The Kinetics of Esterification of Resin Acids[1]

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For more than three-quarters of a century the esterification of resin acids (rosin) has been a commercially important process. Yet surprisingly little has been published on the subject. Commercial esterifications are generally carried out in concentrated solution (that is, essentially equivalent amounts of resin acid and polyhydric alcohol) at temperatures between 250 and 300°C. The usual esterification catalysts, such as sulfuric acid, cannot be used since they promote decarboxylation and color formation. Instead the catalysts are generally salts of metals in groups I and II of the periodic table.

Many kinetic studies have been made of the esterification of fatty and aromatic acids, both uncatalyzed and catalyzed with hydrogen-ions, and the mechanism is well understood. Only fragmentary rate data however have been published on the esterification of resin acids, and no discussion has been given of the mechanism. In this paper are presented kinetic data measured over a wide temperature range for the esterification of resin acids in both concentrated and dilute solutions. Both uncatalyzed esterifications and esterifications catalyzed with hydrogen-ions and metallic salts were studied. These studies showed no fundamental difference between the mechanism for the esterification of resin acids and of other hindered acids. For catalysis by metal salts the kinetic data suggest that the rate-controlling step is a reaction between metallic resinate and alcohol to form a basic resinate and ester.

The kinetic studies of Flory (1) and Hinshelwood (2) have shown that an uncatalyzed esterification is second order in acid and first order in alcohol. When catalyzed by the solvated proton, SH^+, esterifications are first order in both acid and alcohol. If the water formed is not removed however, a correction must be applied, as shown by Goldschmidt (3), because of the inhibitory effect of this water.

Several kinetic investigations of the esterification of fatty acids with glycerol and pentaerythritol have been published (4, 5, 6). The kinetics are complicated and sometimes show fractional orders that change with temperature and extent of reaction. Similar effects were found by Flory (1) and Davies and Hill (7) in studying the polyesterification of dibasic acids with glycols. Flory attributed the change in order with the extent of reaction to a medium effect since the system becomes progressively less polar as the reaction proceeds. For esterifications with glycerol the different reactivities of the primary and secondary alcoholic groups introduce a further complication.

Thus many complications might be expected in a kinetic study of the esterification of resin acids with polyhydric alcohols when no solvent is used and when the reactants are present in nearly equivalent amounts.

Experimental

Procedure. All esterifications were carried out in a constant temperature bath regulated to ± 0.1°C., as measured by mercury-in-glass thermometers. Esterifications in concentrated solution were carried out in three-necked flasks equipped with condenser and stirrer. The condenser was heated electrically to 110 and 150°C. to facilitate the escape of the water liberated. The stirrer was operated at a constant rate since it was found that the esterification rate varied slightly with stirring rate. Dilute-solution esterifications were ordinarily carried out in the same apparatus even though a few experiments in unstirred, closed flasks gave about the same rates. Esterifications in methanol were made in 100-ml. volumetric flasks.

To follow the esterification, samples were withdrawn periodically from the reaction mixture, dissolved in a carbon dioxide-free methanol—benzene solvent, and titrated with alcoholic potassium hydroxide to a phenolphthalein end-point. When acid catalysts were also present, appropriate corrections were applied in calculating the amount of resin acid present.

Materials. Resin 731S (disproportionated rosin, Hercules trademark): acid number, 165; saponification number, 168; 50–51% dehydroabietic acid and 0.3% retene by ultraviolet analysis.

Pentaerythritol: monopentaerythritol, 49.5% hydroxyl; maximum ash, 0.1%.

Perhydrogenated rosin: acid number, 182; hydrogen absorption 0.05–0.1%.

Dehydroabietic acid: purity 99–100% by ultraviolet analysis.

Methanol was dried by the method of Lund and Bjerrum (8) and distilled. The middle fraction was refluxed with anhydrous copper sulfate to remove traces of amines and then redistilled.

Lauryl alcohol and lauric acid: Eastman Kodak Company Nos. 873 and 933 were used without further purification.

p-Toluenesulfonic acid: recrystallized twice from concentrated hydrochloric acid and dried in a vacuum desiccator in the presence of sodium hydroxide pellets to give the monohydrate. The monohydrate was converted into the anhydrous acid by drying in an Abderhalden pistol under vacuum at 115°C.

Lithium resinate was prepared *in situ* by adding metallic lithium to a solution of Resin 731S in lauryl alcohol.

Calcium resinate was prepared by neutralizing Resin 731S with calcium hydroxide in a benzene-alcohol solvent, filtering, and drying the resulting precipitate.

Zinc, manganese, magnesium, and cadmium resinates were prepared by mixing an aqueous solution of either the metallic nitrate or chloride with an aqueous solution of the potassium salt of Resin 731S, filtering the resulting precipitate, and drying it in a vacuum oven at 65°C. The metal resinates were analyzed for metal content, and the concentrations present in esterifications were based on actual metal content.

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Esterifications in Concentrated Solutions

Preliminary esterifications of pentaerythritol (PE) with WG wood rosin were carried out at 260, 280, and 300°C. At 260°C. the reaction followed second-order kinetics whereas at 300°C. the reaction appeared to be third order. At 280°C. the rate data could be satisfactorily fitted to either the second- or third-order rate equation. Second-order rate constants were calculated at 260 and 280°C. from the integrated rate equation, and an initial second-order constant was computed at 300°C. from the third-order constant. Figure 1 shows the logarithm of the rate constants plotted against the reciprocal of the absolute temperature. For comparison, second-order constants calculated from the data reported by Carter (9) are shown. The results are in reasonably good agreement, particularly since laboratory data are being compared with the data obtained in large-scale equipment by Carter. Our data fit the Arrhenius equation with a pre-exponential or frequency factor of 7.94×10^6 and an activation energy of 28,300 cal./mole. The corresponding factors for Carter's data are 3.72×10^5 and 24,500 cal./mole. (The units for the pre-exponential factor are kg. mole^{-1} sec.$^{-1}$)

