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 probable formation of a-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 GS_2A were unaffected by the carbonate washing procedure of Hilditch and Lea. However the GS_2U were found to hydrolyze considerably in Hilditch's oxidation. The GSU_2 were hydrolyzed appreciably in Kartha's oxidation procedure whereas the GS_2U were very slightly affected. As a result of this, Kartha's method, when applied to the GSU_2 concentrates, gave an increase in GS_2U and GU_3 contents and a decrease in GSU_2 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 reexamined.

Acknowledgments

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Catalyzed Esterification of Oleic Acid [1]

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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 Othmer and Rao (3) in the esterification of oleic 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-toluene 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.
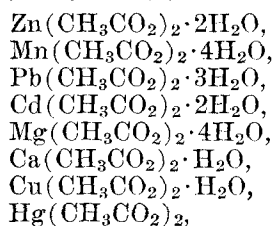
Blagonravova and Lazarev (6) showed that the rate of esterification of a mixture of C_{18} acids was the same as that of the individual ones. Sudborough and Gittins (7) had found earlier that oleic and other long-chain saturated and unsaturated acids had about the same esterification rate. Goldsmith (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 mono- and polyhydric; the reasons for these differences are not yet clear.

Experimental

Materials. Oleic acid was Emery Industries Emersol LL 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), General Aniline and Film; dodecanol, 300 (301), octadecanol, 212 (207), 1,10-decanediol, 663 (630), Eastman Kodak; 1,3-propane diol, Eastman Kodak practical, redistilled and the middle fraction used, b.p. 213-215°C., 1273 (1475); neopentyl glycol, 1083 (1077), Tennessee Eastman; 1,5-pentanediol 1085 (1077), diethylene glycol, 1073 (1058), triethylene glycol, 754 (747), 2,2-diethyl 1,3-propanediol 844 (849), Union Carbide Chemicals; ethylene glycol, 1762 (1808), Fisher Scientific; monopentaerythritol, 1614 (1648) Hercules Powder; trimethylol ethane, 1347 (1402), trimethylol propane, 1244 (1255) Trojan Powder; glycerol, U.S.P. 99.5%, 1798 (1828), Shell Chemical.
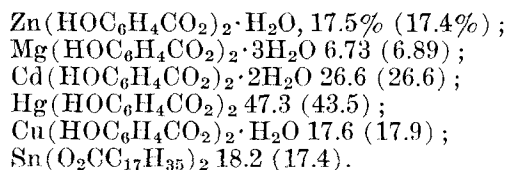
Metal acetates used and the supplier were as follows:

$Zn(CH_3CO_2)_2 \cdot 2H_2O$,
$Mn(CH_3CO_2)_2 \cdot 4H_2O$,
$Pb(CH_3CO_2)_2 \cdot 3H_2O$,
$Cd(CH_3CO_2)_2 \cdot 2H_2O$,
$Mg(CH_3CO_2)_2 \cdot 4H_2O$,
$Ca(CH_3CO_2)_2 \cdot H_2O$,
$Cu(CH_3CO_2)_2 \cdot H_2O$,
$Hg(CH_3CO_2)_2$,

Fisher Certified Reagents; $C_6H_5Hg(CH_3CO_2)$, 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 $Cu(OH)_2$ 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:

$Zn(HOC_6H_4CO_2)_2 \cdot H_2O$, 17.5% (17.4%);
$Mg(HOC_6H_4CO_2)_2 \cdot 3H_2O$ 6.73 (6.89);
$Cd(HOC_6H_4CO_2)_2 \cdot 2H_2O$ 26.6 (26.6);
$Hg(HOC_6H_4CO_2)_2$ 47.3 (43.5);
$Cu(HOC_6H_4CO_2)_2 \cdot H_2O$ 17.6 (17.9);
$Sn(O_2CC_{17}H_{35})_2$ 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-toluenesulfonic 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 alkyd 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 tared flasks, and dissolved in 50 ml. of 0.25% solution of tetrasodium 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.

