Nickel-catalyzed Hydrogenation: A Study of the Poisoning Effect of Halogen-containing Compounds

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ABSTRACT

The poisoning effect of various halogen compounds on a nickel-based hydrogenation catalyst has been investigated. While alkyl monochlorides did not affect the catalyst activity, alkyl monobromide and -iodide had a strong poisonous effect. Vicinal dichlorides, 1,1-dichlorides, and HCl also poisoned the catalyst. It is shown that with chlorine containing compounds, the poisoning mechanism involves a fission of the carbon-chlorine bond with the formation of HCl, while bromine and iodine compounds adsorb to the catalyst surface as such in a simple equilibrium reaction. A mackerel oil previously shown to exhibit three kinetically distinguishable poisoning effects has been further examined, and it is shown that its content of halogens can probably account for the observed poisoning pattern.

INTRODUCTION

Most fatty oils contain trace amounts of catalyst poisons. This is especially true for oils of marine origin. Even after refining, the amount of poisons remains at a level that necessitates a considerable increase in catalyst concentration.

Effective catalyst poisons for nickel catalysts are generally found in compounds of the elements in groups V and VI possessing lone electron pairs, the coordinate link being established by electron donation to the metal d-bond. Sulphur compounds are no doubt the most prominent representatives, as is also evident from recent papers (1-6) on this subject. Somewhat surprisingly, the elements of group VII are scarcely mentioned in connection with the poisoning of nickel hydrogenation catalysts.

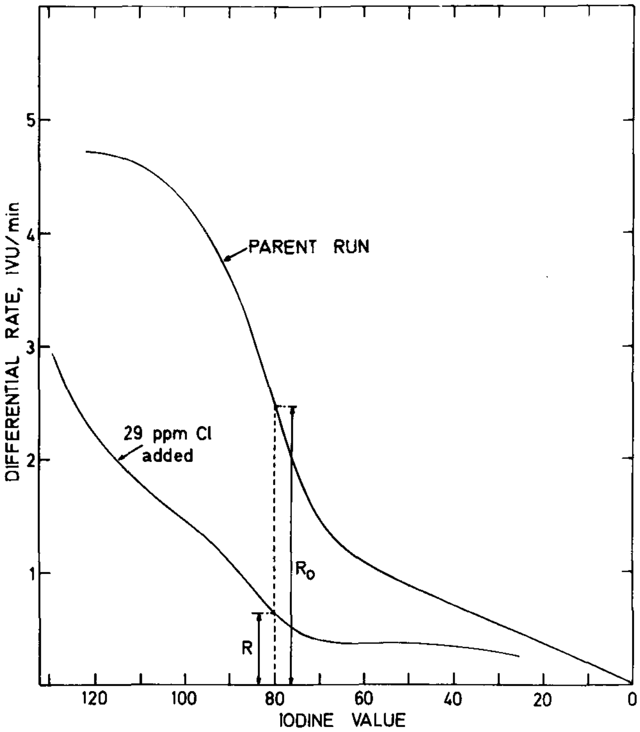


FIG. 1. Differential rates of hydrogenation vs. iodine value. Soybean oil, 170 C, 1 atm, 0.04% Ni; chlorine added as chlorinated soybean oil. IVU = iodine value units.

In a previous paper (5), a kinetic investigation of the nickel-catalyzed hydrogenation of mackerel and capelin oil revealed the existence of three kinetically distinguishable poisoning effects: an "initial" poisoning which was ascribed to the comparatively low sulphur content (ca. 4 ppm) of these oils, a "primary" poisoning completed within the first few minutes of hydrogenation, and a slower "secondary" poisoning which seemed to reach a state of equilibrium after 25-30 min. It was concluded that the two last mentioned effects would have to account for a major part of the total catalyst deactivation, which amounted to ca. 80% of the 0.06% Ni used in these experiments.

Later neutron activation analysis of this mackerel oil has shown that it contains substantial amounts of halogen compounds, with chlorine being the dominating component. This is in accordance with analysis carried out on several other fish oils (7,8).