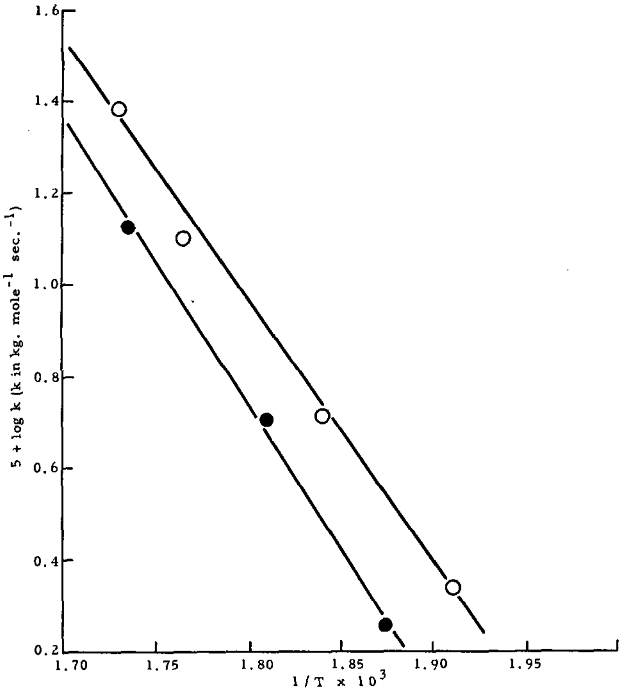

FIG. 1. Rate data for uncatalyzed esterification of WG wood rosin: ○, calculated from data reported by Carter (9); ●, this work.

Similar experiments were carried out on the esterification of Resin 731S with PE, both uncatalyzed and catalyzed, with lithium, sodium, calcium, magnesium, manganese, and zinc acetates. At the high reaction temperatures the acetates were no doubt converted to the corresponding resinates. Many of these esterifications appeared to follow second-order kinetics, particularly when metallic acetates had been added. Many esterifications however showed fractional orders and orders that varied with temperature. A few esterifications with the most effective catalysts, such as zinc acetate, even showed fractional over-all orders of less than two, which seemed anomalous until the data reported subsequently were obtained. Fractional orders between 2 and 3 however were not surprising as the uncatalyzed and catalyzed reactions were assumed to be third and second order, respectively. Because the rate of the uncatalyzed reaction was not negligible compared with the rate of the catalyzed reaction, over-all fractional orders were expected. In addition, the temperature coefficients of the two concurrent reactions are different, which qualitatively accounted for the shift in order with temperature. Whereas most results could be qualitatively explained, particularly when the possible effects of changing medium with the extent of reaction were considered, the quantitative isolation of the various factors in the kinetics was impossible. To avoid some of the complexities, all further rate studies discussed in this paper were made in dilute alcoholic solutions.

Esterifications in Dilute Alcoholic Solutions

In dilute alcoholic solutions uncatalyzed esterifications are pseudo-second order, and esterifications catalyzed by the solvated proton follow the Goldschmidt (3) equation

$$k_c = \frac{2.303\,[(a + r)\log a/(a - x)] - x}{crt}$$

where k_c is the catalytic rate constant, a the initial concentration of acid, x the amount of ester at time t, and c the concentration of the solvated proton, ROH_2^+. The quantity r is a constant defined as

$$r = \frac{[ROH]}{K} = \frac{[ROH_2^+]\,[H_2O]}{[H_3O^+]}$$

where K is the equilibrium constant for the reaction

$$ROH_2^+ + H_2O \rightleftharpoons H_3O^+ + ROH$$

The temperature dependence of the various rate constants can be treated according to Eyring's transition-state theory (10). According to this theory, a rate constant k is given by

$$k = \frac{k'T}{h}\,e^{\Delta S^{\neq}/R}\,e^{-\Delta H^{\neq}/RT}$$

where k′ is Boltzman's constant, h is Planck's constant, $\Delta S^{\neq}$ the entrophy of activation, and $\Delta H^{\neq}$ the heat of activation. According to this equation, a plot of log k/T *versus* 1/T should be linear with the slope $\Delta H^{\neq}/2.3R$.

Acid-Catalyzed Esterifications. The acid-catalyzed esterification of resin acids was studied briefly. To check experimental techniques the esterification rate of lauric acid in methanol when catalyzed by hydrogen chloride was measured at 25°C. for comparison with the results of H. A. Smith (11). A catalytic rate constant of 3.01×10^{-2} liters mole^{-1} sec.$^{-1}$ was obtained, which is in excellent agreement with 3.0×10^{-2} reported by Smith (11). This indicated that our methanol was anhydrous and contained no basic impurities.

An attempt was made to measure the esterification rate of dehydroabietic acid when catalyzed by hydrogen chloride, but hydrogen chloride reacted faster with methanol than the dehydroabietic acid esterified. Consequently p-toluenesulfonic acid (PTSA) was substituted for hydrogen chloride because detectable reaction was observed between PTSA and methanol after three days at 50°C. Since PTSA may not be completely dissociated in methanol, as implied by conductivity measurements (12), and since PTSA often contains trace amounts of moisture, catalyzed esterifications of lauric acid in methanol were studied at 25 and 50°C. to compare the catalytic activity of PTSA with that of hydrogen chloride. In these experiments, as well as in those with hydrogen chloride, the initial concentration of lauric acid and the concentration of catalyst were about 0.1 *N* and 0.005 *N*, respectively. The rate data with PTSA, shown as Goldschmidt plots in Figure 2, gave k_c = 2.6 × 10^{-2} liters $mole^{-1}$ $sec.^{-1}$ at 25°C., which is 13% lower than the value obtained with hydrogen chloride as catalyst. The 50°C. data do not pass through the origin, for no apparent reason, but the slope of the line gives $k_c = 0.104$ liters $mole^{-1}$ $sec.^{-1}$, which is about 7% lower than the value of 0.112 reported by Smith (11). These low values may indicate that PTSA is not completely dissociated in methanol or that it contained traces of moisture since special precautions were not taken in transferring stock solutions. Conductivity measurements however have shown that benzenesulfonic acid in methanol is slightly undissociated (12) and PTSA would be expected to behave similarly.