Second-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^{-1} 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 coördination 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 coördinated and uncoördinated catalysts might be observed. All of the catalysts were soluble in the reaction medium. In

TABLE I

Second-Order Rate Constants (Weight Percentage^{-1} Hour^{-1}) for the Esterification of Ethylene Glycol-Oleic Acid at 180°C. with .005M Metal Salts/100 g. Oleic Acid as Catalyst

	Acetates	Salicylates	Others
Zn^{++}	0.0192	0.0202	0.0202 [a]
Mn^{++}	0.0133	....	....
Pb^{++}	0.0130	....	....
Cd^{++}	0.0121	0.0119	....
Mg^{++}	0.0096	0.0089	....
Ca^{++}	0.0092	....	....
Cu^{++}	0.0072	0.0076	....
Hg^{++}	0.0067	0.0074	....
TiCl$_4$	....	....	0.0093
Phenyl mercuric acetate			0.0076
No added catalyst			0.0060

[a] Zinc stearate.

Table I are listed the reaction-rate constants for the various catalysts and for no added catalyst. The rate constant calculations were based on second order kinetics. Since under our conditions water is removed as rapidly as it reaches the surface and nearly as rapidly as it is formed, we believe the use of the Goldschmidt equation (12) and the calculation of r where $r = (R'OH_2)(H_2O)/(H_3O)^+$ is unnecessary.
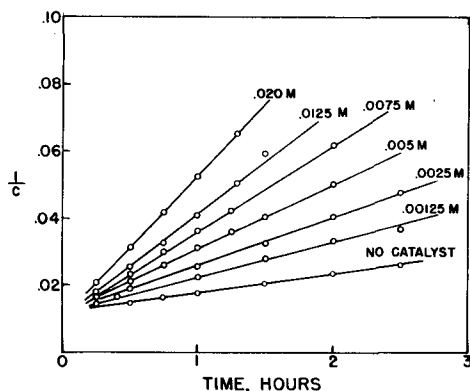

FIG. 1. Rates of esterification, zinc acetate catalyst.

Figure 1 shows the relation between the reciprocal of the concentration and time for various amounts of zinc acetate catalyst and for no catalyst. The straight lines obtained show that these metal-catalyzed esterifications follow second-order kinetics throughout as do acid-catalyzed ones. The self-catalyzed reaction does so in the early stages of reaction. Flory (1) and others have shown that self-catalyzed esterifications become third order at later stages of reaction. Just recently Tang and Yao (13) in Chang Chun, China, have calculated that self-catalyzed esterification follows two-and-a-half order kinetics throughout and propose a mechanism. We avoided these complications by stopping the self-catalyzed reaction at the time the other esterifications were nearly complete.

The reaction rate increases with the concentration of added catalyst but not entirely in direct proportion. Figure 2 shows the initial curvature in the plot of rate vs. concentration. A linear relationship for acid catalysis has been observed by Rubin (4) and by Othmer (3) for esterification and by Flory (14) for alcoholysis and ester interchange but in some cases over a smaller range of concentration. Our reactions were carried out in the absence of solvent, and the effective concentration of the catalyst may not have been uniform.
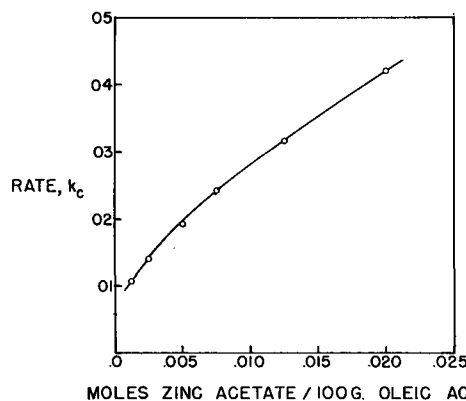

FIG. 2. Change in esterification rate with catalyst concentration

In Figure 3 is shown the effect of change in temperature on the rate of esterification. From these data the energy of activation was calculated to be 14.8 kilocalories per mole. This is somewhat higher than some values, but there are other data which show an energy of 15 kilocalories; Tang and Yao found values of 14 kilocalories.

In order to provide some basis of comparison between the catalysts listed in Table I and acidic types, the rates of esterification were studied by using p-toluenesulfonic acid and zinc chloride. The results are shown in Figure 4. Also is shown the curve for stannous stearate and for zinc acetate. The behavior of the first three is not as simple as that of the zinc acetate because they did not follow second-order kinetics smoothly throughout the reaction. The acid is a much more active catalyst than the metal salts. Stannous stearate is unusually active (the acetate could not be prepared in satisfactory purity) and shows increased activity after the first half hour. After 1.5 hrs. the rate with stannous stearate is about four times and that with p-toluenesulfonic acid about six times that with zinc acetate, at the same molar concentration. Zinc chloride also gave anomalous results, showing a small upward trend. The over-all rate was not greatly different from that for zinc acetate. Under our conditions it caused some discoloration, as did p-toluenesulfonic acid, whereas stannous stearate did not.

