Apparatus.—The preparations and cleavages of the alcoholates were carried out in a 1.8 × 8.5-cm. cylindrical flask fitted to a 0.7 × 12-cm. total-condensation variable-take-off column packed with 1/8-inch glass helices. Distillate was collected in a 15-ml. tube cooled in ice. Evolved gases were led to a 30-ml. trap cooled by liquid nitrogen. A slow stream of nitrogen gas was passed across a T-tube at the outlet of the trap to prevent condensation of air and moisture. Temperature was measured by an iron–constantan thermocouple placed in a well inside the flask. Condensed gases were expanded for measurement into a storage system consisting of a manifold to which was attached two 1-liter flasks, manometer, and stopcocks leading to a vacuum pump and a 10-cm. gas cell for infrared measurements.

Preparation of Alkoxides.—A weighed quantity of the tertiary alcohol was converted under nitrogen in the apparatus to the lithium, sodium or potassium alcoholate. Metallic potassium, powdered lithium hydride (Maywood Chemical Co.), ethereal sodium triphenylmethide and sodium amide (Farchan Research Laboratories) were employed as bases. The temperature was increased sufficiently to produce reaction. Ammonia or ether, when present, was removed by distillation into a separate trap.

Cleavage of Alkoxides.—The procedure is illustrated by one example, cleavage of the potassium salt of diisopropyl-*t*-butyl carbinol. The alkoxide was prepared from 6.406 g., 0.0372 mole, of carbinol and 0.658 g., 0.0168 mole, of potassium. Cleavage began at 180° in the presence of the excess carbinol. The temperature in the flask then fell to 160° during the next 8 hours even though that of the surrounding air-bath was increased from 185 to 250°. A few drops of distillate were collected during this period. Finally, distillation occurred rapidly at a flask temperature of 177–182°. The residue then was heated for 80 min. at 190–196°, but no additional distillate was collected.

The distillate, 2.146 g., was a clear, colorless liquid with a sweet odor. A 0.132-g. aliquot was diluted to 10.0 ml. with carbon tetrachloride for infrared analysis. The spectrum showed the presence of only diisopropyl ketone and isopropyl t-butyl ketone; characteristic peaks for diisopropyl-*t*-butylcarbinol at 2.80, 10.44 and 10.50 μ were absent. Absorbances at 9.45 and 9.73 μ were 0.424 and 0.471, respectively. Specific absorbances for diisopropyl ketone at these wave lengths are 0.11 and 1.35 l. g.$^{-1}$ cm.$^{-1}$. For isopropyl *t*-butyl ketone, the values are 0.92 and 0.056 l. g.$^{-1}$ cm.$^{-1}$. Solution of simultaneous equations gave 0.0058 g./ml. for diisopropyl ketone and 0.0080 g./ml. for isopropyl *t*-butyl ketone corresponding to 0.0082 and 0.0100 mole of each, respectively.

The residue, 3.033 g., was a cream-colored solid. After hydrolysis with 20 ml. of water, the mixture was extracted with 10-ml., 5-ml., 5-ml. and 3-ml. portions of carbon tetrachloride. The combined extract was washed with 7 ml. of water, diluted to 25.0 ml. with carbon tetrachloride and dried over Drierite. Again, the spectrum showed the presence of only the two ketones. The absorbances were 0.800 at 9.45 μ and 4.98 at 9.73 μ corresponding to 0.014 mole of diisopropyl ketone and 0.0031 mole of isopropyl *t*-butyl ketone.

Expansion of the condensed gases gave 783 ml. of hydrocarbon gas at S.T.P. The following composition was obtained by infrared analysis: isobutane, 460 ml., 0.021 mole; propane, 270 ml., 0.016 mole; isobutylene, 3 ml., 0.00012 mole; and methane, 50 ml., 0.00022 mole. The over-all results are summarized in Table II.

Infrared Spectra and Analyses.—Spectra were measured with a Perkin–Elmer model-21 double-beam spectrophotometer equipped with sodium chloride optics. Analyses of liquid products in carbon tetrachloride solution were made by determination of a base line with solvent in two 0.52-mm. matched cells, then by substitution of the solution for the solvent in one cell. Absorbances were measured at frequencies characteristic of each product present, and concentrations were determined by solution of simultaneous equations. Spectra of all pure alcohols, ketones and hydrocarbon gases were measured separately at three or more concentrations and found to follow Beer's law at the wave lengths used for analysis. Benzene and neopentane were measured in both gas and distillate.

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[CONTRIBUTION FROM THE COLGATE–PALMOLIVE CO.]

The Reaction of Lauric Acid Esters with Sulfuric Acid

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Reversibility of the reaction of methyl laurate with sulfuric acid to form lauric acid and methyl sulfuric acid has been demonstrated, and concentration equilibrium constants have been calculated for the reaction at 30.5 and 40.7°. The effect of water and of sulfuric anhydride was observed. Diesters of lauric acid and ethylene, propylene, trimethylene and pentamethylene glycols were prepared and allowed to react with 100% sulfuric acid. The reactions of ethylene glycol monolaurate and of sodium lauroxyethyl sulfate with sulfuric acid also were studied. Stepwise rapid cleavage of lauric acid from the diesters was observed, and, except in the case of pentamethylene glycol dilaurate, one of the principal products obtained on quenching the reaction with water was the glycol monolaurate. A cyclic carbonium ion mechanism is suggested to account for the results.

Previous work on the reaction of simple esters with concentrated sulfuric acid has established that a product is formed which yields a carboxylic acid on dilution with water, and that the rate and extent of formation of this product varies with the structure of the ester.[2] The structure of this product has been given variously as RCO^+ (in the case of mesitoates and certain related esters),[3,4] $RCOH_2^+$ [5] or $RCOOSO_3H$.[6] Cryoscopic evidence for the instability of the acetyl and benzoyl cations in sulfuric acid of concentration 100% or less has been obtained by Leisten.[7] The postulation of the mixed anhydride $RCOOSO_3H$ he shows to be unnecessary, leaving the protonated carboxylic acid as the most likely structure of the stable species from unhindered esters. The other product of the reaction is an alkyl sulfuric acid, which, at least for the methyl and ethyl esters, has been found to be completely stable in sulfuric acid.[8]

The only clear-cut evidence for a mechanism is that of Leisten[9] who assigns the unimolecular acyl–oxygen fission mechanism (AAc1) to the solvolysis of methyl and ethyl benzoates and the corresponding alkyl–oxygen fission mechanism (AAl1)

(1) University of Vienna, Vienna, Austria.

