

tions. For example, Pedersen (18) showed that, of the oxidation products of N, N' diphenyl-p-phenylene diamine, the quinone diimine N, N' dioxide was a more effective antioxidant than the quinone diimine.

Similarly the active species formed when thio- and dithio-compounds are used as antioxidants, are considered to be sulfoxides and thiosulfates by Barnard et al. (19). The antioxidant effectiveness of seleno-compounds is similarly thought to be due to the synthesis of oxidized intermediates (20,21).

Whether substituted hydroxylamines are of practical significance as antioxidants for edible oils remains to be determined. Very little is known about their toxicological properties. Also it is not yet known whether a mechanism related to that described here may explain the synergistic effects of phospholipids (22) and other nitrogenous food constituents. Experiments designed to pursue these topics are in progress.

#### ACKNOWLEDGMENTS

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# Homogeneous Catalytic Hydrogenation of Unsaturated Fats: Metal Acetylacetonates<sup>1</sup>

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#### Abstract

Hydrogenation of linseed and soybean methyl esters was achieved at 100–180°C, 100–1000 psi H<sub>2</sub> and 0.05–0.25 moles catalyst per mole of ester. The relative activity of metal acetylacetonates in decreasing order was: nickel(III), cobalt(III), copper(II) and iron(III). Reduction occurred readily in methanol solution but only slowly in dimethylformamide and acetic acid. No reduction occurred in the absence of solvents. Soybean oil was also hydrogenated rapidly with nickel(III) acetylacetonate in methanol, but in this system the triglycerides were converted to methyl esters. Nickel(III) acetylacetonate was the most selective catalyst toward linolenate hydrogenation. Methyl linoleate and linolenate hydrogenated with nickel(III) acetylacetonate were fractionated into monoenes, dienes and trienes. The *cis* monoenes separated in 62 to 68% yield had double bonds in the original position. The remaining *trans* monoenes had extensively scattered unsaturation. The dienes and trienes showed no conjugation, but some of the double bonds in the dienes were not conjugatable with alkali. Little stearate was formed.

#### Introduction

IN A PROGRAM at this Laboratory to find selective catalysts for the hydrogenation of linolenate in soybean oil, bis- and tris (2,4-pentanedione) metal complexes were investigated. These complexes, com-

monly known as metal acetylacetonates, are soluble hydrogenation catalysts rather than heterogeneous as normally used in commercial operations. In the past, olefinic compounds have been successfully reduced by soluble hydrogenation catalysts (11–13). Soluble metal complexes previously used to hydrogenate polyunsaturated fats include iron and cobalt carbonyls (8–10), pentacyanocobaltate (17,18) and triphenylphosphine derivatives of platinum(II) and tin(II), (1).

#### Experimental

##### Materials

Methyl esters of fatty acids of commercially refined and bleached soybean and linseed oils were obtained by transesterification with methanol and potassium hydroxide and were distilled under vacuum (soybean methyl esters IV 135; linseed methyl esters IV 183). Methyl linoleate (IV 172.4) was obtained from The Hormel Institute. Methyl linolenate (IV 260.1) was prepared by countercurrent distribution (CCD) of distilled linseed methyl esters (21). Gas-liquid chromatography (GLC) showed the methyl linoleate and linolenate to be 100% pure. Nickel(III), cobalt(III), copper(II) and iron(III) acetylacetonates were obtained from the Pearsal Company and used without purification. Small amounts of methanol-insoluble impurities were present, but they exhibited no catalytic activity.

*Hydrogenations* were carried out in a Magne-Dash high-pressure 150-ml, or 300-ml, stainless steel autoclave or a rocking autoclave fitted with a six 10-ml compartment stainless steel insert (6). The catalyst was decomposed after hydrogenation with dilute HCl (2:1) as described previously (10).

<sup>1</sup> Presented at AOCS meeting in Chicago, 1964.

<sup>2</sup> No. Util. Res. and Dev. Div., ARS, USDA.

