flow of water. Applying the Arrhenius equation to the rates represented by the experimental quantities, D_0/T and $1/\eta$, at 1 and 25° (*cf.* Eyring's equations IX-28 and IX-112[25]), we find that the activation energy for diffusion at infinite dilution is 4275 cal./mole, while the activation energy for viscous flow of water is 4476 cal./mole. As it is unlikely that participation by the glycine molecule in the rate-determining step would decrease the activation energy for the process, it appears that the energy of activation may have been lowered by the breakdown of water structure in the vicinity of glycine molecules. It is of interest to note that the corresponding activation energy for the diffusion of sucrose[8] is 4641 cal./mole.

Thus the qualitative explanation of the observed concentration dependence of the diffusion coefficient of glycine in terms of the breakdown in structure of the water brought about by the presence of the solute is in accord with the interpretation of available results of entropy, viscosity, and volume determinations as well as with the conclusions to be drawn from the temperature dependence of the diffusion coefficient at infinite dilution.[26]

Acknowledgments.—The authors wish to express their appreciation of the interest and suggestions of Dr. J. W. Williams throughout the course of this research. They would also like to thank Dr. L. J. Gosting for permission to use the results of two diffusion experiments performed by him at 1°, and for his kindness in reading the manuscript of this paper. The research was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

Summary

The Gouy method for diffusiometry has been applied to the measurement of diffusion coefficients of glycine in aqueous solutions of concentrations up to 4.8 g. glycine per 100 ml. solution at 1 and 25°. Refractive index increments have been calculated from the results of the same experiments, and density and viscosity data were also obtained for glycine solutions at 1°.

The concentration dependence of the diffusion coefficients is not predicted correctly by Gordon's empirical equation, but the experimental behavior may be qualitatively explained by the suggestion of Robinson that glycine causes a breakdown in the ice-like structure of water.

MADISON, WISCONSIN RECEIVED MARCH 6, 1950

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[26] The negative apparent molal compressibility reported for glycine by Gucker, Lamb, Marsh and Haag, THIS JOURNAL, **72**, 310 (1950), constitutes further evidence in support of Robinson's suggestion.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Kinetics of the Base-catalyzed Methanolysis of Ortho, Meta and Para Substituted *l*-Menthyl Benzoates[1,2]

BY ROBERT W. TAFT, JR.,[3] MELVIN S. NEWMAN AND FRANK H. VERHOEK

Although the basic hydrolysis of esters has been the subject of numerous kinetic studies,[4] only one previous study of the kinetics and temperature coefficients of basic ester interchange[5a,b] has been made, and this involved a pseudo ester.[6] The present investigation was undertaken to provide quantitative data concerning the ester interchange reaction for esters of substituted benzoic acids. The kinetics of the reaction, the position of fission, and the effect of substituents in the acyl component of the ester on the rate were studied for the sodium methylate catalyzed reaction of a series of seventeen *ortho*, *meta* and *para* substituted *l*-menthyl benzoates with methanol. The rates of the ester interchange were measured at 30, 40 and 50°, enabling activation energies and $\log_{10} PZ$ factors to be calculated for each ester.

The *l*-menthyl esters were chosen in order that the rate of the reactions could be followed polarimetrically. Furthermore, by use of these esters it was possible to establish the position of fission in the methanolysis.

The effect on the reaction rates of the addition of water was also investigated.

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[1] Taken from the dissertation submitted by Robert Wheaton Taft, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate school of the Ohio State University, 1949.

[2] Presented before the Organic Division of the American Chemical Society at Atlantic City, New Jersey, September 20, 1949.

[3] Chemistry Department, Columbia University, New York, N. Y.

[4] For references see (a) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York and London, 1940, pp. 121, 184-197, 204, 211, 354-356 and 408-422; (b) Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, 2nd Ed., 1949, pp. 324, 408-422; also see Tomilla, *Ann. Acad. Sci. Fennicae*, Ser. A 57, No. 13, 3-24 (1941); No. 9, 3-12 (1941); No. 3, 3-34 (1942).

[5] (a) For equilibrium studies on alcoholysis of esters see Fehlandt and Adkins, THIS JOURNAL, **57**, 193 (1935); (b) kinetic studies of acid catalyzed ester interchange include the following: Dasannacharya, THIS JOURNAL, **46**, 1627 (1924); Patel and Watson, *J. Indian Inst. Sci.*, **16A**, 55-67 (1933); Rao, *J. Indian Chem. Soc.*, **20**, 69-75 (1943); Ducasse, *Bull. Soc. Chim.*, **12**, 918-920 (1945); Harfenist and Baltzly, THIS JOURNAL, **69**, 362 (1947); Farkas, Schachter and Vromen, *ibid.*, **71**, 1991 (1949).