(2) R. J. Gillespie and J. A. Leisten, *Quart. Revs.*, **8**, 40 (1954).

(3) H. P. Treffers and L. P. Hammett, THIS JOURNAL, **59**, 1708 (1937).

(4) M. S. Newman, *ibid.*, **63**, 2341 (1941).

(5) M. S. Newman, R. A. Craig and A. B. Garrett, *ibid.*, **71**, 869 (1949).

(6) L. P. Kuhn and A. H. Corwin, *ibid.*, **70**, 3370 (1948).

(7) J. A. Leisten, *J. Chem. Soc.*, 298 (1955).

(8) R. J. Gillespie, *ibid.*, 2542 (1950).

(9) J. A. Leisten, *ibid.*, 1572 (1956).

to the solvolysis of isopropyl and *t*-butyl benzoates—this on the basis of the effects of substituents and of water on the over-all rate. Actually this work establishes that the reaction is of zero order in bisulfate ion or in water, and not that it is truly unimolecular, since sulfuric acid was used in such large excess.

In this paper we present evidence for the existence of an equilibrium in the sulfuric acid solvolysis of aliphatic esters. We also report the first study of the behavior of several glycol esters of lauric acid in sulfuric acid and present a hypothesis for the nature of the novel reactions and the products.

Experimental

Materials.—Sulfuric acid of 100% strength was prepared by mixing commercial 96.2% acid with sulfur trioxide (Sulfan B) until both Karl Fischer aquametry[10] and alkalimetry gave results of 100.0 to 100.1%. Commercial methyl laurate of about 95% purity was fractionated and the material to be used was collected at b.p. 117–118° (5 mm.), $n^{25}D$ 1.43042. Lauric acid was prepared by alcoholic saponification of the pure methyl laurate and crystallized from acetone, m.p. 43.5–44.0°.

All glycol mono- and diesters were prepared by transesterification of pure methyl laurate and the appropriate glycol (distilled before use). They were purified by distillation and crystallization. Purity was established by partition column chromatography with the system powdered rubber–methanol, monitored by an automatic recording differential refractometer (model 5602, Phoenix Precision Instrument Co.), which system was capable of separating cleanly the mono- and diesters. In addition to ethylene glycol monolaurate[11] and dilaurate,[12] propylene glycol dilaurate[12] and trimethylene glycol dilaurate,[13] which have been described previously, several more esters were prepared.

Propylene Glycol Monolaurate.—A mixture of 152 g. of propylene glycol, 214 g. of methyl laurate and 1 g. of sodium hydroxide was heated in a current of nitrogen to 117°, when distillation of methanol began. The temperature was increased over two hours to 175°, when distillation of methanol ceased. The reaction mixture was cooled, washed free of catalyst, dried, and distilled. The fraction boiling at 133–137° (0.6 mm.) weighed 184 g. (The residue from distillation contained 110 g. of propylene glycol dilaurate.) After low temperature crystallization from Skellysolve B, the product melted at 5–6°. No attempt was made to separate possible isomers.

Anal. Calcd. for $C_{15}H_{30}O_3$: C, 69.72; H, 11.70. Found: C, 69.72; H, 11.80.

Trimethylene Glycol Monolaurate.—A mixture of 114 g. of trimethylene glycol, 214 g. of methyl laurate and 1 g. of sodium hydroxide was heated under nitrogen to 100°, when distillation of methanol began. During two hours the temperature was raised to 200°, and 34 ml. of methanol was collected. It was found necessary in this case to crystallize once from methanol prior to distillation to avoid decomposition. The yield was 125 g. of monoester and 90 g. of diester. Further crystallization of the monoester from Skellysolve B gave a product with m.p. 22–23°, $n^{25}D$ 1.44582.

Anal. Calcd. for $C_{15}H_{30}O_3$: C, 69.72; H, 11.70; OH, 6.58; sapn. equiv., 258.4. Found: C, 69.69; H, 12.03; OH, 6.72; sapn. equiv., 257.4.

Pentamethylene Glycol Dilaurate.—A mixture of 52 g. of pentamethylene glycol, 300 g. of methyl laurate and 2 g. of sodium hydroxide was heated under nitrogen to 200–220° for 3 hours, allowing methanol to distil out. The reaction mixture was cooled, taken up in Skellysolve B, filtered, and the diester allowed to crystallize. The 200 g. of material thus obtained was recrystallized several times from methanol, m.p. 29.0–29.5°.

Anal. Calcd. for $C_{29}H_{56}O_4$: C, 74.31; H, 12.04. Found: C, 74.62; H, 11.96.

Sodium Lauroxyethyl Sulfate.—A stirred mixture of 80 g. of ethylene glycol monolaurate and 175 ml. of ethylene chloride was treated at 10° with 20 ml. of chlorosulfonic acid. The reaction mixture was poured into ice-water and neutralized to *p*H 4 with sodium hydroxide. The aqueous layer was separated and extracted with *n*-butyl alcohol. The alcoholic solution was concentrated *in vacuo* until crystallization began. The product was recrystallized from methanol in 41.5 g. yield.

Anal. Calcd. for $C_{14}H_{27}O_6SNa$: S, 9.26; sapn. equiv., 173.2. Found: S, 9.24; sapn. equiv., 171.3.

Methods.—Weighed quantities of sulfuric acid and the ester were mixed in 100-ml. volumetric flasks with magnetic stirring and heating or cooling as needed to maintain the desired temperature. The stoppered flask of homogeneous reaction mixture was kept in a constant temperature bath and agitated periodically. Samples of approximately 5-ml. volume were withdrawn, weighed, and quenched in 30 ml. of ice-water. Neutralization in the presence of 10 ml. of methanol was immediate using sodium hydroxide solution. Ethyl ether-soluble components were removed by rapidly performed, repeated extraction, whereupon the aqueous solution was adjusted to *p*H 6–7 and diluted up to 250 ml. in a volumetric flask.