TABLE I  
 Hydrogenation of Linseed Methyl Esters  
 with Metal Acetylacetonates<sup>a</sup>

| Catalyst              | Temp.,<br>C | Concn.,<br>M <sup>b</sup> | Percent |      |      |      | IV    | <i>trans</i> ,<br>% elai-<br>date |
|-----------------------|-------------|---------------------------|---------|------|------|------|-------|-----------------------------------|
|                       |             |                           | St      | M    | D    | T    |       |                                   |
| Control               | .....       | .....                     | 3.6     | 23.6 | 18.0 | 52.0 | 183   | 0.0                               |
| Ni(acac) <sub>3</sub> | 150         | 0.10                      | 24.8    | 50.2 | 19.5 | 0.0  | 76.5  | 25.2                              |
| Co(acac) <sub>3</sub> | 150         | 0.10                      | 13.8    | 44.2 | 31.2 | 4.8  | 104.3 | 23.3                              |
| Cu(acac) <sub>2</sub> | 150         | 0.10                      | 5.7     | 26.4 | 14.9 | 46.5 | 179.5 | 16.1                              |
| Fe(acac) <sub>3</sub> | 150         | 0.25                      | 3.6     | 23.6 | 18.0 | 52.0 | 183   | 0.0                               |
| Cu(acac) <sub>2</sub> | 180         | 0.25                      | 27.1    | 38.6 | 25.6 | 3.3  | 85.6  | 27.2                              |
| Fe(acac) <sub>3</sub> | 180         | 0.25                      | 12.9    | 39.8 | 34.2 | 11.2 | 122.1 | 29.9                              |

<sup>a</sup> Conditions: 1,000 psi H<sub>2</sub>; 3 hr; methanol, 10 ml per g ester. Abbreviations: St, stearate; M, monoene; D, diene; T, triene; and acac, acetylacetonate.

<sup>b</sup> Per mole of fatty esters.

### Analyses

Methodology relating to GLC, IR, UV, alkali conjugation, CCD, capillary GLC, silver-resin column chromatography and KMnO<sub>4</sub>-KIO<sub>4</sub> cleavage was the same as described previously (9).

### Results

Hydrogenation of unsaturated fatty esters was catalyzed with the metal acetylacetonate complexes of nickel(III), cobalt(III), copper(II) and iron(III). Table I shows that nickel(III) acetylacetonate was the most effective catalyst. Relative activities of the other acetylacetonate catalysts in decreasing order were cobalt(III), copper(II) and iron(III). The amount of *trans* unsaturation seemed to reach a maximum at 25 to 30% after the triene had been largely reduced. This level of *trans* isomerization was reached independently of the catalyst used. The metal acetylacetonates exhibited varying degrees of thermal instability as shown by the formation of black precipitates. At 125–150C nickel acetylacetonate decomposed slightly; cobalt and copper acetylacetonates to a greater extent; and ferric acetylacetonate almost completely.

The possibility was checked that the precipitate from the metal acetylacetonates would have catalytic activity. A typical reduction of linseed esters with nickel acetylacetonate at 125C and 100 psi hydrogen was interrupted after 1.5 hr. The precipitate formed was isolated by decanting the methanol soluble material, care being taken to keep the precipitate always covered with solvent. The precipitate was washed and the methanol decanted seven times to remove all the soluble catalyst and esters. No hydrogenation of the linseed esters was observed when the precipitate was used as the catalyst at temperatures of 125C and 100 psi hydrogen. Results from this experiment indicated that the precipitate was catalytically inactive. The solution from which the precipitate was isolated was filtered to remove any traces of precipitate. When