The aim of the present study has been to determine the extent to which various halogen compounds may act as catalyst poisons and if possible to establish whether the previously observed poisoning pattern for mackerel oil may be related to its content of halogens.

EXPERIMENTAL PROCEDURES

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 liters/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, University of Lund, Sweden; 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. Reproducibility was generally better than ±10%. The method was found unsatisfactory for the analysis of bromine and iodine due to a large frequency of bad reproducibility.

Materials

The nickel catalyst was Nysel (3201-F) obtained from Harshaw Chemie (De Meern, Holland). Refined and bleached soybean oil was delivered by A/S Denofa & Lilleborg Fabriker (Fredrikstad, Norway). n-Hexadecyl halogens were Merck p.a. Chlorinated soybean oil was prepared according to King (9).

RESULTS AND DISCUSSION

The ability of various halogen-containing substances to act as poisons for Ni catalysts was determined by measuring their effect on the differential rates of hydrogenation of soybean oil. Hydrogen consumption was recorded as a function of time, and the results were converted to differential rate vs. iodine value curves as described previously (5).

The poisoning effect of a given additive was then evaluated in terms of the relative catalyst activity (a_r), defined as the ratio of the rate of hydrogenation of the poisoned oil to that of pure soybean oil, both rates taken at the same iodine value in order to eliminate the effect of oil unsaturation. This is illustrated in Figure 1, which gives the rate curves (rates in iodine value units per minute) for pure soybean oil and for a run poisoned with an amount of chlorinated soybean oil (Cl-SBO) corresponding to 29 ppm Cl (on total oil basis). At an iodine value of 80, corresponding to ca. 36 min of hydrogenation of the poisoned oil, the relative catalyst activity is $a_r = R/R_0 = 0.26$.

Figure 2 gives the relative activity vs. time curves obtained with various amounts of Cl-SBO added. It is seen that the catalyst activity decreases less than proportional to ppm Cl added, thus indicating an equilibrium adsorption. Furthermore, the curves pass through a minimum, after which the catalyst activity apparently increases with time. This effect seems more pronounced the lower the amount of Cl-SBO added. Because the hydrogenation system includes recirculation of hydrogen through an active carbon column, a possible explanation of this phenomenon may be that chlorine is removed from the oil, most likely as HCl. This assumption was checked by inserting a water trap in the recirculation system prior to the carbon column. The water was analyzed for HCl after various times of hydrogenation, and simultaneously the chlorine content of the oil was determined by the combustion method.

Figure 3 gives the results for a series of runs with 116 ppm Cl added. Each hydrogenation time represents a separate experiment. The dashed line is obtained by a mass balance with respect to Cl and indicates the amount of chlorine on the catalyst, irrespective of whether the chlorine atom is adsorbed as such or is part of another molecule. These results strongly suggest that Cl-SBO adsorbs to the nickel catalyst followed by fission of the carbon-chlorine bond. HCl then desorbs from the catalyst surface and is stripped off the oil by the hydrogen gas.

Further support for this reaction sequence was obtained from the following experiments:

1. The 60 min run illustrated in Figure 3 was repeated, but this time without the addition of nickel catalyst. No change in the chlorine content of the oil was observed, so evidently the catalyst participates in the formation of HCl.

2. The same kind of experiment was then carried out with 0.2% Ni, but nitrogen was used instead of hydrogen. After 60 min, the chlorine content of the oil had decreased with a modest 5 ppm, but no HCl was produced. As it is known that commercial catalysts may be partly passivated, reactivation taking place rapidly in the presence of hydrogen at ordinary hydrogenation temperatures, the experiment was repeated with a reactivated catalyst. Reactivation was carried out by hydrogenating soybean oil for 5 min followed by stripping with nitrogen for 30 min. Then an amount of Cl-SBO corresponding to 116 ppm Cl was added. After 60 min in nitrogen atmosphere, a 22 ppm decrease in the chlorine content of the oil was observed, but still no HCl could be detected in the water trap. Apparently, both hydrogen and Ni-catalysts are necessary in order to produce HCl. Further, it seems reasonable to assume that the 22 ppm Cl is present as Cl-SBO on the catalyst, as 22 ppm Cl adsorbed on 0.2% Ni corresponds to ca. 4.5 ppm Cl on 0.04% Ni, concentration effects neglected. Figure 3 indicates the presence of ca. 18 ppm Cl on the 0.04% Ni in an actual hydrogenation experiment. The difference of ca. 13.5 ppm Cl qualitatively indicates the amount of chlorine adsorbed to the catalyst as atoms or as HCl.