In order to determine if any of these catalysts were esterifying the glycol, the hydroxyl content was determined frequently during the esterification. In the case of p-toluenesulfonic acid, stannous stearate, and zinc acetate the decrease in hydroxyl content was exactly equivalent to the decrease in acid content.
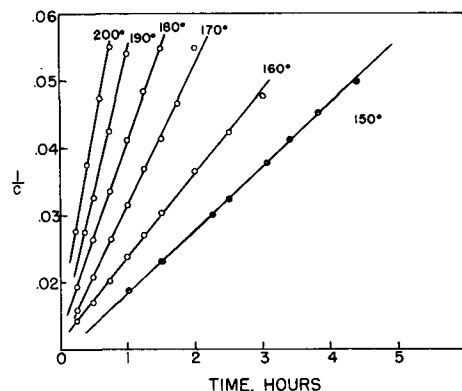

FIG. 3. Rates of esterification at various temperatures.

TABLE II
Catalyzed Esterification of Oleic Acid .005 M Catalyst/100 g. Acid

Time (hours)	Zinc acetate			Zinc chloride		Stannous stearate		p-Toluene[a] sulfonic acid	
	Acid No.(1)	Acid No.(2)	Hydroxyl No.(1)	Acid No.	Hydroxyl No.	Acid No.	Hydroxyl No.	Acid No.	Hydroxyl No.
0	179	179	......	178	......	177	......	177	175
15	......	132	......	150	144	96	94	67	65
19	126	......	125	......	......	......	......	......	......
30	......	103	......	128	......	59	......	49	......
45	84	......	......	109	......	39	......	40	......
60	70	69	67	91	......	27	......	34	......
90	55	53	......	64	......	13	......	31	27
120	42	43	......	49	......	6	5	......	......
150	36	37	......	38	......	......	......	......	......
180	31	32	......	28	......	......	......	......	......
210	......	......	......	22	10	......	......	......	......

[a] .0005 M catalyst per 100 g. of oleic acid.

In the case of zinc chloride there was a small additional loss of hydroxyl. Data for these catalysts are shown in Table II.

Oleic acid was esterified with equivalent amounts of alcohol at 180°C. and 0.005 mole zinc acetate per 100 g. of acid. In Table III are listed the alcohols used

TABLE III
Second-Order Rate Constants, 180°C., 0.005 M Zn (OAc)₂/100 g. of Oleic Acid

Alcohol	Rate constant %/hr.
1,4-Butanediol	.050
Dodecanol (lauryl alcohol)	.048
Octadecanol (stearyl alcohol)	.047
1,10-Decanediol	.041
1,5-Pentanediol	.040
1,3-Propanediol	.038
Ethylene glycol	.033
Pentaerythritol	.035
Trimethylol propane	.034
Trimethylol ethane	.033
Diethylene glycol	.032
Triethylene glycol	.025
2,2-Dimethyl 1,3-propanediol	.026
2,2-Diethyl 1,3-propanediol	.026
Glycerol	.023

and their rate constants. At the top of the list the most rapidly esterifying alcohol under these conditions was the 1,4-diol. Although no mineral acid was present, we were fearful lest the catalyst and fatty acid might cause etherification with the formation of tetrahydrofuran. However there was no loss of hydroxyl groups other than by esterification, as shown by determination of both hydroxyl number and acid number at frequent intervals. The monohydric alcohols octadecanol and dodecanol have the same esterification rate. There is no significant difference in the esterification rates of 1,10-diol, 1,5-diol and 1,3-diol, but the rates of these three are distinctly less than that of 1,4-butanediol. The 1,2-diol ethylene glycol is
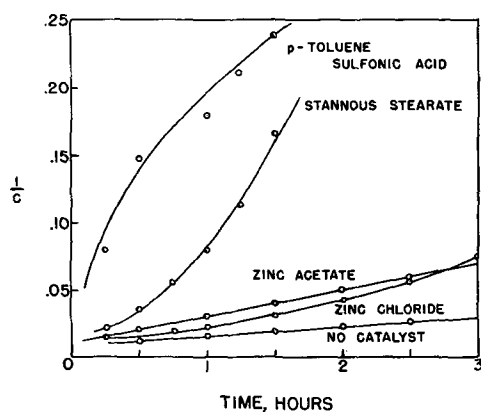