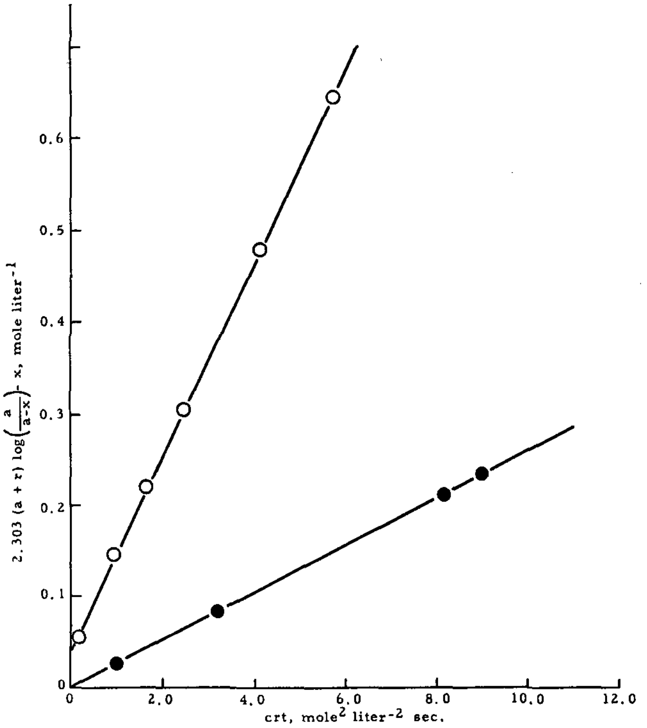

FIG. 2. p-Toluenesulfonic acid-catalyzed esterification of lauric acid in methanol: ●, at 25.0°C.; ○, at 50.0°C.

Figure 3 shows similar results for the PTSA-catalyzed esterification of dehydroabietic acid and perhydrogenated rosin in methanol at 50°C. The initial concentration of resin acid was again about 0.1 *N*, but the concentration of PTSA was 0.084 *N*. The data for dehydroabietic acid, like that for lauric acid, do not pass through the origin. From the slopes however, the catalytic rate constants are 1.08 × 10^{-5} liters $mole^{-1}$ $sec.^{-1}$ for dehydroabietic acid and 0.81 × 10^{-5} liters $mole^{-1}$ $sec.^{-1}$ for perhydrogenated rosin. These rate constants at 50°C. are apparently the lowest that have been reported for catalyzed esterifications in methanol. They can be compared qualitatively with 20.1 × 10^{-5} and 38.7 × 10^{-5} liters $mole^{-1}$ $sec.^{-1}$ for di-isobutylacetic acid and dibutylacetic acid, respectively, in methanol at 25°C. (13). In cyclohexanol at 55°C. however the rate constants for benzoic and o-iodobenzoic acids are 1.56 × 10^{-5} and 0.66 × 10^{-5} liters $mole^{-1}$ $sec.^{-1}$, respectively (14).

Several conclusions may be drawn from these results. Since the esterification of resin acids follows the Goldschmidt equation, this suggests no profound difference between the mechanism of resin acid and fatty acid esterification. In addition, since the rate constants for dehydroabietic acid and perhydrogenated rosin differ by only 20%, the effects observed in concentrated solution esterifications are probably not caused by differences in esterification rates of the different acids in rosin; the mixture of acids in Resin 731S should behave kinetically as a single substance.

Our experiments in methanol, while demonstrating several important points, were carried out under conditions which are markedly different from those used in the commercial esterification of rosin. Thus esterifications were carried out in lauryl alcohol to approach more nearly the conditions of the industrial processes and also to avoid difficulties in getting precise kinetic data because of the physical properties of pentaerythritol. In addition, lauryl alcohol is monohydric whereas pentaerythritol is tetrahydric. Although no evidence was found in this or other work (15) to indicate that the hydroxyls in pentaerythritol are not equivalent kinetically, the hydroxyls remaining in pentaerythritol after partial esterification with bulky resin acid molecules could possibly react with reduced rates. This possibility was avoided by using lauryl alcohol.

Although the hydrogen type of acids is not suitable as catalysts for the commercial esterification of rosin, a few esterifications of Resin 731S catalyzed by PTSA were carried out in lauryl alcohol between 125 and 170°C. The data followed pseudo-first-order kinetics,

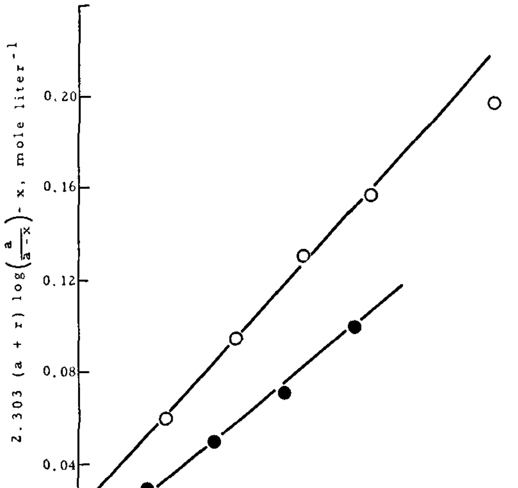

FIG. 3. p-Toluenesulfonic acid-catalyzed esterification of resin acids at 50.0°C.: ○, dehydroabietic acid; ●, perhydrogenated rosin.

and catalytic constants k_c were calculated by dividing the first-order constants by the concentration of PTSA. Figure 4 shows a plot of log k_c/T against $1/T$, from which $\Delta H^{\neq}$ was found to be 13,500 cal./mole and $\Delta S^{\neq}$ was −38.3 e.u. The value of $\Delta H^{\neq}$ is roughly the same as for the esterification of benzoic acid in methanol, but $\Delta S^{\neq}$ is smaller by about 10 e.u. (Table II).