 TABLE II  
 Hydrogenation of Linseed Methyl Esters  
 with 0.10M Ni(acac)<sub>3</sub> in Methanol<sup>a</sup>

| Run No. | Temp.,<br>C | Pressure,<br>psi H <sub>2</sub> | Time,<br>hr | IV    | Percent |      |      |      | <i>trans</i> ,<br>% |
|---------|-------------|---------------------------------|-------------|-------|---------|------|------|------|---------------------|
|         |             |                                 |             |       | St      | M    | D    | T    |                     |
| Control | .....       | .....                           | .....       | 183.0 | 3.6     | 23.6 | 18.0 | 52.0 | 0.0                 |
| 1       | 100         | 100-MD                          | 4           | 153.7 | 4.7     | 28.5 | 35.6 | 26.1 | 19.2                |
| 2       | 100         | 100-MD                          | 5           | 135.5 | 5.6     | 34.6 | 41.5 | 13.2 | 29.5                |
| 3       | 125         | 500-MD                          | 2           | 104.4 | 6.2     | 46.2 | 35.1 | 2.4  | 20.6                |
| 4       | 125         | 1000-R                          | 3           | 82.2  | 20.2    | 54.0 | 20.9 | 0.0  | 25.2                |
| 5       | 150         | 500-MD                          | 2           | 102   | 7.6     | 55.2 | 31.4 | 0.0  | 30.8                |
| 6       | 150         | 1000-R                          | 3           | 76.5  | 24.8    | 50.2 | 19.5 | 0.0  | 25.2                |
| 7       | 180         | 1000-R                          | 3           | 64.2  | 32.5    | 50.2 | 12.3 | 0.0  | 24.9                |

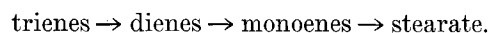
<sup>a</sup> Abbreviations: See footnote a of Table I. Also, MD = Magne-Dash, R = Rocker.

this solution was reheated to 125C and 100 psi hydrogen, the hydrogenation resumed at approximately the same rate as before interruption. These results indicate that the reduction is catalyzed by the metal acetylacetonate in solution and not by the precipitates formed by thermal decomposition.

The effect of reaction conditions was studied with nickel(III) acetylacetonate (Table II). Temperature and reaction time were the major variables affecting the extent of reaction. No hydrogenation was obtained at temperatures below 100C and a catalyst concentration of less than 0.05 mole per mole ester. Between 0.10 and 0.25 moles catalyst the extent of hydrogenation observed was approximately the same. Monoenes were the main products formed as long as some trienes remained in the reaction mixture. Once the trienes had been reduced, stearate became an important product. *Trans* values generally leveled off at 25 to 30%. A higher rate of reduction was obtained with the Magne-Dash autoclave than with the rocker bomb, probably because of more efficient agitation.

Extensive reduction of the esters occurred only when methanol was used as a solvent. Small amounts of hydrogenation occurred with dimethylformamide (DMF) and acetic acid. However, no reduction was observed when cyclohexane, benzene, acetone, pyridine, acetylacetone, chloroform and heptanoic acid were used as solvents.

The relative selectivity of the catalysts was calculated by simulating the reaction rates with an analog computer (3,4), assuming the consecutive reaction of



Linseed methyl esters afforded more accurate estimates of selectivity than soybean methyl esters because the large amounts of methyl linolenate permitted more reliable analysis by GLC. Table III shows the calculated selectivity ratios for methyl linolenate versus methyl linoleate ( $K_{Ln}/K_{Lo}$ ) and for methyl linoleate versus methyl oleate ( $K_{Lo}/K_{Ol}$ ). Nickel acetylacetonate was the most selective catalyst followed by