[6] Schaefgen, Verhoek and Newman, *ibid.*, **67**, 253 (1945) (see also reference 13).

Table I

Physical Constants and Analyses for Substituted-menthyl Benzoates

Substituent and position	$[\alpha]^{40}_{546}$ (methanol c = 2.0-4.0)	Liquids B. p., °C.	Mm.	M. p., °C.	n^{25}D	Carbon, %[a] Calcd.	Found	Hydrogen %[a] Calcd.	Found
o-Cl	− 79.5°	129	0.3-0.4		1.5158	69.2	69.2	7.9	7.8
m-Cl	− 90.0°	137	0.5		1.5145	69.2	69.3	7.9	7.9
p-Cl	− 92.8°	156	1		1.5180	69.2	69.4	7.9	7.9
o-Br	− 71.2°	146–147	0.6		1.5283	60.2	60.5	6.8	7.0
m-Br	− 83.4°	146–147	0.5		1.5292	60.2	60.3	6.8	6.8
p-Br	− 78.3°	151–152	0.5		1.5309	60.2	60.1	6.8	6.8
o-CH_3	− 95.9°	134–135	0.3		1.5085	78.8	78.8	9.6	9.5
m-CH_3	−102.9°	109–110	0.1–0.2		1.5070	78.8	78.6	9.6	9.5
m-OCH_3	−100.0°	130	0.2-0.3		1.5118	74.5	74.5	9.1	9.0
p-OCH_3	− 95.4	138–140	0.3		1.5177	74.5	74.8	9.1	9.2
m-NO_2	− 96.4°	149–150	0.3		1.5217	66.9	66.8	7.6	7.6
H	−107.8°	118–121	0.3–0.5	53.5–54.0[b]		..	..	...	...
p-CH_3	−100.5°	121–122	0.2	39.0–39.5		78.8	78.8	9.6	9.3
o-OCH_3	− 70.9°	166–167	1	41.5–42.5		74.5	74.7	9.1	9.0
o-NO_2	−172.3°	162–163	0.4	61.0–61.5		66.9	66.9	7.6	7.3
p-NO_2	− 92.6°	191–192	2	61.0–61.3[c]		66.9	66.6	7.6	7.6
p-CN	− 96.0°	Approx. 185 (sublimes)	1	48.5–49.1		75.8	75.8	8.1	8.2

[a] Analysis by E. H. Klotz of this Laboratory. [b] Schaefgen, Verhoek and Newman give m. p. 53.8–54.8°; Beckmann and Pleisner (*Ann.*, **262**, 31 (1891), *J. prakt. Chem.*, [3] **55**, 16 (1897)), give m. p. 53–54°. [c] Read, Grubb and Malcolm, *J. Chem. Soc.*, 170, 173 (1933), give m. p. 61–62°.

Experimental

A. Preparation of Esters.—The acids were esterified directly (Method I) or by means of the acid chlorides (Method II). By Method I best results were obtained by refluxing (3–12 days) one-third mole of acid and one-half mole of *l*-menthol in approximately one liter using a small amount of benzenesulfonic acid as catalyst. Water was removed as formed. When no excess of *l*-menthol was used poor yields were obtained, probably because of an accompanying dehydration of the alcohol. Yields of 50 to 100% were obtained by Method I; the yields of the para derivatives were generally 25 to 30% lower than those for *ortho* and *meta* substituted esters because of the low solubility of the acids. In Method II the acid chlorides, prepared with phosphorus pentachloride, were refluxed with *l*-menthol in dry benzene giving over-all yields of 70–75%.

B. **Materials—Acids.**—Recrystallized commercial acids[7] were used in most cases to prepare the esters.

***l*-Menthol.**—The reagent-grade commercial product[8] having m. p. 41.5–42.5°, $[\alpha]^{40}$D −48.8°, $[\alpha]^{40}_{546}$ mμ −58.3° (methanol, c = 1.2) was used in the preparations.

Methanol and sodium methylate solutions were prepared as previously described.[6]

Esters.—Those esters which were viscous non-crystalline oils were doubly distilled from a Claisen flask with a ten-inch Vigreux column at 0.1 to 2 mm. pressure. In the second distillation only a middle constant-boiling cut was retained. The crystalline esters were recrystallized to constant melting point from methanol–water solutions, and dried "*in vacuo*." Physical constants and analyses for each ester are listed in Table I.

