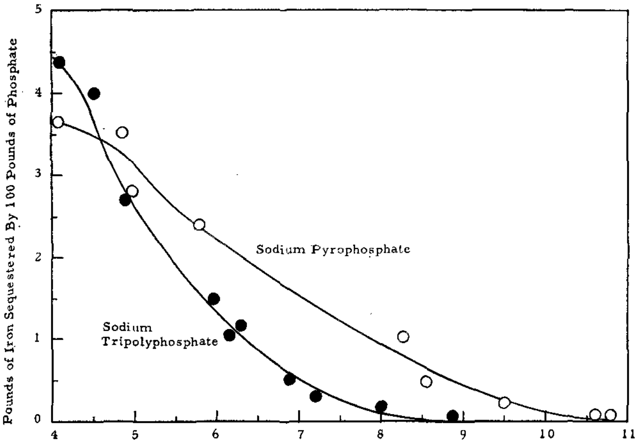

FIG. 2. Sequestration of Iron (II).

ing the stability constants, the stability constant for ferric ethylenediamine tetraacetate (EDTA) was determined and found to be:

$$\frac{(Fe^{3+})(EDTA^{4-})}{(FeEDTA^{-})} = 10^{-26.7\pm0.4} \qquad (6)$$

as compared with a literature (6,8) value of $10^{-25.1}$, obtained with more sophisticated methods. The agreement suggests that our assumptions are not grossly in error.

Ferrous Sequestration. The results for ferrous iron sequestration, shown in Figure 2, were obtained by allowing 1000 ppm of iron from $FeCl_2$ to come to equilibrium with 5000 ppm of sodium polyphosphates at various pH values.

Many authors listed in reference (2) found the solubility product of ferrous hydroxide to be in the range of 10^{-12} to 10^{-21}, depending on time of equilibration and degree of oxidation of ferrous ions. Our data cannot be rigorously interpreted with these values because in the pH region of 2–8, we found less dissolved iron in the presence of polyphosphates or EDTA than would be predicted from the solubility product of the ferrous hydroxide by itself. This must lead us to conclude that, though not detectable, some ferrous oxidation took place in our system leading to the formation of the more insoluble ferrosic hydroxides, $Fe(OH)_2 \cdot \times Fe(OH)_3$. However, rough estimates show ferrous polyphosphate complexes to have dissociation constants larger than 10^{-14}.

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Hydrogenation of Linolenate. VIII. Effects of Catalyst Concentration and of Temperature on Rate, Selectivity, and *Trans* Formation[1]

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Abstract

The effects of catalyst concentration and of temperature on linolenate selectivity, *trans* formation, and rate of hydrogenation have been studied for a commercial electrolytic nickel catalyst. Results obtained with an equimixture of linoleate and linolenate, following the procedure previously described, are presented as isometric drawings, which cover the experimentally practicable temperature ranges from 70–230C and nickel concentration from 0.05–10%. Whereas the rate of hydrogenation depends upon both temperature and catalyst concentration, *trans* formation is essentially a function of temperature while selectivity is little influenced by either parameter.

Introduction

A PREVIOUS INVESTIGATION has shown that statistically significant differences do exist between commercially available catalysts in their linolenate selectivity and isomerization characteristics (8). The present phase of a continuing search for linolenate selectivity in reduction of linolenoyl groups and for low isomerizing tendencies concerns the influence of the parameters of temperature and percentage catalyst. It is part of a utilization research program aimed at the production of flavor-stable products high in linoleic acid by hydrogenation of soybean oil.

Experimental

A procedure to evaluate catalysts for selectivity has been previously described (5) and its applicability demonstrated in a survey of commercial catalysts (8). The specific details of manometric manipulation, gas-liquid chromatography, and infrared spectrometry were presented by Johnston et al. (8). Diene conjugation was determined on weighed samples in isooctane using a Carey Model 14 spectrophotometer. The catalyst selected for more intensive study from among those surveyed, because it demonstrated high-linolenate selectivity and moderate isomerization characteristics, is 25% nickel in cottonseed flakes prepared by electrolytic precipitation.

Results and Discussion

Experimental data from this investigation are presented in the form of three isometric drawings (Figs. 1, 2, and 3). In these three dimensional diagrams temperature and nickel concentration are plotted on

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[1] Presented at the AOCS meeting in New Orleans, La., 1962.
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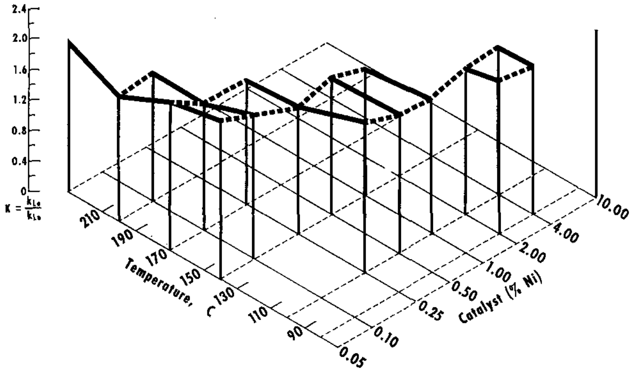

FIG. 1. Plot of linolenate-selectivity ratio, K (vertical axis), as temperature and log of nickel concentration (horizontal axes) change.

the two horizontal axes. Experimentally practical temperatures ranged from 70–230C and nickel concentrations from 0.05–10%. These ranges are bounded by no reaction on one side and are too rapid to measure accurately on the other. Selectivity ($K = \frac{k_{le}}{k_{lo}}$ defined here as the ratio of the reaction constants for linolenate to the reaction constants for linoleate) rate of hydrogen uptake, and formation of isolated *trans* are plotted in Figures 1, 2, and 3, respectively, as the vertical axis.