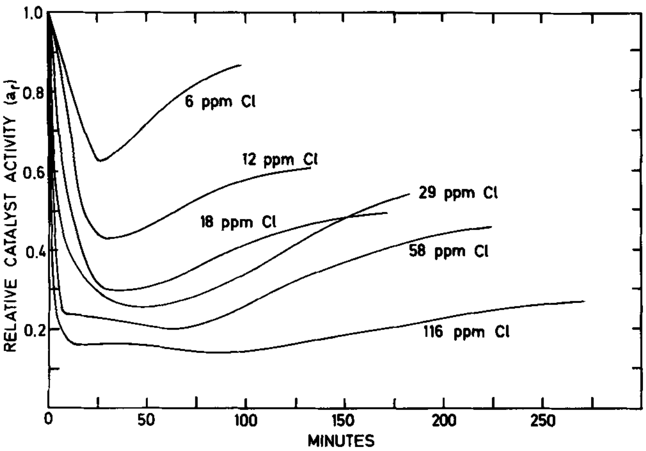


FIG. 2. Relative catalyst activity vs. time. Chlorine added as chlorinated soybean oil; soybean oil, 170 C, 1 atm, 0.04% Ni.

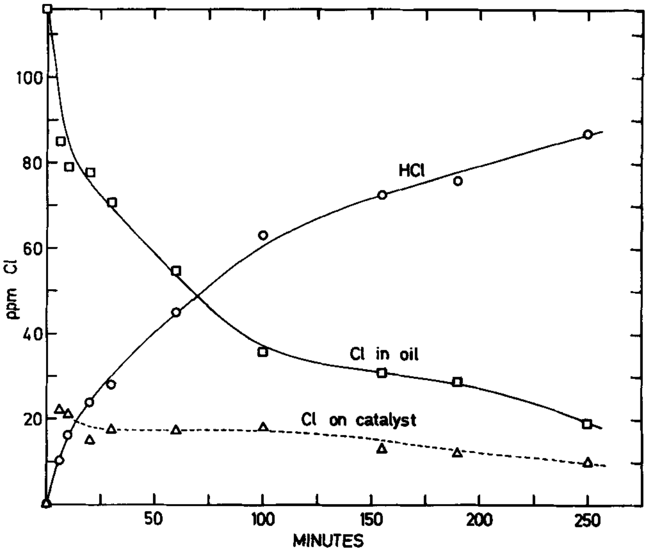


FIG. 3. Distribution of chlorine during hydrogenation. Soybean oil with 116 ppm Cl (as chlorinated soybean oil) added; 170 C, 1 atm, 0.04% Ni.

3. Accordingly, HCl should act as a catalyst poison, probably through a reaction sequence like:

$$HCl \rightleftharpoons (HCl)_{ads} \rightleftharpoons (H)_{ads} + (Cl)_{ads}$$

This was verified in a hydrogenation experiment in which 1 ml gaseous HCl, corresponding to ca. 50 ppm Cl, was injected through a rubber septum into the hydrogen gas stream in front of the reactor. From Figure 4 it is seen that the HCl, which was injected at an iodine value of 70, causes a marked decrease in the rate of hydrogenation. It is also evident that the relative activity of the catalyst increases with time in accordance with the results presented in Figure 2.

