neutral triglycerides from the acidic and hydrolysis products of oxidation. By this procedure both oxidation methods gave values higher than the actual for the trisaturated glyceride content of the concentrates. This increase was shown to be due to the formation of α-ketols from the unsaturated acids in Hilditch’s oxidation and the corresponding acetyl derivatives in Kartha’s oxidation. These incompletely oxidized glycerides were formed to a greater extent in Kartha’s oxidation than in Hilditch’s oxidation.

The saturated acid content was determined accurately by Kartha’s oxidation and Bertram separation procedure whereas Hilditch’s oxidation gave slightly lower values. The GS2A were unaffected by the carbonate washing procedure of Hilditch and Lea. However the GS2U were found to hydrolyze considerably in Hilditch’s oxidation. The GS2U were hydrolyzed appreciably in Kartha’s oxidation procedure whereas the GS2U were very slightly affected. As a result of this, Kartha’s method, when applied to the GS2U concentrates, gave an increase in GS2U and U3G contents and a decrease in GS2U content.

The effects of incomplete oxidation and hydrolysis on the determination of glyceride composition were demonstrated. This investigation explains the differences in the results obtained by Hilditch’s crystallization method and Kartha’s oxidation method. As the experimental basis of Kartha’s restricted random distribution theory is unsound, this theory must be re-examined.

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Catalyzed Esterification of Oleic Acid1

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The purpose of this study was to determine quantitatively the effects of type and concentration of catalyst and temperature on the rate of esterification of oleic acid with ethylene glycol. The catalysts used were salts of divalent metals. In addition, a study was made of the rate of the catalyzed esterification of oleic acid by a variety of mono- and polyhydric alcohols. Some comments are made on the mechanism of esterification. There have been many studies of catalysis of esterification, and no attempt will be made here to review them. Most of them are qualitative; some measure the time to reach a given low acid number. Flory (1, 2) showed that self-catalyzed esterification follows, for the most part, third-order kinetics; esterification catalyzed with p-toluenesulfonic acid follows second-order kinetics. This was also found by Otsuka (3) and Rao (4) in the esterification of fatty acid with butanol, using sulfuric acid catalyst. Rubin (4) calculated rate constants for the esterification of fatty acid with polyhydric epoxy resins, both self-catalyzed and catalyzed with acids or salts. He found no difference in rate between litharge and lead naphthenate; p-toluen sulfonic acid was about 30% faster. Calcium naphthenate was about 50% slower and its rate only a little greater than that of the self-catalyzed reaction. Feuge, Kraemer, and Bailey (5) compared the effectiveness of a variety of catalysts for the esterification of fatty acids with glycerol. They found zinc or tin chlorides the most effective and practical.

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Blagonravova and Lazarev (6) showed that the rate of esterification of a mixture of C_{18} acids was the same as that of the individual ones. Sudborough and Gittins (7) had found earlier that oleic and other long-chain saturated and unsaturated acids had about the same esterification rate. Goldsmith (8) collected many references to studies of catalyzed esterifications but indicated that no systematic investigation of the merits of various catalysts had been recorded.

Even fewer quantitative studies have been made of the rates of esterification of the various alcohols. Newman (9) presents evidence showing that the acid-catalyzed rate of esterification of ethanol is less than that of methanol. Tommila (10) studied the saponification rates of various esters of benzoic acid and found some differences among the primary monohydric alcohols. We have found some significant differences in the esterification rates of a number of alcohols both monohydric and polyhydric; the reasons for these differences are not yet clear.

**Experimental**

**Materials.** Oleic acid was Emery Industries Emersol V.I. 233 (low linoleic), A.N. 200, equivalent weight 281, I.V. 89.7. Alcohols, glycols, and polyols, with the exception of 1,3-propanediol, were used as received. Each was analyzed for hydroxyl content and the equivalent weight was calculated. The actual hydroxyl numbers and theoretical (in parentheses) for each alcohol, and the supplier follow: 1,4-butanediol, 1247 (1246); ethylene glycol, 1083 (1077), Tennessee Eastman; 1,5-pentanediol 1085 (1077), diethylene glycol, 1073 (1058), triethylene glycol, 754 (747), 2,2-diyetyl 1,3-propanediol 844 (849), Union Carbide Chemicals; ethylene glycol, 1776 (1080), Fisher Scientific; monopentaerythritol, 1614 (1648) Herenues Powder; trimethylol ethane, 1347 (1402), trimethylol propane, 1244 (1255) Trojan Powder; glycerol, U.S.P. 99.5%, 1798 (1828), Shell Chemical.