C. **Apparatus—Polarimeter Tubes.**—Specially prepared polarimeter tubes were used. These all-pyrex tubes were five decimeters in length, seventeen millimeters in diameter with sealed glass end plates, and were constructed with a filling tube sealed at the top center of the tube. The entire length of the tube (to within a few mm. of the end plates) was enclosed by a glass jacket through which water could be circulated. The capacity of the polarimeter tubes was approximately 95 ml.[9]

Polarimeter.—A Schmidt and Haensch Precision Polarimeter with spectroscope monochromator was used. Readings were accurate to ±0.02°. All readings were taken using a mercury line of approximately 545 mμ wave length. The purpose of using this wave length rather than the D line of sodium was to secure a greater difference in the rotations of the *l*-menthyl esters and *l*-menthol, and to be able to make readings with greater precision.

D. **Procedure.**—The desired amount of ester was weighed into the longer arm of an inverted Y reaction tube and 100 ml. of anhydrous methanol was introduced into this arm from a calibrated Machlett buret. The short arm of the reaction tube was then filled with methanolic sodium methylate solution from a calibrated gravity-feed micro buret, or, in certain cases, from an Exax pipet. Only 0.5 to 3.5 ml. of relatively concentrated sodium methylate solution was used so that this component represented only a few per cent. of the final total volume. For reactions at 30 and 40° the filled reaction tube was brought to reaction temperature in a thermostat. The contents were shaken together at zero time, and immediately poured into a polarimeter tube which was then securely stoppered and placed in the thermostat. For reactions at 50°, the reactants were shaken together at room temperature, and the filled polarimeter tube placed immediately in the thermostat.

The polarimeter tube was kept in the thermostat except for the comparatively short time when it was removed for polarimetric readings. To take a reading the polarimeter tube was transferred to the platform of the polarimeter, and water from a small thermostat was circulated through the glass jacket keeping the contents at the reaction temperature. The temperature control of the reaction thermostat was accurate to ±0.05°.

Ten or more points were generally taken during the course of each experiment (five or six polarimeter readings were taken per point—the average reading and average time were used) and in almost every case the reaction was followed to at least 65% (and in some cases up to 90%) of completion. At least one experiment for each ester (except *l*-menthyl orthotoluate) was allowed to go to completion. The observed final rotation was within 0.00 to 0.05° of the calculated value in most cases with a maximum deviation of 0.12° in one experiment. The total change in rotation was usually 6 to 7°.

In order to obtain the volumes of the solutions at reac-

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(7) Eastman Kodak Company, Rochester, New York.

(8) Orr, Brown and Price Company, Columbus, Ohio.

(9) These tubes were made by the Scientific Glass Apparatus Company, Bloomfield, N. J.