 TABLE III  
 Selectivity of Metal Acetylacetonates

| Catalyst              | Methyl Ester         | Solvent | Temp.,<br>C | Pressure,<br>psi H <sub>2</sub> | <i>trans</i> ,<br>% | Concn.,<br>M <sup>a</sup> | ΔIV | Selectivity     |                 |
|-----------------------|----------------------|---------|-------------|---------------------------------|---------------------|---------------------------|-----|-----------------|-----------------|
|                       |                      |         |             |                                 |                     |                           |     | $K_{Ln}/K_{Lo}$ | $K_{Lo}/K_{Ol}$ |
| Ni(acac) <sub>3</sub> | Soybean <sup>b</sup> | MeOH    | 100         | 100                             | 11.5                | 0.1                       | 33  | 3.4             | 20.0            |
| Ni(acac) <sub>3</sub> | Soybean              | DMF     | 100         | 100                             | 9.5                 | 0.1                       | 24  | 4.8             | 13.3            |
| Ni(acac) <sub>3</sub> | Linseed <sup>c</sup> | MeOH    | 100         | 100                             | 31.8                | 0.1                       | 66  | 3.6             | 8.5             |
| Ni(acac) <sub>3</sub> | Linseed              | MeOH    | 125         | 500                             | 20.6                | 0.05                      | 75  | 3.9             | 13.2            |
| Ni(acac) <sub>3</sub> | Linseed              | DMF     | 125         | 1,000                           | 10.0                | 0.1                       | 20  | 3.1             | .....           |
| Ni(acac) <sub>3</sub> | Linseed              | MeOH    | 150         | 500                             | 26.7                | 0.1                       | 59  | 4.1             | 25.7            |
| Ni(acac) <sub>3</sub> | Linseed              | MeOH    | 180         | 1,000                           | 21.5                | 0.25                      | 117 | 3.5             | 2.2             |
| Co(acac) <sub>3</sub> | Linseed              | MeOH    | 150         | 1,000                           | 23.4                | 0.1                       | 77  | 2.4             | 3.6             |
| Co(acac) <sub>3</sub> | Linseed              | MeOH    | 180         | 1,000                           | 23.3                | 0.1                       | 35  | 2.7             | 10.0            |
| Cu(acac) <sub>2</sub> | Linseed              | MeOH    | 150         | 1,000                           | 16.1                | 0.1                       | 4   | 1.0             | 5.8             |
| Fe(acac) <sub>3</sub> | Linseed              | MeOH    | 180         | 1,000                           | 16.3                | 0.1                       | 14  | 2.0             | 2.0             |

<sup>a</sup> See footnote b, Table I.

<sup>b</sup> Soybean—IV = 135.

<sup>c</sup> Linseed—IV = 183.

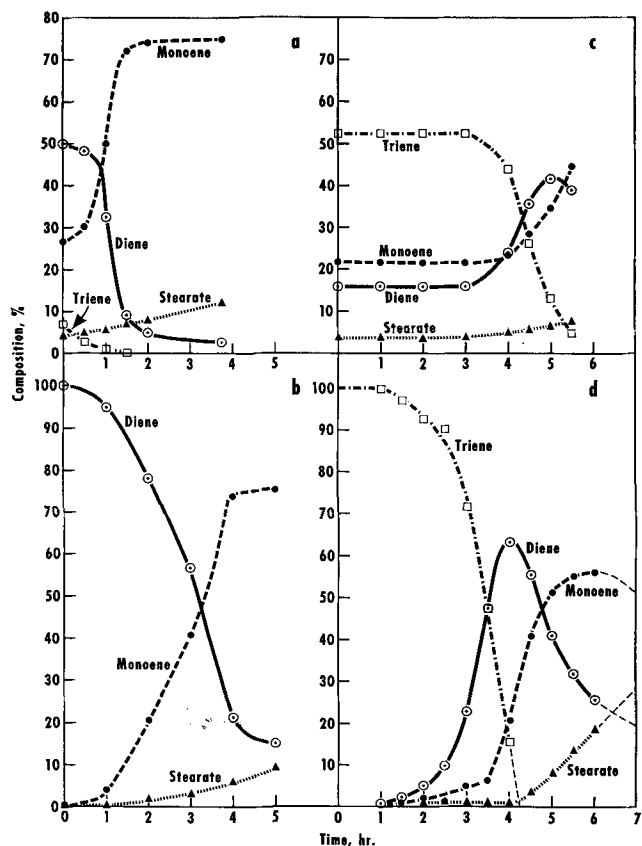


FIG. 1. Reaction rate curves for the hydrogenation of fatty acid esters using 0.1M Ni(acac)<sub>3</sub> (100C, 100 psi H<sub>2</sub>): a, soybean methyl esters; b, methyl linoleate; c, linseed methyl esters; d, methyl linolenate.