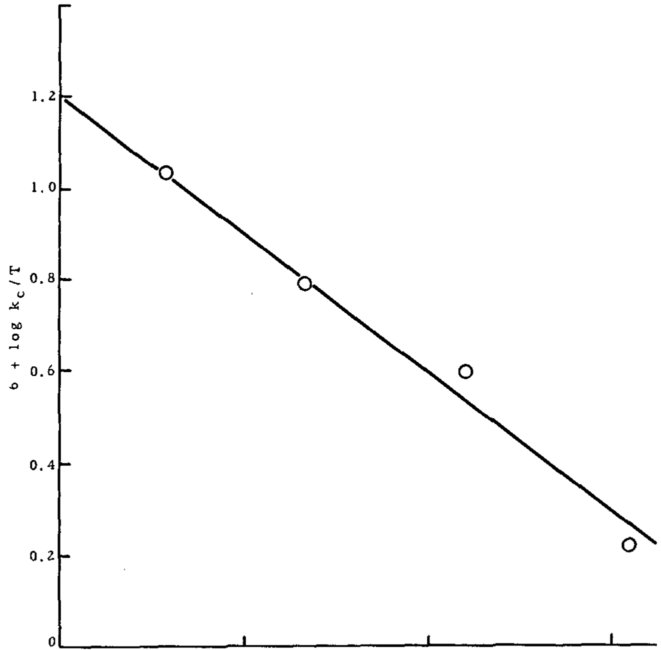

Fig. 4. Temperature dependence of catalytic rate constants for esterification of Resin 731S in lauryl alcohol (p-toluenesulfonic acid catalyst).

Uncatalyzed Esterification. The rates of esterification of Resin 731S and perhydrogenated rosin were measured in lauryl alcohol over the temperature range 230 to 260°C. The esterifications followed pseudo-second-order kinetics as expected. Plots of $1/c - 1/c_0$ against time were linear as shown in Figure 5 for perhydrogenated rosin, where c is the concentration of acid and c_0 the original concentration. Similar results were obtained for Resin 731S. From the plots of log k/T *versus* $1/T$ shown in Figure 6, $\Delta H^{\neq}$ was found to be 17,200 cal./mole for Rosin 731S and 16,200 cal./mole for perhydrogenated rosin. The $\Delta S^{\neq}$ values are −45.2 and −47.7 e.u. for Resin 731S and perhydrogenated rosin, respectively. From the data in Table II it can be calculated that, at 260°C., Resin 731S reacts more slowly with lauryl alcohol by a factor of 2 than does benzoic acid with methanol and more slowly by a factor of 3 than does myristic acid with ethanol.

TABLE I

Catalytic Rate Constants for Esterification of Resin 731S in Lauryl Alcohol

Temperature, °C.	$k_c \times 10^3$ liter mole^{-1} sec.$^{-1}$	
	Calcium resinate	Lithium resinate
220	0.097	0.142
240	0.41	0.387
250	0.84	......
260	1.04	0.848

Metallic Resinate-Catalyzed Esterifications. When catalyzed by metallic resinates, esterifications in dilute lauryl alcohol solution were found to be different and more complex than when catalyzed by hydrogen-ions. An accurate analysis of the kinetic data was difficult since the rate of the uncatalyzed reaction was not negligible compared with catalyzed reaction.

The metallic resinates decreased the over-all order of the reaction. The rate data often followed zero-order kinetics during the first 30 to 40% of the esterification, and then the apparent order increased. The same rate data however followed first-order kinetics to a greater extent of reaction, then the apparent order decreased. As rather accurate rate measurements are needed to differentiate between zero- and first-order kinetics during the first 30% of a reaction, it was thus not possible to decide what the initial order was. Since the uncatalyzed reaction is second order, this simultaneous reaction would tend to increase the observed order. But since the over-all order often became less than first as the reaction progressed, it was concluded that the catalyzed reaction is not simple first-order and must have a lower apparent order.

The first-order rate constant evaluated at zero time varied inversely with the initial concentration of resin acid, especially with zinc resinate as catalyst. To check for surface catalysis, experiments were made with broken glass in the reaction flask, but little or no effect on the rate data was observed. Also calcium resinate reacts slowly with lauryl alcohol at elevated temperatures to form a basic solution.