Analysis.—The ether solution was found to contain monoester, diester and lauric acid. The latter was determined alkalimetrically and then removed from the mixture by adsorption on a moderately basic ion exchange resin (Duolite A-30) from solution in 3A ethyl alcohol. In the resulting mixture of glycol mono- and dilaurate the former was determined by way of quantitative acetylation[14] and the latter by difference. This method was checked frequently by hydrolyzing the ester mixture and determining the liberated acid by titration and the glycol by periodate oxidation.

The aqueous solution was found to contain sodium sulfate, glycol monolaurate monosulfate and glycol sulfates. No free glycol ever was found. The monolaurate monosulfate was determined by titration with cetylpyridinium bromide to a methylene blue phase-transfer end-point.[15] Glycol sulfates (mono- and disulfates were not distinguished) were determined by way of the glycol liberated on acid hydrolysis, correcting for the glycol monolaurate monosulfate present.

Results and Discussion

Methyl Laurate.—Preliminary experiments on the reaction of methyl laurate with 100% sulfuric acid revealed the presence in the reaction mixture of lauric acid, methyl sulfuric acid and starting materials. From acid and ester analyses on material isolated from mixtures of methyl laurate and sulfuric acid allowed to stand for 20 hours at 30.5 and 40.7°, concentration equilibrium constants were calculated from the expression

$$(C_{11}H_{23}COOH)(CH_3HSO_4)/(C_{11}H_{23}COOCH_3)(H_2SO_4)$$

These data are in Table I.

Aside from a small drift in values for K of about 10% over the range studied, which may be ascribable to the neglect of activity coefficients in quite concentrated solutions, the results definitely indicate the existence of the equilibrium 1

$$RCOOMe + H_2SO_4 \rightleftharpoons RCOOH + MeHSO_4 \quad (1)$$

where the formulas are meant to represent the products obtained on dilution with water and not the species actually present in the sulfuric acid solution.

Additional evidence for the equilibrium was obtained by running the reverse reaction, *i.e.*, dissolv-

(10) J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 245.

(11) P. E. Verkade, F. D. Tollenaar and T. A. P. Posthumus, *Rec. trav. chim.*, **61**, 373 (1942).

(12) H. Staudinger and H. Schwalenstoecker, *Ber.*, **68**, 727 (1935).

(13) H. Staudinger and H. Moser, *ibid.*, **69B**, 208 (1936).

(14) C. L. Ogg, W. L. Porter and C. O. Willits, *Ind. Eng. Chem., Anal. Ed.*, **17**, 394 (1945).

(15) S. R. Epton, *Trans. Faraday Soc.*, **44**, 226 (1948).

TABLE I

Moles H_2SO_4 / Moles RCOOMe	$K^{30.5°}$	Moles H_2SO_4 / Moles RCOOMe	$K^{40.7°}$
3.16	0.298	3.06	0.346
4.04	.301	3.06	.344
4.26	.304	4.09	.327
5.01	.297	4.10	.324
5.87	.295	6.08	.321
11.77	.271	6.10	.318
12.08	.275	12.27	.302
19.21	.257	12.28	.303
19.44	.266	20.48	.294
		20.54	.298

ing methanol in sulfuric acid and then adding lauric acid. That methanol is completely sulfated by three moles of sulfuric acid in three hours at 30.5° is shown by the data of Table II.

TABLE II

MeOH, mmoles	H_2SO_4, mmoles	H_2SO_4 / MeOH	Meq. acid Start	Meq. acid Finish	Reaction, %
18.54	18.66	1.006	37.32	24.19	70.8
17.89	18.90	1.056	37.80	25.42	69.2
18.54	37.32	2.013	74.64	57.44	92.3
17.92	37.77	2.107	75.54	58.97	92.4
18.54	55.98	3.019	111.96	93.55	99.3
17.95	56.23	3.133	112.46	94.67	99.2

The lauric acid recovered after seventeen hours of reaction at 30.5° of equimolar quantities of lauric acid with methylsulfuric acid in sulfuric acid is compared in Table III with the lauric acid formed under similar conditions from methyl laurate in sulfuric acid.

TABLE III

Moles H_2SO_4 / Moles RCOOH(Me)	% RCOOH recovered in reverse reacn.	% RCOOH formed in forward reacn.
1.94	47.4	44.7
2.94	57.1	54.5
5.88	70.3	67.5

Although in the reverse reaction there is present a mole of water, formed in the reaction of the methanol with sulfuric acid, and this might be supposed to affect the equilibrium, such is not the case. As shown in Table IV the addition of water in amounts up to equimolar with ester in three moles of sulfuric acid does not alter the extent of solvolysis in a 20-hour period.

TABLE IV

Moles H_2O added	% H_2SO_4 resulting	Conversion of ester to acid
0	100	56.6
0.22	98.7	56.9
.44	97.4	56.6
.88	94.8	56.8
1.0	94.2	56.8
3.0	84.4	51.7
4.0	80.3	50.6

When the reaction was run in oleum of strengths up to 25%, the sulfur trioxide present appeared not to affect seriously the proportion of ester solvolyzed. However, some of the lauric acid formed was converted to a water-soluble product, stable in acid solution and titratable with cetylpyridinium bromide. This is most likely a sulfonation product, such as 2-sulfolauric acid.

Glycol Laurates.—In extending the work to glycol esters we might expect, analogous to 1, the establishment of equilibria 2 and 3.

$$RCOOCH_2CH_2OCOR + H_2SO_4 \rightleftharpoons \underset{\text{I}}{RCOOCH_2CH_2OSO_3H} + RCOOH \quad (2)$$

$$RCOOCH_2CH_2OSO_3H + H_2SO_4 \rightleftharpoons \underset{\text{II}}{HO_3SOCH_2CH_2OSO_3H} + RCOOH \quad (3)$$

In test runs on ethylene glycol dilaurate the three postulated products were indeed found, but a fourth major product also was isolated—ethylene glycol monolaurate. This substance did not arise from hydrolysis of I during the work-up, since, despite its sensitivity to acid, Compound I was shown to be decomposed to the extent of less than 1% under the particular conditions obtaining. Finding monoester confirms an observation of Grün[16] who reported obtaining some monoester from the reaction of 3-chloro-1,2-propanediol distearate with 98% sulfuric acid.