cobalt and then copper acetylacetonate. This order corresponds approximately to their degree of catalytic activity. Copper acetylacetonate showed little selectivity under the conditions used. Varying the reaction temperature, pressure, time and catalyst concentration did not affect the selectivity of the catalysts much. In one run, using DMF<sup>1</sup> as the solvent produced higher selectivity ratios than methanol although the amount of reduction was comparatively small (IV drop, 24).

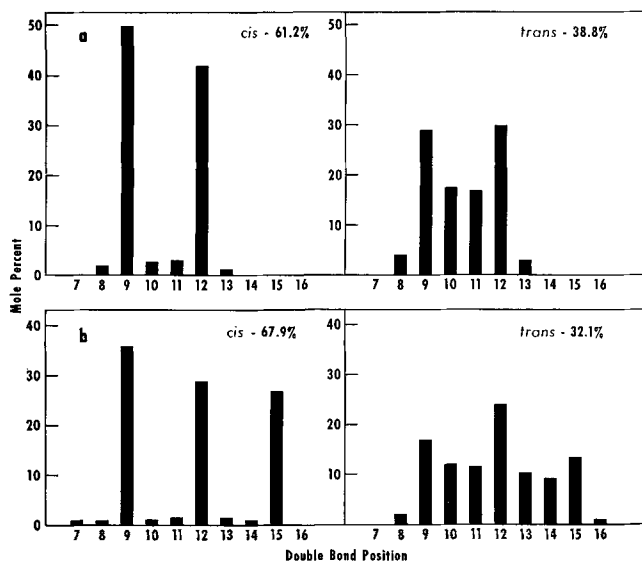


FIG. 2. Oxidative cleavage analysis (dibasic acids): a, the *cis* and *trans* monoenes from reduced methyl linoleate; b, the *cis* and *trans* monenes from reduced methyl linolenate.

Figure 1 shows typical rate curves (a-d) for the reduction of soybean methyl esters, linseed methyl esters, methyl linoleate and methyl linolenate. These curves illustrate the ability of nickel acetylacetonate to hydrogenate selectively the polyunsaturated fatty esters. With soybean methyl esters and methyl linoleate (Fig. 1a,b), the reduction began after an induction period of approximately 0.5 hr. The reaction then proceeded rapidly until about 75% monoene was formed. At this point the reaction leveled off, and little stearate was formed. With linseed methyl esters (Fig. 1c), a longer induction period was observed (~3 hr). The maximum amount of monoene formed was 40% whereas stearate did not exceed 5%. With methyl linolenate (Fig. 1d) the induction period varied from 1 hr to 4.5 hr. Once started, the reaction proceeded rapidly with diene formation reaching a maximum of 63%, followed by monoene leveling off at 55%. The amount of stearate formed was initially small but increased when the triene was completely reduced. In Figure 1d, the high selectivity of the catalyst for trienes is quite apparent and is enhanced by the formation of isomeric dienes, which are not readily reducible to monoenes. Isomer analyses are presented below.

Countercurrent distribution (CCD) between hexane-acetonitrile was used to separate hydrogenated samples into stearate, monoene, diene and triene fractions (20). Table IV gives complete analysis of reduction products from methyl linoleate and methyl linolenate. UV analysis showed no conjugated dienes or trienes. Since a high proportion of the dienes of both methyl linoleate and linolenate was not conjugatable with alkali, the double bonds must be separated by more than one methylene group. The triene fraction of linolenate was completely conjugatable with alkali. About one-third of the monoenes showed isolated *trans* configuration. In the diene and triene fractions, isolated *trans* unsaturation ranged from 20 to 40% of the double bonds.