To explain the experimental observations the following two consecutive reactions are postulated to explain catalysis by a metallic resinate, such as calcium resinate:

$$R'OH + Ca(OOCR)_2 \xrightarrow{k_1} RCOOR' + Ca(OH)(OOCR) \qquad (1)$$

$$Ca(OH)(OOCR) + RCOOH \overset{K'}{\rightleftharpoons} Ca(OOCR)_2 + H_2O \qquad (2)$$

Although equation (1) may appear unlikely, it seems reasonable when it is recalled that resin acids are extremely weak acids, so the reaction of calcium resinate with R'OH at elevated temperatures is analogous to the hydrolysis of the salt of a weak acid. Equation

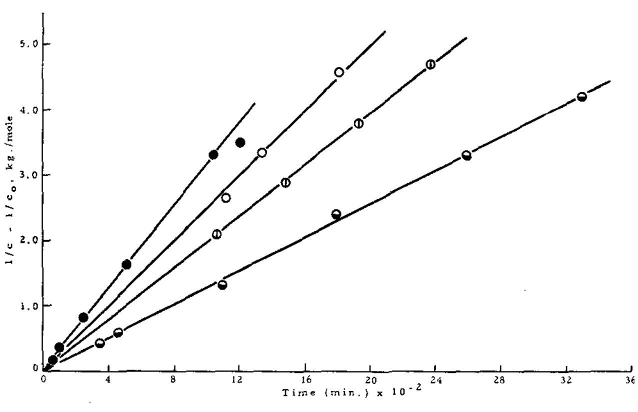

Fig. 5. Uncatalyzed esterification of perhydrogenated rosin in lauryl alcohol: ●, 260°C.; ○, 250°C.; ⦶, 240°C.; ⊖, 230°C.

TABLE II

Values of $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta F^{\neq}$ for Various Esterifications in Dilute Alcoholic Solutions

Catalyst	Esterification reaction	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta F^{\neq}$, calculated values at 260°C.
None	Myristic acid in ethanol [a]	13,900	−49.2	40,100
None	Benzoic acid in methanol [b]	17,400	−43.8	40,700
None	Resin 731S in lauryl alcohol	17,200	−45.2	41,300
None	Perhydrogenated rosin	16,200	−47.7	41,600
HCl	Fatty acids in methanol [a]	10,600	−29.8	26,500
HCl	Benzoic acid in methanol [b]	14,800	−28.4	29,900
PTSA[c]	Resin 731S in lauryl alcohol	13,500	−38.3	33,900
Calcium resinate	Resin 731S in lauryl alcohol	32,900	−11.3	38,920
Lithium resinate	Resin 731S in lauryl alcohol	22,400	−31.5	39,200

[a] Values calculated from data of Fairchild and Hinshelwood (19). [b] Values calculated from data of Hinshelwood and Legard (20). [c] p-Toluenesulfonic acid.

(2) is considered to be an equilibrium although the same final kinetic expressions are obtained if it is assumed that the rate constant for equation (1) is small compared with that for equation (2).

The equilibrium constant for equation (2) is

$$K = \frac{K'}{[H_2O]} = \frac{[S]}{[SOH]\,[RCOOH]} \qquad (3)$$

where S represents calcium resinate and SOH the basic calcium resinate. The concentration of water has been considered to be constant since its solubility in lauryl alcohol at high temperature is not known. As the solutions were stirred during esterification experiments and the reaction flasks were equipped with heated condensers, it was assumed that a steady-state concentration of water was established rapidly. If $[S]_o$ is the total concentration of catalyst, then

$$[S]_o = [S] + [SOH] = [S]\left\{1 + \frac{1}{K\,[RCOOH]}\right\} \qquad (4)$$

The rate of ester formation thus equals

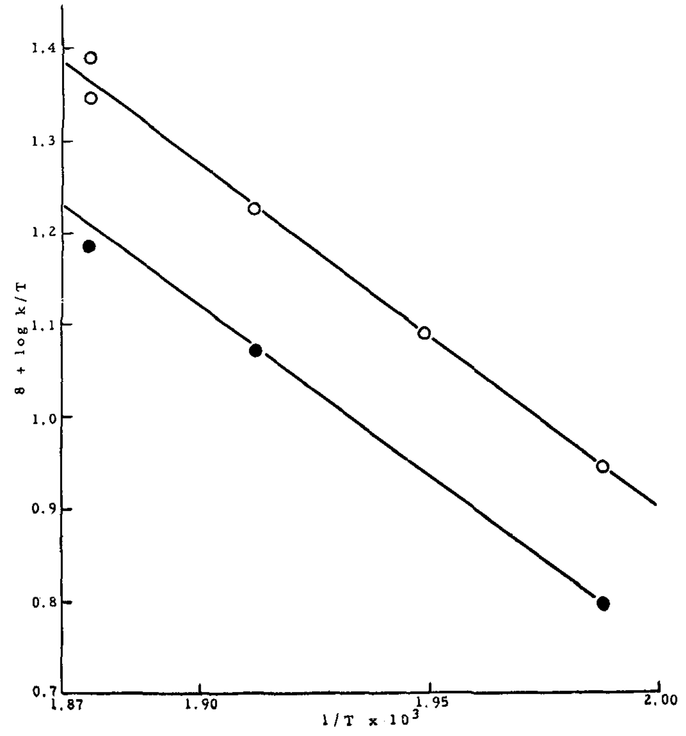

FIG. 6. Temperature dependence of rate constants for uncatalyzed esterifications in lauryl alcohol: ○, Resin 731S; ●, perhydrogenated rosin.

$$\frac{d\,[RCOOR']}{dt} = \frac{k_1\,[S]_o\,[R'OH]\,[RCOOH]}{1 + K\,[RCOOH]} \qquad (5)$$

or when a large excess of alcohol is present

$$\frac{dx}{dt} = \frac{k_c[S]_o\,(a - x)}{1 + K\,(a - x)} \qquad (6)$$

where x is the concentration of ester at time t and a the initial concentration of resin acid. Thus, when $K\,(a - x) >> 1$, the reaction will be zero order but will approach first order as $(a - x)$ goes to zero.

When the contribution of the uncatalyzed reaction is included in the rate equation, equation (6) can be written as

$$\frac{d \ln (a - x)}{dt} = \frac{k_c\,[S]_o}{1 + K\,(a - x)} + k_o\,(a - x) \qquad (7)$$

where k_o is the second-order constant for the uncatalyzed esterification. At zero time, equation (7) can be written in the form

$$\frac{[S]_o}{k_{obs} - k_o a} = \frac{1}{k_c} + \frac{Ka}{k_c} \qquad (8)$$

where k_{obs} is the observed initial first-order constant. Thus k_c and K can be evaluated from the dependence of k_{obs} on initial acid concentration.