Propylene glycol dilaurate (1,2-propanediol dilaurate) behaved very similarly, and in Fig. 1 the effect of increasing amounts of sulfuric acid on the equilibrium concentrations of lauric acid, propylene glycol monolaurate monosulfate (III) and propylene glycol monolaurate (IV) is depicted. The dilauric esters of trimethylene glycol (1,3-propanediol) and pentamethylene glycol (1,5-pentanediol) behaved a little differently as shown in Figs. 2 and 3. Pentamethylene glycol dilaurate behaved most like methyl laurate, and, indeed, concentration equilibrium constants could be calculated from the expression

$$\frac{[HO_3SO(CH_2)_5OSO_3H][RCOOH]^2}{[RCOO(CH_2)_5OCOR][H_2SO_4]^2}$$

which showed a fair degree of constancy (see Table V).

TABLE V

Moles H_2SO_4/moles ester	$K^{40°}$
3.81	0.169
5.63	.139
7.67	.119
13.68	.118

This type of calculation could not be made for the other esters. It would seem that there is some interaction of the two oxygen-bound groups which decreases inversely with the distance between them. These curves also show that differences between the various glycol esters become less, and all tend to approximate the behavior of methyl laurate, at high concentrations of sulfuric acid.

The curves for three of the esters show plateaus in the neighborhood of sulfuric acid to ester mole ratios of 6; hence, this ratio was chosen for time studies. The data obtained at 40° are plotted in Figs. 4–7. The immediate formation in each case of lauric acid and monolaurate monosulfate is evidence for reaction 2. To verify reaction 3 sodium lauroxyethyl sulfate was allowed to react with 8.7 moles of sulfuric acid to produce the results shown in Table VI.

(16) A. Grün and E. Theimer, *Ber.*, **40**, 1792 (1907).

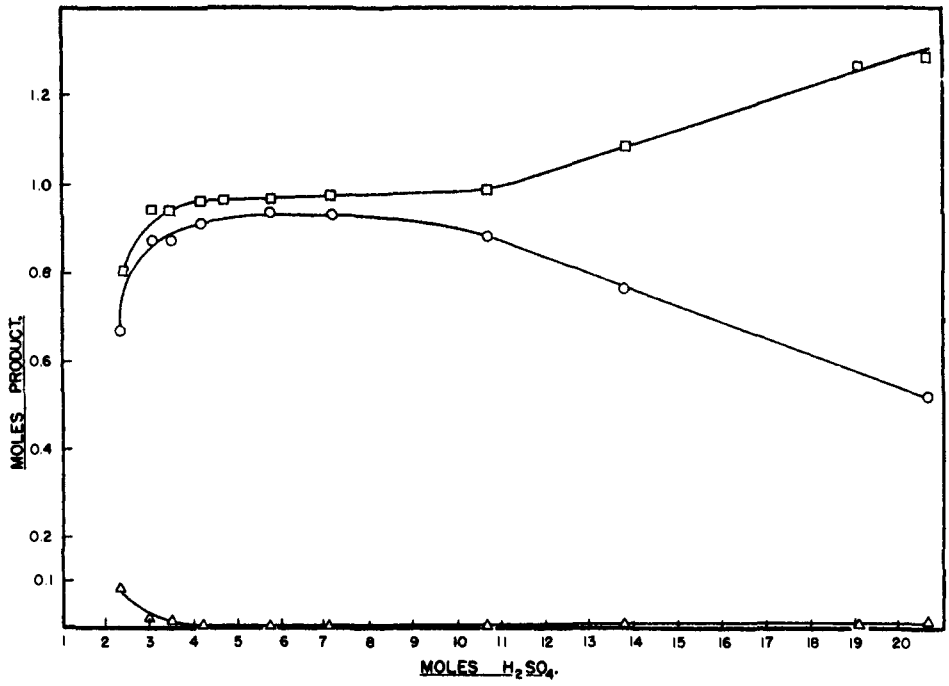


Fig. 1.—Reaction of propylene glycol dilaurate with sulfuric acid for 20 hours at 40°: □, lauric acid; △, monoester monosulfate; O, monoester.

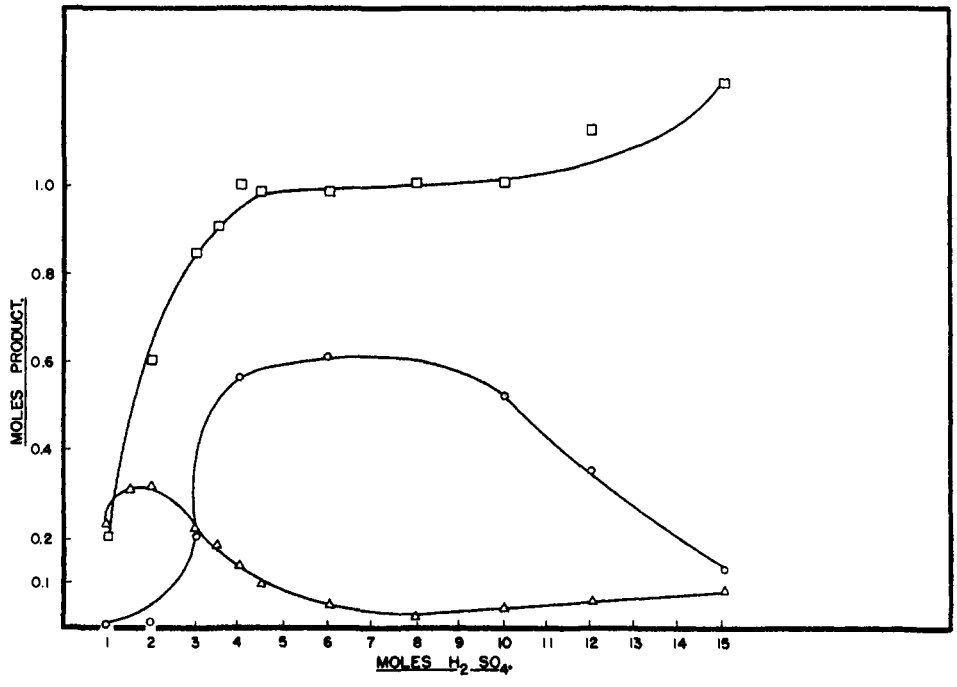


Fig. 2.—Reaction of trimethylene glycol dilaurate with sulfuric acid for 20 hours at 40°: □, lauric acid; △, monoester monosulfate; O, monoester.