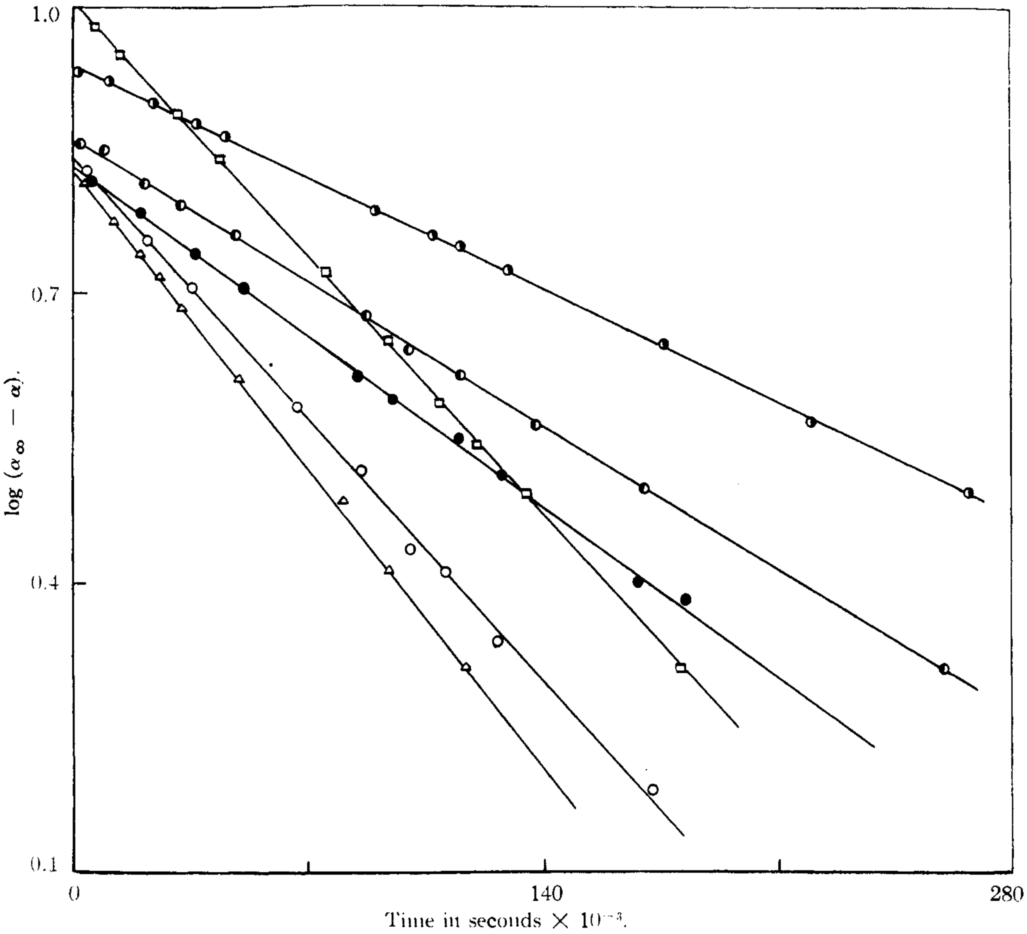

Fig. 1.—Graphs of log (α_∞ − α) against time in the sodium methylate catalyzed ester interchange of *l*-menthyl benzoates:

Symbol	Substituent	Concn. ester, m./l.	Concn. MeONa, m./l.	Temp., °C.
◑	*p*-CH_3	0.0929	0.0694	39.9
□	*m*-OCH_3	.1020	.0523	39.9
◐	*m*-OCH_3	.0728	.0707	30.0
○	*m*-OCH_3	.0698	.0528	39.9
●	*m*-OCH_3	.0688	.0353	39.9
△	*p*-Cl	.0739	.01756	40.0

tion temperatures (from which concentrations were calculated), densities were determined at 30° for solutions of all of the esters at the average concentration used. By assuming that the total volume of these dilute solutions was equal to the sum of the volumes of the methanolic ester and sodium methylate solutions, and that the density change with temperature was the same for these solutions as for pure methanol, it was possible to calculate the concentrations at the reaction temperature for each experiment. Any error thus introduced was within the experimental error of the polarimeter readings.

Usually three or four kinetic experiments were made for each ester at 40° using different concentrations of sodium methylate at approximately the same concentration of ester. Except in the case of *l*-methyl *o*- and *p*-methoxybenzoates and *l*-menthyl *o*-, *m*- and *p*-bromobenzoates, an additional experiment was made in which the concentration of ester was either increased or decreased by approximately three halves. At least one experiment was made at 30 and 50° for each ester, generally at concentrations of ester and sodium methylate nearly the same as for one of the 40° experiments.

Results

For each experiment the logarithm of the rotation calculated for *l*-menthol at the appropriate concentration (α_∞) minus the observed rotation[10] was plotted against the time. The plots yielded straight lines as shown by the representative cases in Fig. 1. The first-order constants, k_1, tabulated in Table II, were obtained from the slopes of the lines. Three cases in which abnormal behavior was observed are discussed later.

The specific rate constants, k, for reactions at 40° were obtained from the slopes of the straight lines which resulted from plotting the first order

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[10] The specific rotation at zero time (calculated from the extrapolated rotation) was the same as that for a methanolic solution of the ester. This is an indication that no complex between ester and methylate ion is formed in detectable amounts. We are indebted to Dr. C. L. Wilson for suggesting this check.