Figure 4 also shows the rate curves obtained with some other chlorine compounds. These curves are consistent with those obtained with Cl-SBO in that the relative catalyst activity increases with time due to HCl formation. It should, however, be noted that the poisoning effect of the additives in Figure 4 are qualitative only. Due to the vola-

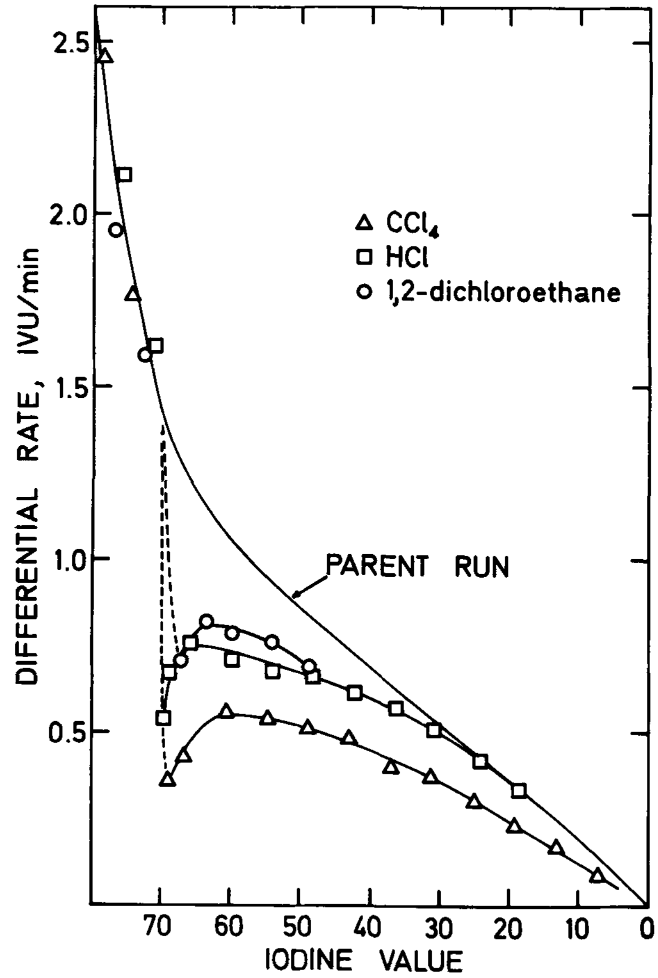


FIG. 4. Effect on differential rate of the addition of CCl_4 (100 ppm Cl), 1,2-dichloroethane (100 ppm Cl), and HCl (50 ppm Cl) at iodine value of 70. Soybean oil, 170 C, 1 atm, 0.04% Ni. IVU = iodine value units.

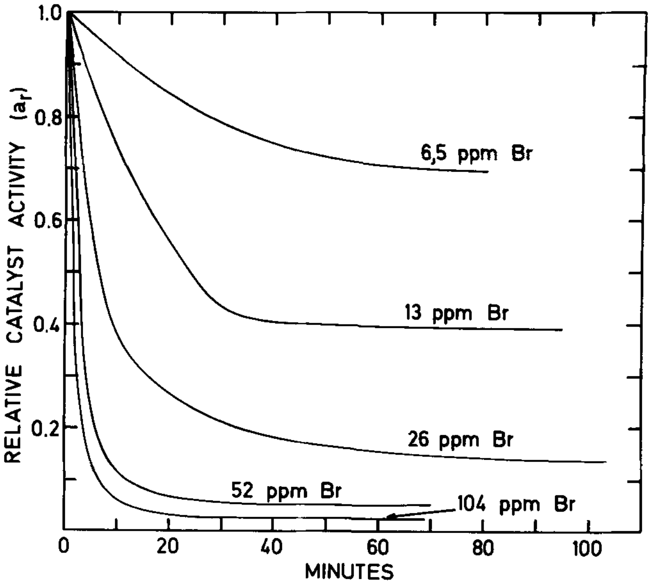
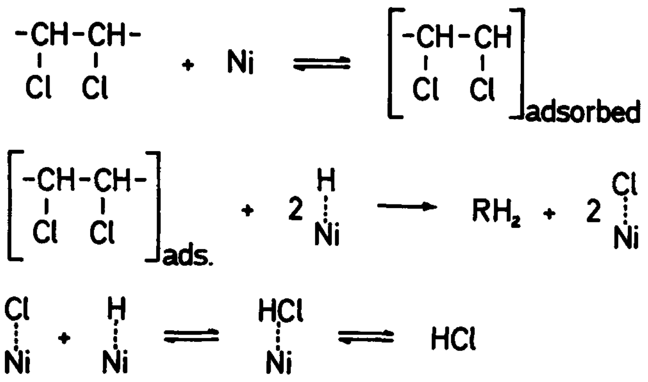


FIG. 5. Relative catalyst activity vs. time. Bromine added as n-hexadecyl bromide; soybean oil, 170 C, 1 atm, 0.04% Ni.

tility of these substances, an unknown fraction will be stripped off by the circulating hydrogen gas and be adsorbed on the active carbon column.