TABLE VI

Time, min.	Temp., °C.	Lauroxyethyl sulfate[a]	Monoester	Lauric acid	Glycol sulfates
6	20	0.228	0.082	0.644	0.713
12	20	.171	.082	.703	.760
20	20	.105	.146	.712	.800
60	40	.095	.250	.623	.641
18 hr.	40	.0	.787	.157	.200

[a] Quantities expressed in mmole.

The monolaurate monosulfate is seen to be quite unstable in sulfuric acid, reacting rapidly to give lauric acid and glycol sulfate as predicted. After a longer time monolaurate becomes the chief product, just as when glycol dilaurate is the starting material. The reversible nature of these reactions was demonstrated by dissolving ethylene glycol in sulfuric acid and then adding lauric acid. All the expected components were found in proportions

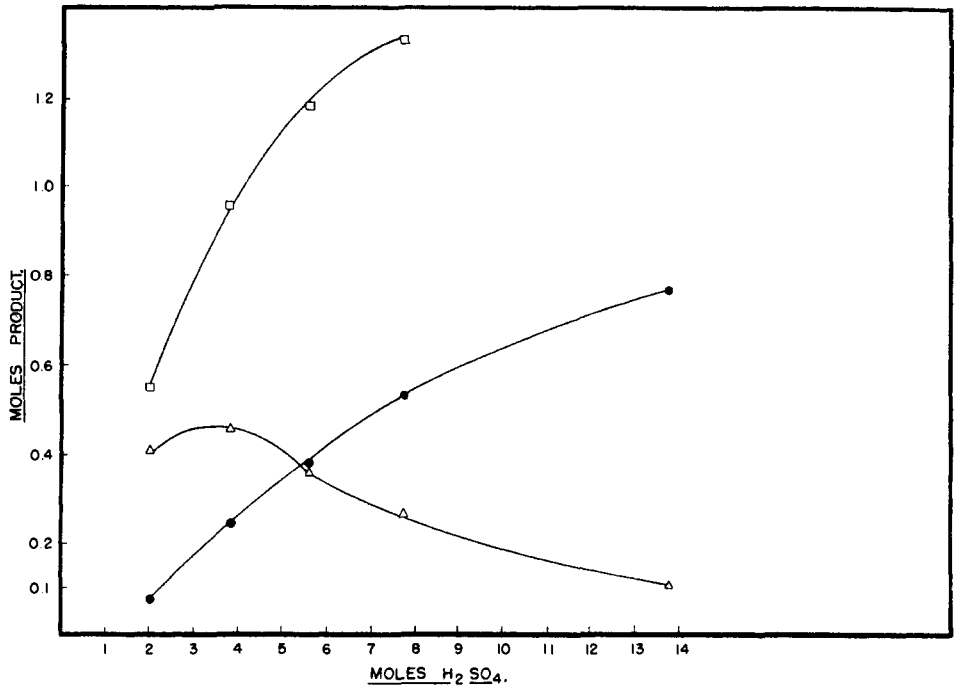


Fig. 3.—Reaction of pentamethylene glycol dilaurate with sulfuric acid for 20 hours at 40°: □, lauric acid; △, monoester monosulfate; ●, glycol sulfate.

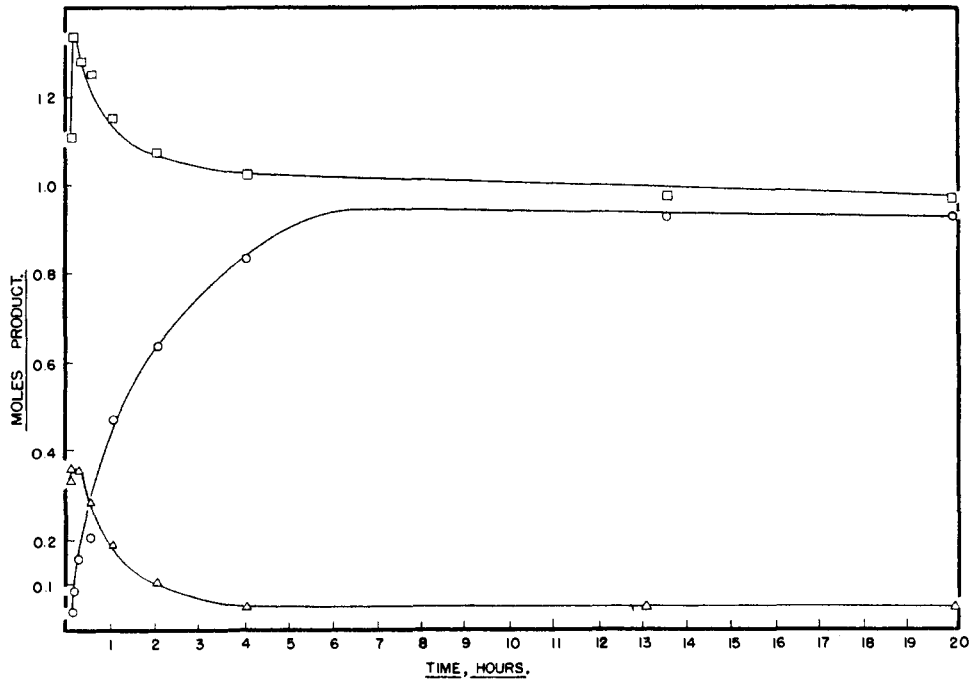


Fig. 4.—Kinetic curve for reaction of ethylene glycol dilaurate with six moles of sulfuric acid at 40°: □, lauric acid; △, monoester monosulfate; O, monoester.

varying with the quantities of starting materials and the duration of the reaction.