From the data of Figure 1 it is evident that catalyst concentration and temperature have little influence upon the linolenate selectivity of the chosen catalyst. In fact the least significant difference for all data considered together is 0.24. This variation is less than 0.3 previously found to be required for least significant difference in comparable experiments (8).

The conclusion drawn from these experiments that temperature and catalyst concentration have no significant influence on linolenate selectivity agrees with the conclusions of Albright and others (1, 10) who observed little effect of either; however, other workers (2,3) found that increased temperature and catalyst concentration do give increased selectivity in a linoleate-oleate system.

Figure 2, which represents the effect of concentration and temperature parameters upon hydrogen uptake, gives results that confirm the literature (1-3, 9,10). The lowest rate of uptake was observed at 0.96 ml per min, 70C, and 10% nickel and the highest at 8.0 ml per min, 170C, and 0.25% nickel. Both increasing temperature and increasing catalyst concentration give increasing rate of hydrogen uptake.

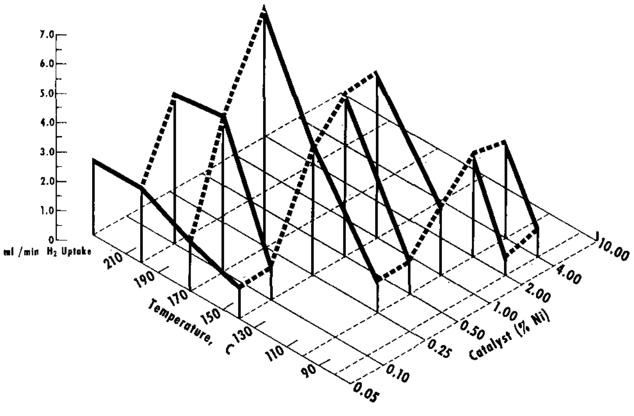

FIG. 2. Plot of rate (vertical axis) as temperature and log of nickel concentration (horizontal axes) change.

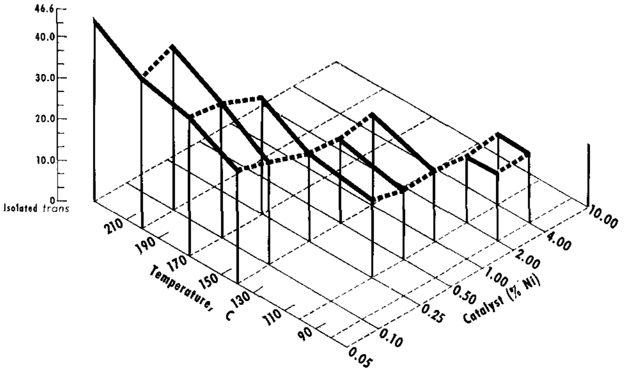

FIG. 3. Plot of isolated *trans* (vertical axis) as temperature and log of nickel concentration (horizontal axes) change.

The influence of temperature parameter and of concentration parameter on isomerization characteristics is shown in Figure 3. It is clearly evident that increasing temperature greatly increases the formation of *trans* isomers; however, increasing concentration of nickel catalyst seems to have little or no effect on isomerization characteristics. These conclusions as to the influence of temperature (2–4,6,7) and of catalyst concentration (1,10) are in agreement with the literature and are supported by numerous other authors. Diene conjugation was measured and although the data were not plotted, the average value was 0.75 at 70, 0.70 at 80, 0.58 at 100, 1.09 at 140, 1.75 at 170, 2.95 at 200, and 5.56% at 230C. *Trans,trans* conjugated diene became evident on gas-liquid chromatographic analyses at higher hydrogenation temperatures thus indicating the predominant source of ultraviolet absorption. As found previously (6), a higher percentage of diene conjugation occurs at higher hydrogenation temperatures.

Conclusions drawn from this study, together with the conclusions of many other reports in the literature, give little hope for altering the parameters of linolenate selectivity by changing temperature and catalyst concentration. From considerations of the physical mechanism used to explain the selectivity of hydrogenation catalysts, it would be expected that selectivity would involve specificity in the adsorption and would thus depend on the structure of the catalyst surface and its relation to catalyst preparation.

The tendency of catalysts to isomerize double bonds is also a function of preparative procedures but, in contrast with selectivity, may be decreased by lowering the temperature. The observations made here and elsewhere that lowering the temperature lowers the *trans* content is currently being extended by investigating hydrogenation at low temperature. By increasing hydrogen pressure, the rate should remain high at low operating temperatures.

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