Similar poisoning effects were found with chlorobenzene and the three isomeric dichlorobenzenes.

On the evidence of the results presented, we suggest that the poisoning mechanism of the chlorine-containing compounds involves the following steps, as visualized for a vicinal dichloride:



$$\underset{\text{Cl}}{\text{-CH}}-\underset{\text{Cl}}{\text{CH-}} + \text{Ni} \rightleftharpoons \left[\underset{\text{Cl}}{\text{-CH}}-\underset{\text{Cl}}{\text{CH}}\right]_{\text{adsorbed}}$$

$$\left[\underset{\text{Cl}}{\text{-CH}}-\underset{\text{Cl}}{\text{CH-}}\right]_{\text{ads.}} + 2\,\underset{\text{Ni}}{\overset{\text{H}}{\vdots}} \longrightarrow RH_2 + 2\,\underset{\text{Ni}}{\overset{\text{Cl}}{\vdots}}$$

$$\underset{\text{Ni}}{\overset{\text{Cl}}{\vdots}} + \underset{\text{Ni}}{\overset{\text{H}}{\vdots}} \rightleftharpoons \underset{\text{Ni}}{\overset{\text{HCl}}{\vdots}} \rightleftharpoons \text{HCl}$$

In contrast to the results presented above, no detectable poisoning effect was found on addition of simple alkyl chlorides, e.g., n-butyl chloride, n-octyl chloride, n-hexadecyl chloride, or 1,4-dichlorobutane. It appears that any noticeable adsorption of a chlorine compound is contingent upon activation of the chlorine atom by another chlorine atom on the same or a neighboring carbon atom. This may seem to contradict the findings of Campbell and Kemball (10), who studied the catalytic hydrogenolysis of ethyl chloride and ethyl bromide on evaporated nickel films at temperatures from 184 to 323 C and found that the main decomposition products were ethane and hydrogen halides. Evidently, in their experiments ethyl chloride chemisorbs to the nickel surface, while in the present investigation the alkyl monochlorides apparently fail to do so to any noticeable extent. This difference, in addition to the different experimental conditions, may probably be explained in terms of a competitive adsorption of the fatty acid double bonds. With additives like HCl, CCl_4 or vicinal dichlorides, the heats of adsorption may be sufficiently high to compete favorably with the double bonds for the active sites on the catalyst surface, while this is not the case with the alkyl monochlorides.

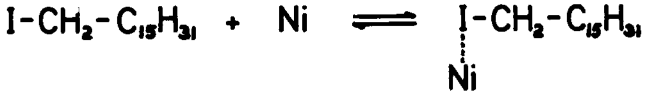
Bromine and Iodine Compounds

Contrary to the results with n-hexadecyl chloride, it was found that n-hexadecyl bromide was a powerful catalyst poison. Figure 5 gives the relative activity vs. time curves obtained on addition of various amounts of n-hexadecyl bromide, expressed as ppm Br on total oil basis. Again the effect of increasing amounts of halogen indicates an equilibrium adsorption. However, the relative activity does not pass through a minimum, as was observed with Cl-SBO. Similar results were obtained on addition of brominated soybean oil.

Furthermore, no bromide ions could be detected when the water trap was inserted in the recirculation line. Apparently, hydrogenolysis with the formation of HBr does not take place.