The remaining product to be accounted for, monolaurate, is, of course, not present as such in the reaction mixture before quenching in water. When pure ethylene glycol monolaurate was mixed with six moles of sulfuric acid at 25°, sulfation occurred rapidly as would be expected of an alcohol; and when such a mixture was quenched after a few minutes of reaction, over half the starting material had disappeared. However, allowing the mixture to stand for several hours before quenching resulted in recovery of 80–90% of the original monoester. This is shown graphically in the kinetic plot of Fig. 8. This indicates formation of a species stable in sulfuric acid and reactive with water to form a glycol monoester. If we consider the acyl–oxygen fission mechanism to apply to aliphatic

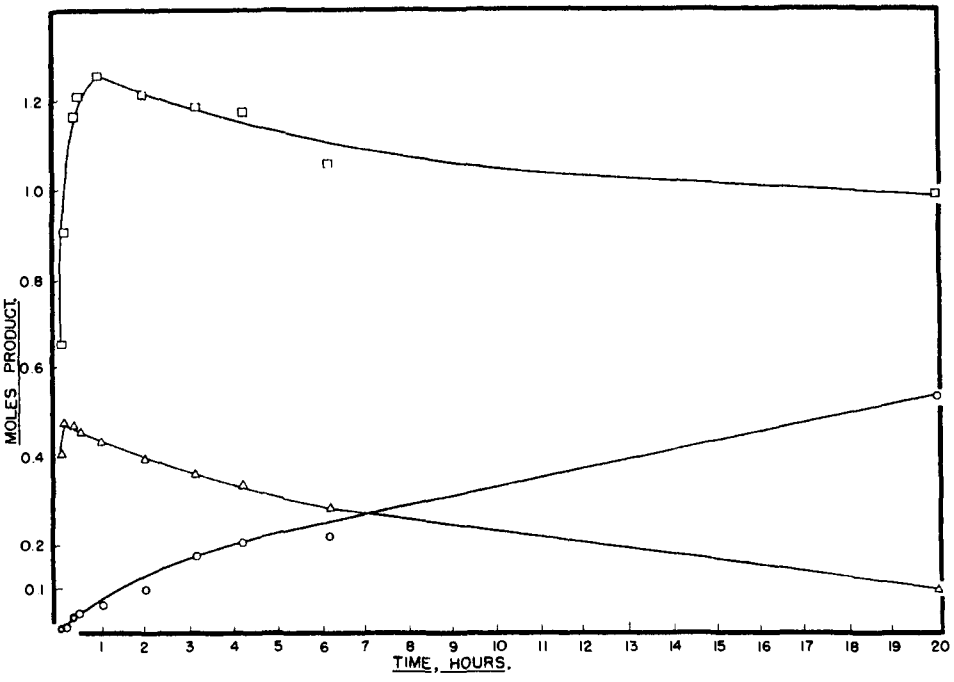


Fig. 5.—Kinetic curve for reaction of trimethylene glycol dilaurate with six moles of sulfuric acid at 40°: □, lauric acid; △, monoester monosulfate; ○, monoester.

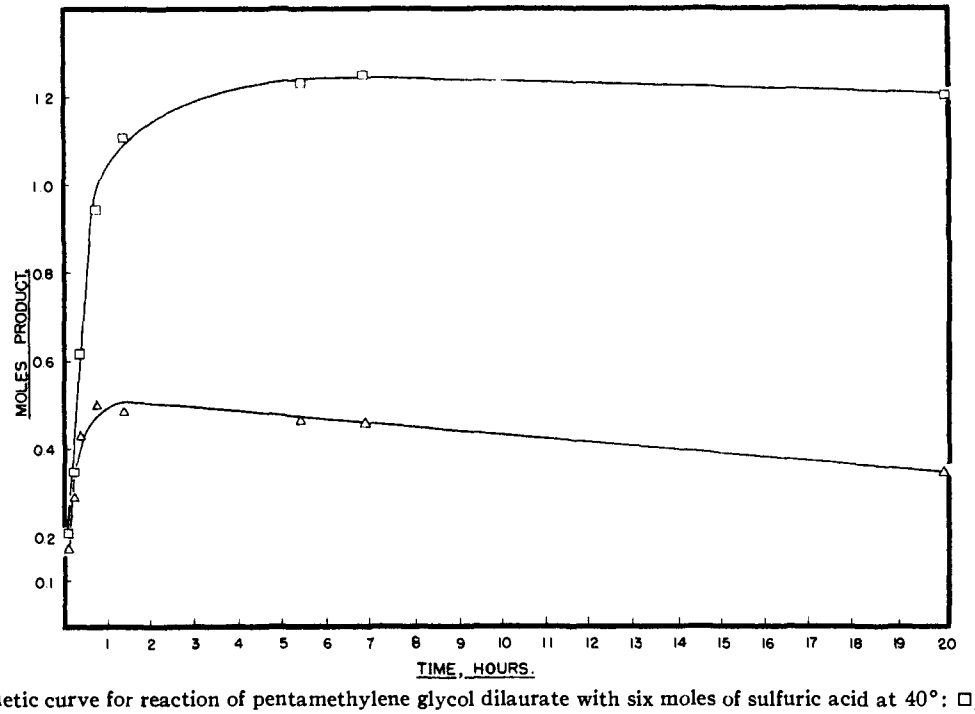


Fig. 6.—Kinetic curve for reaction of pentamethylene glycol dilaurate with six moles of sulfuric acid at 40°: □, lauric acid; △, monoester monosulfate.

esters of glycols, we might write reaction 2 as a series of steps

$$RCOOCH_2CH_2OCOR + H_2SO_4 \rightleftharpoons RCOO(H)CH_2CH_2OCOR^+ + HSO_4^- \quad (4)$$

$$RCOO(H)CH_2CH_2OCOR^+ \rightleftharpoons RCO^+ + RCOOCH_2CH_2OH \quad (5)$$

$$RCOOCH_2CH_2OH + H_2SO_4 \rightleftharpoons RCOOCH_2CH_2OSO_3H + H_2O \quad (6)$$

$$RCO^+ + H_2O \rightleftharpoons RCOOH_2^+ \quad (7)$$

The product of step 6 is still a diester which conceivably could cleave at either end. Loss of the remaining acyl group could occur by repetition of the above sequence. In contrast to carboxylic esters the predominant mode of cleavage of sulfuric esters is alkyl–oxygen fission[17] with the formation of a carbonium ion. Although loss of a proton or reaction with a nucleophilic reagent would ordinarily bring a quick end to the life of the carbonium ion,

(17) A. G. Davies and J. Kenyon, *Quart. Revs.*, **9**, 203 (1955).