Monoenes from reduced methyl linoleate and methyl linolenate were further characterized by separation into *cis* and *trans* isomers by using a silver-saturated ion-exchange resin column (7). Figure 2a shows the bond position of the monoenes from reduced methyl linoleate determined by oxidative cleavage (15). The *cis* monoenes have double bonds in their original position. In the *trans* monoene fraction, the bonds that migrate have moved mainly one carbon to either side of their original 9 and 12 positions. As with linoleate, the bond position of the *cis* monoene from reduced linolenate also shows little or no migration (Fig. 2b). In the *trans* monoene fraction, the bonds that migrate have moved predominantly one carbon on either side of the original 9, 12 and 15 position.

Analysis by capillary GLC of the *cis* monoenes from reduced methyl linoleate and linolenate agrees well with the dibasic acid analysis (Fig. 3). The position of the 9-, 12- and 15-monoene isomers were determined by adding as internal standards the corresponding isomers obtained from hydrazine-reduced methyl linolenate (19). Owing to the greater complexity of the *trans* monoene and to the poor separation of positional *trans* isomers, the *trans* fractions show only one partially resolved peak.

Hydrogenation of unsaturated triglycerides with metal acetylacetonates was also investigated. However, when soybean oil was hydrogenated with nickel acetylacetonate in methanol at 100C and 100 psi hydrogen, the triglycerides were converted to methyl

esters. Therefore, nickel acetylacetonate catalyzes both the hydrogenation and transesterification reactions. The use of nonalcoholic solvents is currently being investigated in an attempt to eliminate the transesterification reaction.

### Discussion

Metal acetylacetonates are effective homogeneous catalysts for the reduction of unsaturated fatty esters. Catalysts containing different transition metals exhibit varying degrees of activity, stability and selectivity. Nickel acetylacetonate was shown to be a highly selective hydrogenation catalyst for methyl linolenate (Table III). In general, the selectivity ratios for methyl linolenate versus methyl linoleate were 2 to 2.5 times higher than those for commercially available heterogeneous catalysts (14). This order of selectivity is the same as that reported by Koritala and Dutton (16), using various solvents, notably DMF, to increase the selectivity of heterogeneous catalysts. In the present study a high selectivity was also observed when DMF was used with nickel acetylacetonate, but the extent of hydrogenation was little with this solvent. Relatively high  $K_{L_0}/K_{O_1}$  selectivity ratios (8.5 to 25.7) were also obtained with nickel acetylacetonate.

Metal carbonyls used previously as homogeneous hydrogenation catalysts produced extensive isomerization of unsaturated fats (9,10). Conjugated polyenes were important products in the iron carbonyl reduction, but minor one in the cobalt carbonyl reduction. In this respect, the metal acetylacetonates are analogous to cobalt carbonyl. However in contrast to both the iron and cobalt carbonyl reductions, the *cis* monoenes, comprising 61 to 68% of the total monoenes, from the nickel acetylacetonate reduction show essentially no movement of double bonds. Therefore, the *cis* monoenes would seem to be formed directly from methyl linoleate and linolenate. Cleavage analyses of the *trans* monoenes, constituting 32 to 39% of the total monoenes, show that geometric isomerization without movement of the double bond is also an important reaction. This reaction would explain the large amount of *trans* unsaturation in the triene fraction from methyl linolenate, which is completely conjugatable. Also, the relatively large proportion of 9, 12 and 15 monoenes in the *trans* monoenes would be expected to be formed by direct geometric isomerization. The total unsaturation remaining in the original position of both the *cis* and *trans* monoene from reduced methyl linoleate and methyl linolenate is calculated to be 79%.