In another experiment, an oil containing 100 ppm Br was treated with 1% Ni in nitrogen atmosphere at 170 C for 30 min. Combustion analysis of the oil indicated that the hexadecyl bromide had been quantitatively removed. This result also supports the above observation, namely, that no noticeable fission of the carbon-bromine bond takes place. Since a carbon-bromine bond is weaker than a carbon-chlorine bond, this may seem surprising. However, it is in accordance with the findings of Campbell and Kemball (10), who determined the activation energy for the decomposition of ethyl bromide on evaporated nickel films to be 26 kcal/mol as compared to 13 kcal/mol for ethyl chloride. Furthermore, in our work the presence of a neighboring chlorine atom in the poisonous dichloro compounds may reduce the bonding energy and thus ease the fission of the carbon-halogen bond.

Figure 6 shows the relative activity vs. time curves obtained on addition of various amounts of n-hexadecyl iodide. Additional experiments confirmed that the iodide acted similarly to the bromide from a mechanistical point of view; i.e., its poisoning effect can be ascribed to a simple adsorption equilibrium:



$$I{-}CH_2{-}C_{15}H_{31} + Ni \rightleftharpoons \underset{\vdots\atop Ni}{I}{-}CH_2{-}C_{15}H_{31}$$

In Figure 7, the poisoning effects of the three halogens are compared on a molar basis. The runs with Cl-SBO are represented by the relative activity at the minimum of the curves in Figure 2, while with bromine and iodine the activity at the flat part of the curves is taken. It is evident that the deactivating effect per mol halogen added increases in the order: Cl < Br < I. The larger poisoning effect of n-hexadecyl iodide as compared to n-hexadecyl bromide is probably due to a higher adsorption equilibrium constant for the iodide. However, the increase from Cl-SBO to n-hexadecyl bromide may have various explanations. In the first place, the poisoning mechanism suggested for Cl-SBO involves several equilibrium constants, of which at least the one for the Cl-SBO molecule is probably low compared to that of the n-hexadecyl bromide. Secondly, a steric factor may well be important, as a major part of the chlorine on the catalyst surface seems to be present as HCl or chlorine atoms while the n-hexadecyl bromide is adsorbed as such. The long alkyl chain may thus reduce the availability of vacant nickel surface towards adsorption of unsaturated triglycerides.

Mackerel Oil

The aforementioned mackerel oil was found to contain ca. 90 ppm Cl, 3 ppm Br, and 2.5 ppm I as determined by neutron activation analysis. This oil was hydrogenated and analyzed for chlorine by the combustion method in a series of experiments similar to those described for soybean oil in Figure 3. The results are given in Figure 8, where the total halogen content is calculated as ppm Cl. This procedure does not introduce any noticeable error, as a neutron activation analysis taken after 5 min of hydrogenation showed only traces (< 0.2 ppm) of iodine, ca. 0.8 ppm Br, and 68 ppm Cl.

It appears that the strong catalyst poisoning previously observed (5) in the hydrogenation of mackerel oil may be ascribed to its content of halogens. Furthermore, the curve giving the amount of chlorine on the catalyst indicates that adsorption equilibrium is attained after ca. 30 min, in agreement with the previous kinetic investigation (5) which suggested the presence of a secondary poisoning effect characterized by reaching a state of equilibrium after 25-30 min. of hydrogenation. The presence of a comparatively fast primary poisoning effect was also proposed. This effect may be at least partly ascribed to a rapid adsorption of the bromine and iodine compounds present in the mackerel oil.

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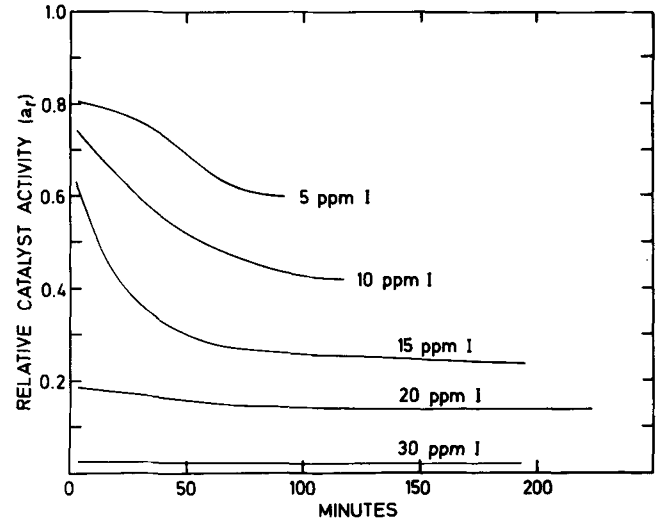

FIG. 6. Relative catalyst activity vs. time. Iodine added as n-hexadecyl iodide; soybean oil, 170 C, 1 atm, 0.04% Ni.