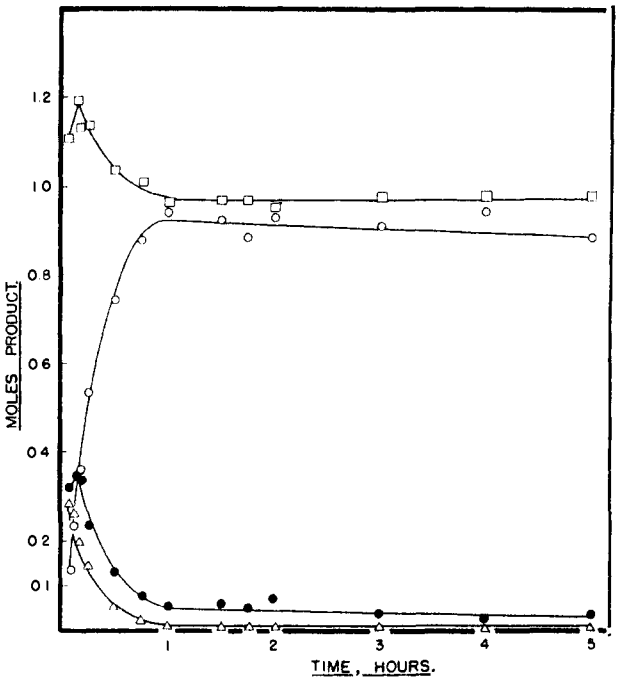
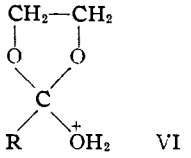


Fig. 7.—Kinetic curve for reaction of propylene glycol dilaurate with six moles of sulfuric acid at 40°: □, lauric acid △, monoester monosulfate; O, monoester; ●, glycol sulfate.

pounds containing adjacent acetoxy and bromo groups,[18] and for the reaction of some 2-alkoxy-1,3-dioxolanes with boron trifluoride.[19] It is possible that V exists not as the free carbonium ion or an ion pair with HSO_4^-, but in the form VI, having extracted a molecule of water from the solvent.



VI

When the reaction mixture is poured into water, either of the ions V or VI would be expected to form $RCOOCH_2CH_2OH$, the product actually obtained.

The reaction to form monoester precursor is slow compared to reactions 2 and 3, as is clear from the plots of kinetic data in Figs. 4–7. In the range of sulfuric acid concentration represented by the plateaus in Figs. 1–3, equilibrium is in favor of the monoester precursor, but in larger excesses of sulfuric acid reaction 3 is driven further to completion, and no sizable amount of the intermediate I accumulates to react by the slower path of equation 8.

If equation 8 is a plausible representation of the reaction, pentamethylene glycol dilaurate would be expected to give no monoester, which was experimentally substantiated, and the order of reactivity

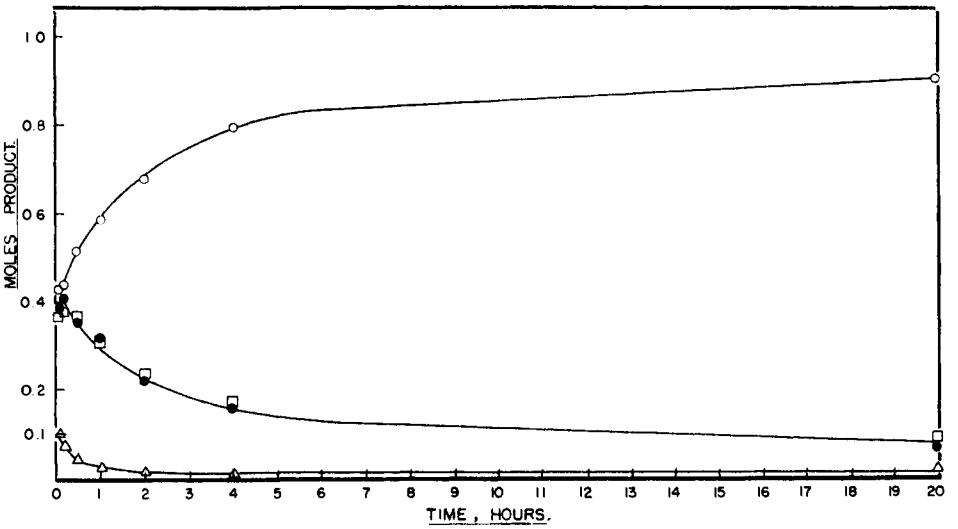
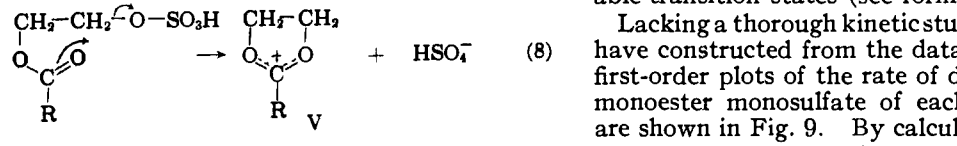


Fig. 8.—Kinetic curve for reaction of ethylene glycol monolaurate with six moles of sulfuric acid at 25°: □, lauric acid; △, monoester monosulfate; O, monoester; ●, glycol sulfate

in this particular case a means of stabilization exists, namely, cyclization with dispersal of the positive charge over two adjacent oxygen atoms.