TIME, HOURS
FIG. 4. Rates of esterification, various catalysts.

distinctly lower. The polyols come next, pentaerythritol, tetramethylol propane, and tetramethylol ethane. There is no significant difference between these and ethylene glycol. Diethylene glycol is next and esterifies at about the same rate as ethylene glycol itself. Its rate, on the other hand, may be contrasted with that of 1,5-pentanediol or 1,4-butanediol where the hydroxyl groups are a corresponding distance away. The effect of the ether oxygen in decreasing the reactivity of the alcohol groups is distinctly noticeable. In the similar instance of the esterification rate of triethylene glycol this decrease in reaction rate by the introduction of ether oxygen is even more noticeable. Still further interesting behavior is shown by the *alpha*-substituted propane diols, 2,2-dimethyl 1,3-propanediol and 2,2-diethyl 1,3-propanediol. These are the slowest of the primary alcohols which were studied, and their behavior is in strong contrast to that of the unsubstituted 1,3-propanediol and of the methylol-substituted trimethylolethane. Certainly this difference can scarcely be explained on the basis of simple steric hindrance, which is not supposed to be particularly effective with primary alcohols in any event.

An attempt was made to compare 2-nitro-2-ethyl 1,3-propanediol with 2,2-diethyl 1,3-propanediol. This nitro glycol unfortunately is not stable at the temperature of 160° and decomposed. We took precautions against violent decomposition, but rapid charring occurred. The rate of esterification did appear to be very slow, but the data are unreliable. Comparisons would have to be made at a lower temperature.

A number of reaction mechanisms have been proposed for acid-catalyzed esterification. One offered by Roberts and Urey (10) is shown in Figure 5.
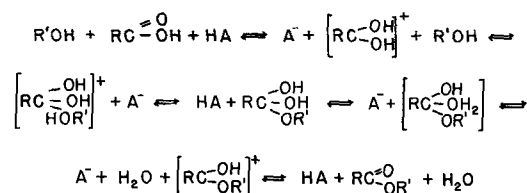

FIG. 5. Possible mechanism for acid catalyzed esterification.

They deduced that the rate-controlling complex must incorporate acid, alcohol, and catalyst or ester, water, and catalyst. The existence of an intermediate is considered probable as the result of the work of Bender (16), who showed that hydrolysis of an ester with O^{18} carbonyl formed H_2O^{18}. H. A. Smith (12) suggests, using Goldschmidt's concept, that the acid catalyst reacts with the alcohol.

$$H^+ + R'OH + RC(O)OH \rightleftharpoons RC(O)OH + R'OH_2^+ \rightleftharpoons RC(O)OR' + H_3O^+$$
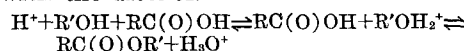
The H_2O formed competes with the alcohol for the proton.

If we combine this with the mechanism of Roberts and Urey, we may write a simplified equilibrium as follows:

$$RC(O)OH+R'OH_2^+ \rightleftharpoons [RC(OH)_2O(H)R]^+ \rightleftharpoons$$
$$RC(O)OR'+H_3O^+$$
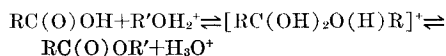
Syrkin and Moiseev (17) reviewed the mechanism of hydrolysis of esters and suggested the equilibrium shown in Figure 6A. The reverse of this would be a mechanism for esterification, Figure 6B.