Some rate data obtained at 260°C., using zinc resinate as catalyst, fit equation (8), as shown in Figure 7. A k_o value of 1.25×10^{-4} liter/mole-sec. was used, the result from uncatalyzed esterifications. The catalyst concentration for data shown by circles varied from 7.05×10^{-3} to 7.9×10^{-3} moles/liter whereas the catalyst concentration for the triangle was 3.75×10^{-3} moles/liter. Thus it appears that the rate may not vary linearly with catalyst concentration. From

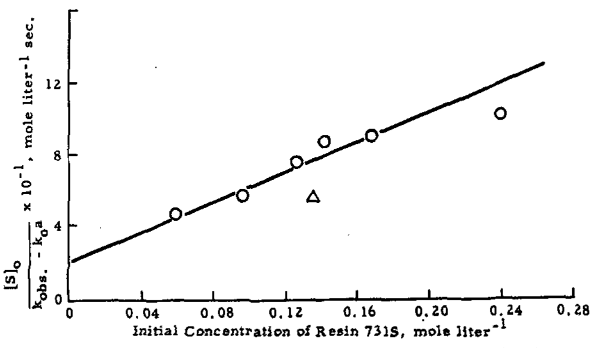

FIG. 7. Dependence of initial rate constant on initial concentration of Resin 731S (zinc resinate catalyst): ○, $0.00705 \leqslant [S]_o \leqslant 0.0079$; △, $0.00375 = [S]_o$.

the slope and intercept of the line, K and k_c were estimated to be 20 and 0.05 liter mole^{-1} sec.$^{-1}$, respectively.

Although some qualitative observations seemed to indicate that the rate of the catalyzed reaction does not vary linearly with catalyst concentration, some quantitative data obtained at 260°C. show that the rate constant does vary linearly with the concentration of calcium resinate. Figure 8 shows a plot of $(k_{obs} - k_oa)$ *versus* catalyst concentration, where k_{obs} is again the observed first-order constant and k_o the uncatalyzed rate constant. For data shown by the circles, the initial acid concentration varied from 0.109 to 0.152 moles/liter. The points shown by triangles, which lie below the line, are for initial acid concentrations between 0.203 and 0.278 moles/liter. Sufficient data were not available to determine whether or not the k_{obs} varied with initial acid concentration in the same manner as found for the zinc resinate-catalyzed esterifications. Since the triangles lie below the line however, it is likely that equation (8) holds for calcium resinate catalysis.

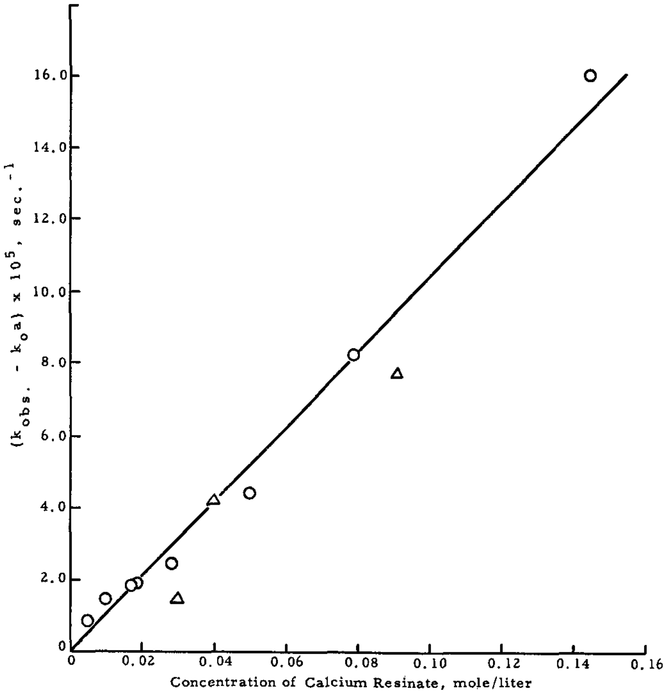

FIG. 8. Dependence of initial rate constant on concentration of calcium resinate: ○, $0.109 \leqslant a \leqslant 0.152$; △ $0.203 \leqslant a \leqslant 0.278$; $k_c = 1.04 \times 10^{-3}$ liter mole^{-1} sec.$^{-1}$.

Although the proposed mechanism is not proven, it is reasonable and is consistent with the kinetic observations.

Less extensive studies were made of catalysis by calcium resinate at 220, 240, and 250°C. and by lithium resinate at 220, 240, and 260°C. First-order rate constants were first calculated from initial rate data, next corrected for the contribution of the uncatalyzed esterification, and then converted into catalytic rate constants by dividing by the concentration of metallic resinate. Average values of the catalytic rate constants are given in Table I and are shown as plots of log k_c/T *versus* $1/T$ in Figure 9. From these plots $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were found to be 32,900 calories/mole and −11.3 e.u. for the esterification catalyzed by calcium resinate and 22,400 calories/mole and −31.5 e.u. for lithium resinate catalysis.