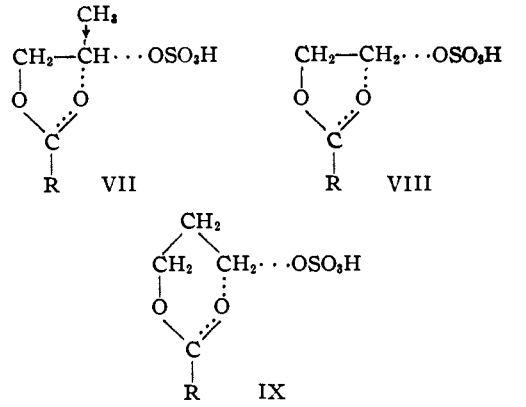
(8)

Written as in 8 the reaction is an example of elimination of a bisulfate ion with neighboring group participation, and, structurally, the suggested carbonium ion resembles the intermediate postulated for the reaction of silver acetate with certain compounds of the other glycol esters would be expected to be propylene glycol > ethylene glycol > trimethylene glycol, in accord with the relative stabilities of the probable transition states (see formulas VII, VIII, IX).

Lacking a thorough kinetic study of the reaction, we have constructed from the data of Figs. 4, 5 and 7 first-order plots of the rate of disappearance of the monoester monosulfate of each glycol, and these are shown in Fig. 9. By calculation from this plot the order of reactivity is VII:VIII:IX = 50:10:1, in agreement with the qualitative prediction.

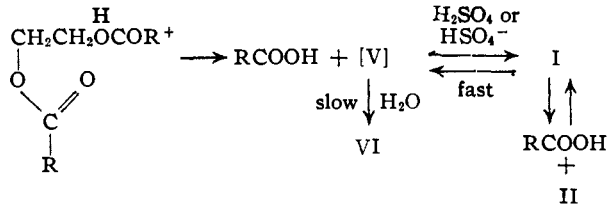
(18) S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2780 (1942).

(19) H. Meerwein, *Angew. Chem.*, **67**, 374 (1955).



VII VIII IX

It is also possible to formulate a mechanism in terms of alkyl–oxygen fission. This seems desirable in view of the apparently large difference in the rate of cleavage of lauric acid from the ethylene and propylene glycol esters as compared with that of pentamethylene glycol dilaurate and methyl laurate. The driving force again would be neighboring group participation to give at once the cyclic carbonium ion V. If, now, this ion is only an unstable intermediate which reacts rapidly with either sulfuric acid or bisulfate ion, the formation of monoester monosulfate can be accounted for. Further cleavage of lauric acid from this compound might be assisted by participation of the sulfate group. The formation of monoester precursor would then consist in a slow but thermodynamically preferred hydration of the ion V to VI. This mechanism is summarized below.



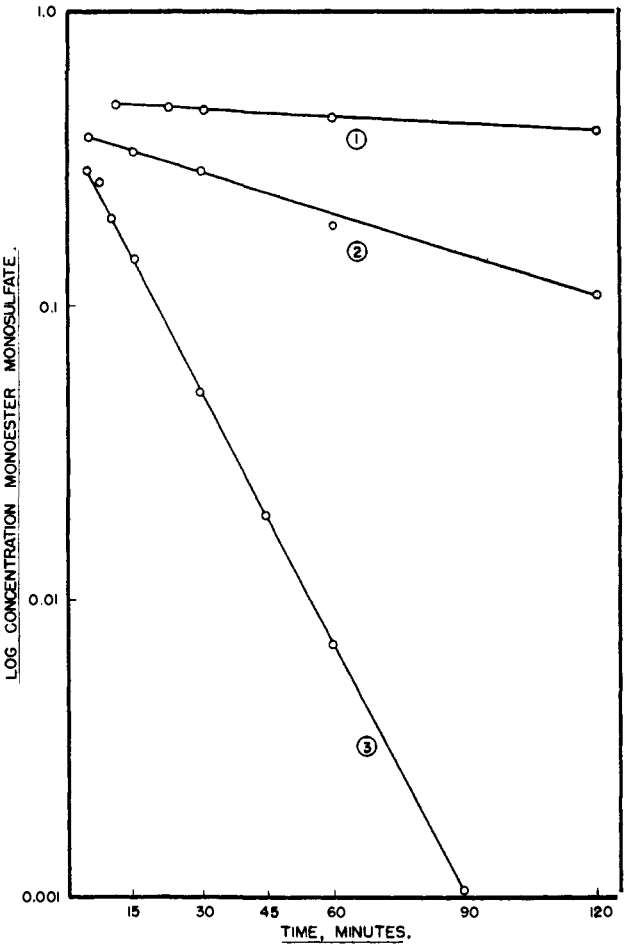


Fig. 9.—Comparative rates of disappearance of monoester monosulfate in the reaction of glycol dilaurates with six moles of sulfuric acid at 40°: dilaurate of trimethylene glycol, 1; ethylene glycol, 2; propylene glycol, 3.

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[CONTRIBUTION NO. 1034 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Phenylation of Esters by Reaction with Bromobenzene and Sodium Amide

BY WILLIAM W. LEAKE[1] AND ROBERT LEVINE

RECEIVED OCTOBER 1, 1958

Five monobasic esters and three malonic esters have been phenylated in fair to good yields by reaction with bromobenzene and excess sodium amide in liquid ammonia solution. The reaction of diethyl malonate with sodium amide, bromobenzene and ethyl bromide gave a mixture of diethyl phenylmalonate, diethyl ethylphenylmalonate and N-ethylaniline.

Recently[2] we reported that ketone anions can be phenylated by reaction with benzyne, the dehydrohalogenated halobenzene. The present paper is concerned with the phenylation of several monobasic and dibasic esters by their reaction with bromobenzene and excess sodium amide in liquid ammonia solution.

The results of the phenylation of the monobasic esters are found in Table I. It can be seen that in each reaction some or all of the following types of products were obtained: (1) monophenylated ester, (2) diphenylated ester, (3) aniline and (4) N-acylaniline. Thus, the phenylation of ethyl acetate gave a mixture of ethyl phenylacetate (I) (42%); ethyl diphenylacetate (II) (14%); aniline (III) (21%) and acetanilide (IV) (15%).

(1) Monsanto Chemical Co. Research Fellow.

(2) W. W. Leake and R. Levine, THIS JOURNAL, **81**, 1169 (1959).