The *trans* monoenes from methyl linoleate and linolenate show movement of double bonds to predominantly one carbon on either side of the original 9, 12 and 15 positions. This isomerization could be accounted for by conjugation prior to reduction as was done for cobalt carbonyl (9). It can be assumed also that conjugated dienes are formed slowly and then are rapidly reduced to monoenes. The presence of substantial amounts of nonconjugatable dienes from the reduced methyl linoleate and linolenate (Table IV) is also consistent with the initial formation of conjugated dienes, which are immediately hydrogenated. The nonconjugatable dienes are expected to be difficult to hydrogenate and would accumulate during the reaction.

Extensive reduction occurred only in methanol, and this condition may indicate that methanol is essential

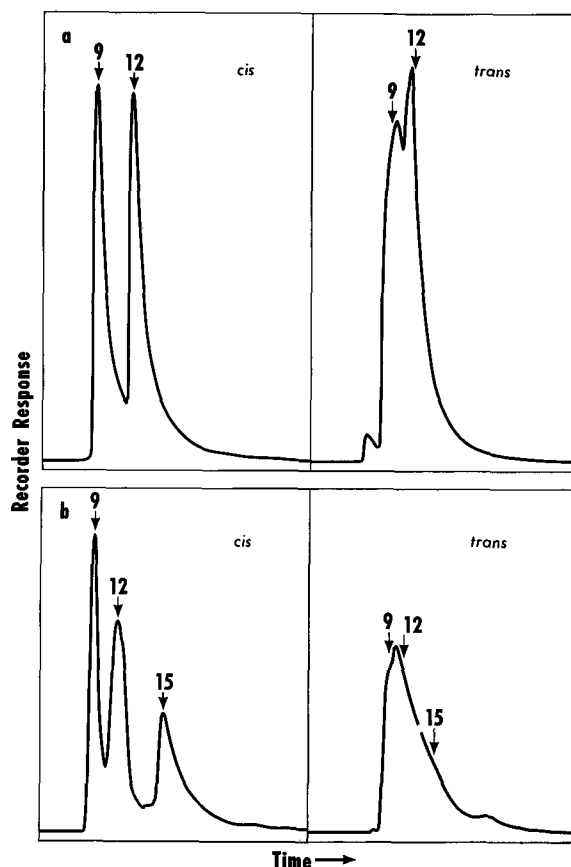
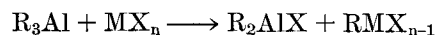


FIG. 3. Capillary gas chromatograms of *cis* and *trans* monoenes from  $Ni(acac)_3$  reduced (a) methyl linoleate and (b) methyl linolenate (arrows indicate retention of 9, 12 and 15 monoenes added as internal stands).

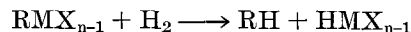
to the reaction. This solvent is considered to be a fairly good ion stabilizing solvent, as are DMF and acetic acid (5). These are the only other solvents in which any reduction occurred. These solvents may stabilize  $H^+$  ion or promote the formation of the metal acetylacetonate hydride. Another indication of solvent activity is the formation of methyl esters from triglycerides during the reduction. This result may be due to formation of the nickel acetylacetonate hydride, which could act as an acid catalyst for transesterification.

Sloan et al. (22) have suggested a mechanism for the reduction of simple olefins using mixtures of metal acetylacetonates and Ziegler catalysts. In their mechanism the following steps were postulated:

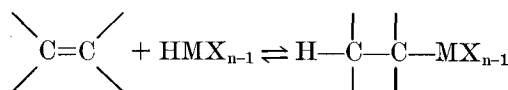
- (1) Alkylation of the metal complex:



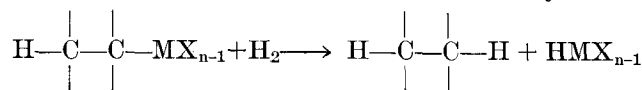
- (2) Hydrogenolysis of the metal-alkyl bond:



- (3) Hydride addition to the olefin:



- (4) Hydrogenolysis of the olefin-metal alkyl bond:



where R = alkyl group, Al = aluminum, M = metal ion, X = ligand.