Table II gives values of $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta F^{\neq}$ at 260°C. for the uncatalyzed, hydrogen acid-catalyzed, and metallic resinate-catalyzed esterifications of resin acids and other acids. For uncatalyzed esterifications $\Delta H^{\neq}$ is similar for benzoic and resin acids, but lower for fatty acids, while $\Delta F^{\neq}$ shows that fatty acids react the fastest and resin acids the slowest. Hydrogen acid catalysts for the three types of acids decrease $\Delta H^{\neq}$ and increase $\Delta S^{\neq}$, and the $\Delta F^{\neq}$ values again show that the esterification rate decreases in going from fatty to benzoic to resin acids. For resin acids the metallic resinate catalysts increase $\Delta H^{\neq}$ over that for the uncatalyzed reaction. But this increase is more than counterbalanced by the increase (more positive) in $\Delta S^{\neq}$ so that $\Delta F^{\neq}$ at 260°C. is decreased and the metallic resinates speed up esterification. With calcium resinate at temperatures below 190°C. however $\Delta F^{\neq}$ is greater for the "catalyzed" than for uncatalyzed esterification. But since the metallic resinate decreases the order of the reaction, an esterification carried out slightly below 190°C. would be completed in less time than in the absence of resinate catalyst. Finally lithium resinate is a better catalyst below 245°C. than calcium resinate, as shown in Figure 9.

No definite conclusions can be drawn regarding relationships between the energies and entropies of activation and the structural properties of the several types of acid molecules since both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ change simultaneously with the type of acid. It should be mentioned however that $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the metallic resinate-catalyzed reactions no doubt contain contributions from the two reactions given by equations (1) and (2). This is true since it appears that equation (2) influences the initial esterification rate and so the temperature dependence of this

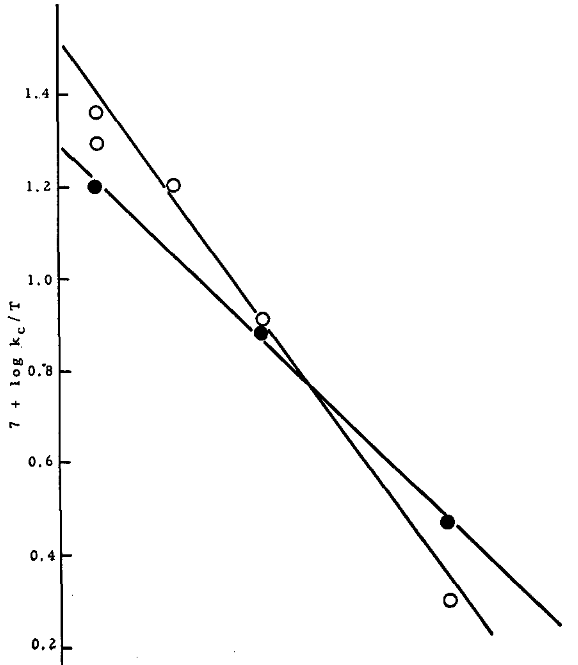

FIG. 9. Catalytic rate constants for esterification of Resin 731S in lauryl alcohol: ○, calcium resinate; ●, lithium resinate.

equilibrium will influence the observed energy and entropy of activation for ester formation.

Brief studies were also made, using magnesium, manganese, cadmium, and lead resinates as catalysts. These salts showed kinetic behavior similar to lithium and calcium resinates in that they reduced the over-all order to less than unity, especially with cadmium and magnesium resinates. When cadmium and lead resinates were used, black metallic-like materials formed during an esterification. These materials were believed to be metallic cadmium and lead because of their appearance and their reaction with dilute nitric acid.

Acidities of Metallic Resinates in Rosin

It has been found (16) that metal resinates may be ranked in order of their Lewis-type acidity in molten rosin by means of indicator (Rhodamine B) measurements. From spectrophotometric measurements an equilibrium constant K may be calculated for the assumed reaction $MA + In \rightleftharpoons MIn^{+}A^{-}$ where MA is the metal resinate, In is the basic form of the indicator, and $MIn^{+}A^{-}$ the metallic resinate-indicator complex. The values of K indicate the tendency of a metallic resinate to accept electrons from the basic form of the indicator.

Values of K were determined for a series of metallic resinates in molten rosin at 200°C. A correction was made for the acidity of the molten rosin medium and its effect on the measured indicator ratios. If the mechanism proposed in equations (1) and (2) is correct, there should be a relationship between the acidities or electron-accepting tendencies of the various metal resinates and their catalytic efficiencies. Figure 10 shows a plot of log K in molten rosin at 200°C. against log k_c for catalyzed esterifications of Resin 731S in lauryl alcohol at 260°C. Lithium and calcium resinates are not shown because only qualitative values of K were obtained because of unfavorable indicator ratios obtained in the acidity measurements on these compounds. But qualitatively the K values for calcium and lithium resinates agreed with the relationship shown in Figure 10. Although the media and temperatures for the K and k_c measurements are markedly different, an essentially straight-line relationship is obtained; those salts with a higher acidity give higher catalytic rate constants hence are more efficient catalysts.

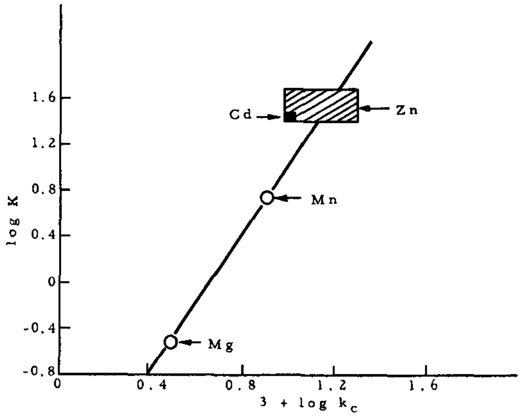

FIG. 10. Variation of catalytic rate constant, k_c, with "acidity" of metallic resinates.

Discussion of Results

The experimental results can be compared with the theory of nucleophilic substitutions given by Swain (17). He considers that nucleophilic substitutions involve a concerted attack of a nucleophilic group (N) and an electrophilic group (E) upon a substrate molecule (S). The formation of the activated complex is a termolecular reaction between N, S, and E. In some reactions however two of these functional groups may exist in the same molecule, consequently the formation of the activated complex is a bimolecular reaction. Within this framework the generally accepted theories for the mechanism for esterification (18) and our proposed mechanism for metallic resinate catalysis may be formulated.