This would agree with the idea that a complex or intermediate is involved between the alcohol, catalyst, and acid. In the case of catalysis by a salt, such as zinc acetate, the first reaction might be the abstraction of a proton from the alcohol, forming an acid which could catalyze normally.

$$R'OH+Zn(OAc)_2 \rightleftharpoons R'OZn(OAc)+AcOH \rightleftharpoons$$
$$(R'O)_2Zn+2AcOH$$
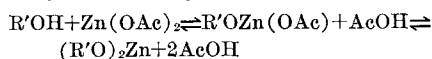
It is also possible to depict structures analogous to Figure 6B which incorporate the zinc complex, Figure 6C. Recently Kapoor and Mehrotra (18) found in the reaction of zirconium tetra-isopropoxide with stearic acid successive formation of the mono-salt trialkoxide, di-salt dialkoxide and tri-salt monoalkoxide, demonstrating the existence of alkoxide-salts. A cadmium methoxide-salt was formed when cadmium acetate was used to catalyze the transesterification of bornyl acetate with methanol (19). The compound $CH_3O-Cd-O(O)CCH_3$ was isolated and identified. These results are in harmony with our interpretation of the function of metal salt catalysts in esterification.

Zinc forms alkoxides fairly readily, cadmium less so, and mercury hardly at all (20). This same order holds true for effectiveness as a catalyst. In Figure 7 rate is plotted against the cube of the ionic radius, and the straight line shows clearly the direct relationship between the two (21).

T. L. Smith and Elliott (22) used metal salt catalysts for esterification of rosin acids at 200°C. They suggest that zinc resinate acts as a comparatively strong Lewis acid under their conditions and that the catalyst forms a complex with the alcohol. We consider it probable that the mechanism for acid catalysis
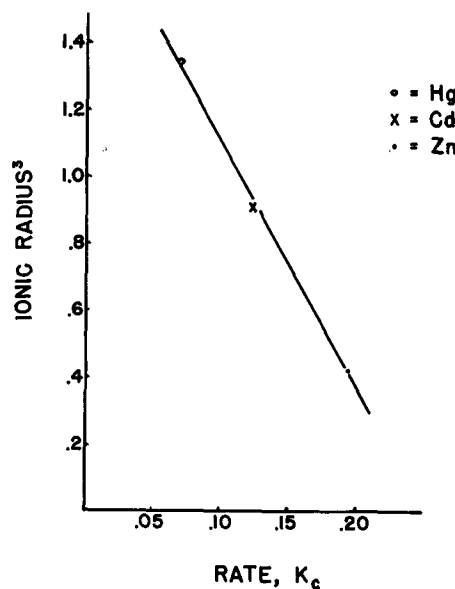

Fig. 7. Relation between rate constant and ionic volume for Group II B metal acetates.

and for metal salt catalysis is similar and that the metal salt acts as an acid in the general sense in these conditions.

Conclusions

It has been shown that the effectiveness of certain divalent metal salts as esterification catalysts can be quantitatively compared and that for the Group II B series their effectiveness is inversely proportional to their ionic volume. The rates of esterification using these metal salts are not as great as for strong acids, but it is probable that the mechanism is similar and that the metal salts act as acids in the general sense.

The rates of esterification differ appreciably for different primary polyols. It is also probable that these differences are related to the comparative acidity or basicity of the alcohols.

It would be particularly desirable to investigate the activity of the catalysts in different alcohols. It is possible that infrared studies might show formation of a complex between the catalyst and either the alcohol or the acid or both. A number of possibilities may be formulated; at present we lack critical evidence to distinguish between them and this area provides a fruitful field for further research.
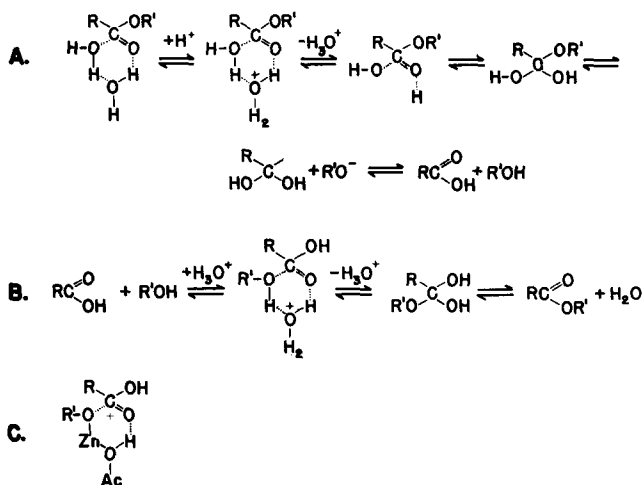

Fig. 6. Possible intermediates for catalyzed hydrolysis and esterification.

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