Metal acetates used and the supplier were as follows:

- **Zn**\(\text{(CH}_3\text{CO}_2\text{)}_2\cdot\text{2H}_2\text{O}\), Mn\(\text{(CH}_3\text{CO}_2\text{)}_2\cdot\text{4H}_2\text{O}\), Pb\(\text{(CH}_3\text{CO}_2\text{)}_2\cdot\text{3H}_2\text{O}\), Cd\(\text{(CH}_3\text{CO}_2\text{)}_2\cdot\text{2H}_2\text{O}\), Mg\(\text{(CH}_3\text{CO}_2\text{)}_2\cdot\text{H}_2\text{O}\), Ca\(\text{(CH}_3\text{CO}_2\text{)}_2\cdot\text{2H}_2\text{O}\), Cu\(\text{(CH}_3\text{CO}_2\text{)}_2\cdot\text{H}_2\text{O}\), Hg\(\text{(CH}_3\text{CO}_2\text{)}_2\).

Fisher Certified Reagents: C_{12}H_{22}Hg\(\text{(CH}_3\text{CO}_2\text{)}_2\), Eastman Kodak practical. Zinc stearate was obtained from Witco Chemical, zinc chloride from Fisher, titanium tetrachloride from Matheson, Coleman and Bell. The concentrations used were based on the metal content given by the supplier.

Metal salicylates were prepared by double transposition of barium salicylate and the metal sulfates. The aqueous filtrates, after removal of BaSO_4, were concentrated; the crystals were removed by filtration, redissolved, and recrystallized from water. Copper salicylate decomposed on concentration; it was prepared by neutralizing freshly precipitated Cu\(\text{(OH)}_2\) with salicylic acid in methanol and evaporating the methanol. The concentration used of each catalyst was based on the metal content, obtained by analysis. The actual and theoretical (in parentheses) metal content for each were as follows:

- Zn\(\text{(HOCH}_2\text{CH}_2\text{CO}_2\text{)}_2\cdot\text{H}_2\text{O}\), 17.5% (17.4%);
- Mg\(\text{(HOCH}_2\text{CH}_2\text{CO}_2\text{)}_2\cdot\text{3H}_2\text{O}\), 6.73 (6.89);
- Cd\(\text{(HOCH}_2\text{CH}_2\text{CO}_2\text{)}_2\cdot\text{2H}_2\text{O}\), 26.6 (26.6);
- Hg\(\text{(CH}_3\text{CO}_2\text{)}_2\), 47.3 (43.5);
- Cu\(\text{(HOCH}_2\text{CH}_2\text{CO}_2\text{)}_2\cdot\text{H}_2\text{O}\), 17.6 (17.9);
- Sn\(\text{(O}_2\text{CC}_1\text{H}_5\text{)}_2\), 18.2 (17.4).

Stannous stearate was prepared by adding an aqueous solution of stannous chloride to one of sodium stearate. The stannous stearate precipitated was removed by filtration, washed, and dried. The p-toluene-sulfonic acid was from Eastman Kodak, white label.

**Procedure.** Esterifications were conducted in a 200-ml, 3-necked flask, fitted with a 2.5-in. Teflon anchor type of stirrer turning at 200 r.p.m. To one side neck was connected a gas inlet tube, through which alkyl grade CO_2 was passed over the surface of the reaction mixture at the rate of 200 ml./min. To provide an inert atmosphere and to remove water. Increasing this rate had no effect on esterification rate. To the other side neck was fitted a 6-in. Vigreaux column electrically heated to 120-140°C to return alcohols. A water trap with a water-cooled reflux condenser was connected to the top of the Vigreaux column. The temperature was measured by an iron-constantan thermocouple and recorded and controlled by a Leeds and Northrup Type G Speedomax.

The oleic acid was heated in the flask to about 10°C above reaction temperature, the equivalent amount of alcohol was added, and then the catalyst. The temperature had dropped to that desired. Samples were withdrawn by pipette, weighed into tarred flasks, and dissolved in 50 ml. of 0.25% solution of tetradsodium salt of ethylenediamine tetracetic acid 2:1 toluene: methanol to complex the metal so that only unesterified oleic acid was titrated by the 0.2 N methanolic KOH with phenolphthalein.

Secondary-order rates of esterification were determined from the slopes of plots of the reciprocal of oleic acid concentration versus time (hours). Oleic acid concentration is expressed as weight percentage, determined from the acid number and average equivalent weight, 281. A correction for loss of water was applied to each sample weight. Reaction constant is expressed as weight percentage-hour\(^{-1}\). In concentrated solution, as in this case, the density changes during esterification so that if concentration in mols per unit volume were used, it would be necessary to determine the density of each sample.

**Discussion**

The divalent metal salts evaluated as catalysts for the esterification of oleic acid and ethylene glycol were used at the same molar (and so equivalent) concentration, at 180°C, as acetates, salicylates, or stearates. The salicylates were used to see if coordination with the metal had any effects on the catalytic activity as found by Langenbeck and Mahrwald (11); but under these conditions there appeared to be no difference between the acetate and the salicylate salts. It is possible that at a lower temperature a significant difference between coordinated and uncoordinated catalysts might be observed. All of the catalysts were soluble in the reaction medium. In