In uncatalyzed esterifications the activated complex contains two molecules of acid and one of alcohol. The alcohol molecule contains the nucleophilic group while one molecule of acid contains the electrophilic group. Both groups form the activated complex along with a second acid molecule. In hydrogen-ion-catalyzed esterifications ROH_2^+ is the electrophilic species which forms an activated complex with an acid molecule while a neutral alcohol molecule is the nucleophilic molecule. ROH_2^+ is a stronger electrophilic species than an uncharged acid molecule so the esterification rate is greater when hydrogen ions are present.

In changing from uncatalyzed to hydrogen-ion-catalyzed esterifications $\Delta H^{\neq}$ decreases and $\Delta S^{\neq}$ becomes more positive. It seems reasonable that $\Delta H^{\neq}$ is reduced because ROH_2^+ is a stronger electrophilic species than RCOOH so less energy is required to form the activated complex. Since the hydrogen ion is labile, it is reasonable that $\Delta S^{\neq}$ is increased (becomes more positive).

According to the mechanism for metallic resinate catalysis proposed in equations (1) and (2), the activated complex contains one molecule of metallic resinate and one of alcohol. But now the substrate and the electrophilic group (metallic ion) are in the same molecule. Since the metallic ions studied are relatively weak electrophilic species, a large amount of energy might be required to form the activated complex which may explain the high values of $\Delta H^{\neq}$. On the other hand, $\Delta S^{\neq}$ is considerably more positive than for hydrogen-ion catalyzed esterifications. This is reasonable since only two molecules instead of three form the activated complex; the probability of two molecules coming together is ordinarily greater than the probability that three will unite. As discussed previously, the increase in $\Delta S^{\neq}$ outweighs the increase in $\Delta H^{\neq}$ in going from uncatalyzed to metallic resinate-catalyzed esterifications so the metallic resinates function as catalysts.

These suggested correlations between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ and the molecular structure of the activated complexes are perhaps tenuous since, in general, heats and entropies of activation involve both kinetic energy and potential energy contributions. It is interesting however and perhaps useful to make these postulates, which are based on the assumption that the major variations in $\Delta H^{\neq}$ result from changes in the potential-energy barriers.

Summary

The kinetics of the esterification of resin acids in both concentrated solutions and dilute alcoholic solu-

tions were studied over a wide temperature range. In concentrated solutions the order of the reaction changes with both the temperature and the extent of reaction, but in dilute solutions the kinetics are similar to those for other organic acids. The uncatalyzed esterification is pseudo-second order while the hydrogen-ion-catalyzed esterification is first order and follows the Goldschmidt equation. Thus the esterification mechanism is probably the same as for other organic acids even though the carboxyl group on a resin acid molecule is highly hindered.

Catalysts by six metallic resinates—especially calcium and lithium—was also studied. The catalytic rate constants at 260°C. varied quantitatively with the "acidity" of the metallic resinates in rosin at 200°C. As esterification catalysts, the metallic resinates increase the activation energy but also increase the activation entropy sufficiently so that the free energy of activation is decreased, especially at high temperatures. The observed kinetic behavior agrees with a rate expression derived by assuming that the rate-controlling step is a reaction of metallic resinate with the alcohol to form an ester and a basic metallic resinate.

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X-Ray Diffraction and Melting-Point Studies on Some Long-Chain Sulfur-Containing Acids[1]

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THIS PAPER reports the x-ray diffraction powder data and melting points of three series of crystalline long-chain sulfur-containing acids, namely, some terminally substituted undecanoic acids. These compounds are

a) sulfones, 11-(*n*-alkylsulfonyl)undecanoic acids, $RSO_2(CH_2)_{10}CO_2H$;
b) sulfoxides, 11-(*n*-alkylsulfinyl)undecanoic acids, $RSO(CH_2)_{10}CO_2H$; and
c) sulfides, 11-(*n*-alkylthio)undecanoic acids, $RS(CH_2)_{10}CO_2H$;

where R is a selected radical from methyl through undecyl. Aside from 11-(carboxymethylthio)undecanoic acid (2) there seems to be no x-ray diffraction data available on the effect on the solid-state structure of interrupting long-chain aliphatic compounds with a sulfide, sulfoxide, or sulfone group.

Experimental

Preparation. The compounds studied had the general formulas given above. They were recrystallized solids of high purity unless otherwise indicated. In addition to the acids previously reported (2, 3, 6) the new compounds listed in Table I were also used; these were prepared by the published methods.

X-Ray Technique. All samples were run on a G. E. XRD-3 direct-recording diffraction unit, using nickel-filtered CuK_α radiation ($\lambda = 1.5405$ Å), 1° beam slit, 0.1° detector slit, medium resolution Soller slit, 2°-per-min. scanning speed, 60 in./hr. chart speed, linear scale, and 2-sec. time constant. For the powder data reported in Tables II, III, and IV samples were carefully ground in an agate mortar to insure random orientation and packed into the recess of a plastic holder approximately 1.0 in. long, 0.5 in. wide, and 0.015 in. deep. The intensities of the diffraction lines reported were measured as counts/sec. at the peak height minus counts/sec. of the background, and then expressed on a relative scale ($I_{Rel.}$) with the strongest line arbitrarily given a value of 1,000.

The long spacings reported in Table V were obtained from oriented samples. Unground samples were placed in a thin layer on a glass slide and firmly pressed to insure adherence. The exposed surface on the glass slides was about 0.5 in. wide by 0.5 in. long. In general, particularly sharp and intense peaks were obtained, and in a number of cases 20 or more orders of the long spacing were observed. At least five orders are included in each average reported in Table V. The first and sometimes the second orders were not included in the average because of the limited accuracy

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