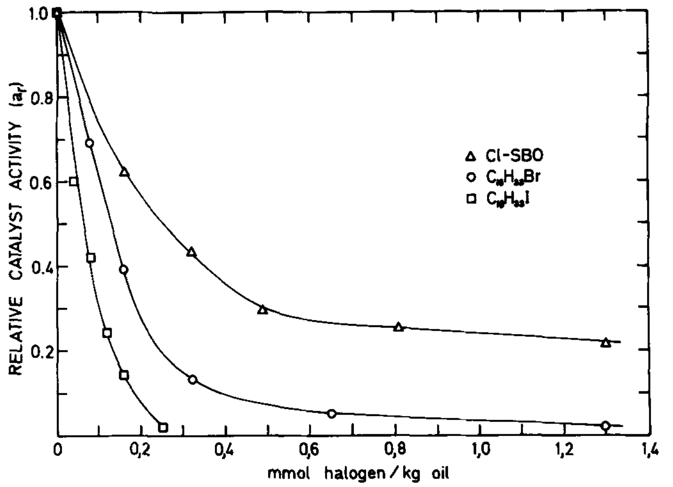

FIG. 7. Relative catalyst activity vs. mmol halogen added. Comparison of the deactivating effect of the various halogens. Cl-SBO = chlorinated soybean oil.

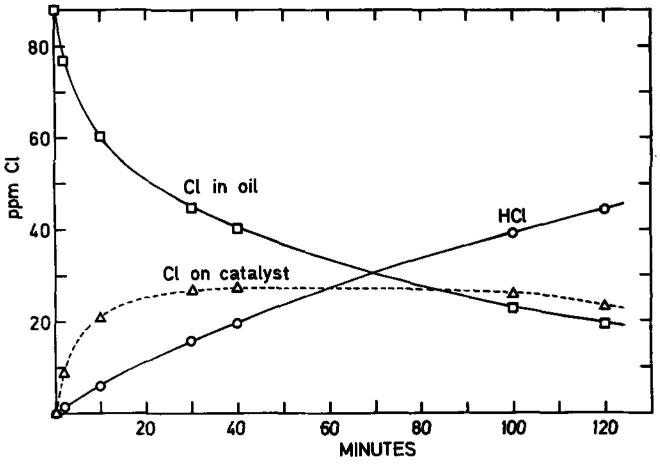

FIG. 8. Distribution of chlorine during hydrogenation of mackerel oil. 170 C, 1 atm, 0.08% Ni.

REFERENCES

1. Drozdowski, R., H. Niewiadomski, and E. Szukalska, Przem. Chem. 52:556 (1973).
2. Babuchowski, K., and A. Rutkowski, Seifen-Oele-Fette-Wachse 95:27 (1969).

3. Coenen, J.W.E., and B.G. Linsen, in "Physical and Chemical Aspects of Adsorbents and Catalysts," Edited by B.G. Linsen, Academic Press, London, England, 1970, p. 496.
4. Ottesen, I., Paper presented at the 6th Scandinavian Symposium on Fats and Oils, Grena, Denmark, 1971.
5. Mφrk, P.C., JAOCS 49:426 (1972).
6. Notevarp, O., R. Storleer, and A. Helgerud, Proceedings of the 7th Scandinavian Symposium on Lipids, Edited by Lipidforum, SIK, Fack S-40021, Gothenburg, Sweden, 1973, p. 169.
7. Tananger, A., and O. Jordal, Ibid., p. 176.
8. Lunde, G., Ibid., p. 183.
9. King, G., J. Chem. Soc. 1817 (1949).
10. Campbell, J.S., and C. Kemball, Trans. Faraday Soc. 57:809 (1961).

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