TABLE IV  
OCD Analysis: Fatty Esters Reduced with Ni(acac)<sub>3</sub>

| Analysis                           | Percent  |         |       |        |
|------------------------------------|----------|---------|-------|--------|
|                                    | Stearate | Monoene | Diene | Triene |
| Methyl linoleate                   |          |         |       |        |
| Weight                             | 9.0      | 75.3    | 15.0  | .....  |
| <i>trans</i> (as elaidate)         | .....    | 38.8    | 83.1  | .....  |
| Conjugated                         | .....    | .....   | 0.0   | .....  |
| Conjugatable (alkali) <sup>a</sup> | .....    | .....   | 45.5  | .....  |
| Methyl linolenate                  |          |         |       |        |
| Weight                             | 1.0      | 15.1    | 59.8  | 24.2   |
| <i>trans</i> (as elaidate)         | .....    | 32.1    | 57.4  | 68.2   |
| Conjugated                         | .....    | .....   | 0.0   | 0.0    |
| Conjugatable (alkali) <sup>b</sup> | .....    | .....   | 35.3  | 100.0  |
| Conjugated diene-triene            | .....    | .....   | ..... | 1.0    |

<sup>a</sup> Relative to pure methyl linoleate.

<sup>b</sup> Relative to pure methyl linolenate.

Their mechanism may be extended to the hydrogenation of unsaturated fatty esters catalyzed by metal acetylacetonates. The first step may be modified to allow for the absence of the Ziegler catalyst. Since methanol or a suitable protonating or hydride-stabilizing solvent is apparently necessary for the reaction, it may be postulated that one of the acetylacetonate ligands is replaced with methanol. This reaction has a precedence with copper acetylacetonate (2). The solvated acetylacetonate would then assume the same role as the alkylated (RMX<sub>n-1</sub>) intermediate in the initial step. Subsequent reactions in the mechanism would remain the same with the metal acetylacetonate-methanol system. Basic studies are needed to elucidate further the mode of action of this new class of hydrogenation catalysts.

## ACKNOWLEDGMENT

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## Foam Generation Method for Evaluating Biodegradability<sup>1</sup>

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### Abstract

Mechanization of a simple laboratory test for foam generation capacity has resulted in a sensitive research tool and a valuable method for investigating biodegradation of surfactants. By standardizing energy input, temperature and other parameters, very acceptably reproducible foam generation capacity and foam decay measurements are obtained.

The method is suitable for organic materials capable of producing foams in aqueous solutions at very low concentrations such as 0.2-30 mg/liter. It is particularly suitable for individual or mixed surfactants and detergent formulations but has broader scope. It is fully adaptable to River Dieaway and Shake Flask Culture biodegradation test procedures and probably to others. The working range of concentrations is substantially that of interest in studies of water pollution by surfactants, and extends well below that for which most physical and chemical methods are suited. The method is broader in application and in information gained than an analytical method alone can be. The two may but do not necessarily yield parallel results. Both examinations are desirable.

### Introduction

A LONG BUT MORE DESCRIPTIVE title for this paper would be "Method of Following Surfactant Biodegradation by Foam Generation Capacity and Stability Evaluation." In simple terms, the ancient art of shaking a foamable solution in a graduated cylinder for observation of the foam developed and its decay has been mechanized. After plenty of adverse experience with hand shaking methods, the more important variables have been standardized. The very acceptable degree of reproducibility achieved for diverse surfactant materials has been applied to individual or mixed surfactants or to detergent formulations (but has broader scope in that the foam generation and decay patterns derived characterize not only an individual surfactant but combinations of its decaying remainder, degradation products and other materials present). It shows some promise of becoming one of the few research tools well suited to very low concentrations of surfactants such as 0.2-30 ppm.

Methods of generating foams in reproducible manner have been classified as follows (1):

1. Shaking solutions
2. Beating in air, as by rotating stirrers or moving a perforated disc up and down (2)
3. Bubbling air or other gas through a column of liquid (3,4).
4. Dropping the liquid from a height (5-7).

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