TABLE II

FIRST ORDER RATE CONSTANTS FOR THE METHANOLYSIS OF SUBSTITUTED *l*-MENTHYL BENZOATE IN THE PRESENCE OF SODIUM METHYLATE

Temp., °C.	Ester, m./l.	MeONa, m./l.	k_1, sec.$^{-1}$ × 10^6
l-Menthyl benzoate			
30.0	0.0725	0.0712	3.70
39.9	.0733	.01774	2.25
	.0732	.03530	4.59
	.0714^a	.0518	6.53
	.0728	.0527	6.84
	.0725^b	.0699	8.94
	.0703	.0699	9.02
	.0383^c	.0707	8.98
	.1079	.0692	8.91
	.0727^d	.0701	7.98
50.0	.0697	.0714	22.5
	.0721^e	.0700	21.9
l-Menthyl *o*-toluate			
30.0	.0941	.1049	0.403
39.9	.0912	.1032	1.030
50.0	.0929	.0962	2.39
	.0914	.1048	2.62
l-Menthyl *m*-toluate			
30.0	.0943	.1036	4.02
39.9	.0945	.0523	4.97
	.0930	.0694	6.71
	.0926	.0865	8.49
	.1374	.1017	9.87
50.0	.0918	.1038	24.9
l-Menthyl *p*-toluate			
30.0	.0936	.1048	2.28
39.9	.0938	.03504	1.849
	.0929	.0694	3.85
	.0924	.0863	5.10
	.0920	.1031	5.81
50.0	.0916	.1034	14.33
l-Menthyl *o*-bromobenzoate			
30.0	.0839	.1061	2.21
39.9	.0840	.0706	4.17
	.0838	.0878	5.43
	.0836	.1049	6.93
50.0	.0818	.1062	16.91
l-Menthyl *m*-bromobenzoate			
30.0	.0800	.01444	8.30
39.9	.0795	.00891	12.06
	.0791	.01430	15.97
	.0780	.01768	24.0
50.0	.0785	.01445	44.2
l-Methyl *p*-bromobenzoate			
30.0	0.0800	0.02523	7.13
39.9	.0806	.01077	6.98
	.0796	.02148	14.26
	.0791	.03566	24.0
50.0	.0790	.02172	34.1
l-Menthyl *p*-cyanobenzoate			
30.0	0.759	.002847	9.09
	.0757	.003010	9.62
40.0	.0754	.002218	15.36
	.0716	.002993	22.3
	.0756	.003720	26.1
	.1111	.004338	31.1
50.0	.0744	[illegible]	48.1
l-Menthyl *o*-methoxybenzoate			
39.9	.0957	.0862	2.09
	.0958	.1026	2.58
	.0958	.1195	3.12
50.0	.0953	.1047	6.38
l-Menthyl *m*-methoxybenzoate			
30.0	.0728	.0708	4.85
39.9	.0724	.01769	2.88
	.0688	.03531	5.92
	.1020	.0523	8.74
	.0698	.0528	9.09
	.0707	.0698	12.30
50.0	.0706	.0722	29.4
l-Menthyl *p*-methoxybenzoate			
30.0	.1020	.1045	1.169
39.9	.0970	.0863	2.52
	.0970	.1031	2.99
	.0962	.1190	3.70
50.0	.0990	.1074	8.16
	.0994^f	.1089	8.27
l-Menthyl *o*-chlorobenzoate			
30.0	.0738	.0872	3.21
39.9	.0703	.03531	3.02
	.0705	.0527	4.70
	.1052	.0711	6.25
	.0722	.0869	7.79
50.0	.0731	.0873	18.49
l-Menthyl *m*-chlorobenzoate			
30.0	0.0740	0.01447	8.41
40.0	.0738	.00589	7.80
	.1081	.00877	11.32
	.0746	.01071	14.88
	.0722	.01164	15.43
	.0731	.01415	19.47
50.0	0.726	.01446	44.7
l-Menthyl *p*-chlorobenzoate			
30.0	.0798	.02335	5.51
40.0	.0730	.00707	3.88
	.0720	.01399	7.98
	.0739	.01756	10.21
	.1086	.02305	13.19
	.0740	.03527	20.1
50.0	.0776	.02346	31.1
l-Menthyl *p*-nitrobenzoate			
30.0	.0820	.04991	7.26
40.0	.0812	.01769	5.96
	.0831	.02774	9.68
	.0810	.03524	12.23
	.0806	.04910	17.58
	.1181	.0686	24.6
50.0	.0794	.04941	40.8
l-Menthyl *m*-nitrobenzoate			
30.0	.0847	.002839	11.86
40.0	.0763	.001381	12.74
	.0800	.001762	16.12
	.0862	.002076	19.54
	.1211	.003426	32.6
50.0	.0859	.001355	27.3
l-Menthyl *p*-nitrobenzoate			
30.0	.0751	.002850	16.78
40.0	.0751	.000698	8.90
	.0749	.001053	13.30
	.0744	.001381	17.67
	.1106	.001735	21.7
50.0	.0731	.001360	36.7

[a] 1.04 molar in H_2O. [b] 0.525 molar in H_2O. [c] 1.06 molar in H_2O. [d] 5.27 molar in H_2O. [e] 0.0522 molar in H_2O. [f] 0.23 g. NaCl added.

constants for a given ester against sodium methylate concentrations (see Fig. 2). The specific rate constants at 30 and 50° were obtained by dividing the first order constant by the corresponding sodium methylate concentration. Specific rate constants for each ester at 30, 40 and 50° are given in Table III. Judging from the reproducibility, the error involved in the rate constants is 1 to 4%. The rate constants for the ortho substituted esters are less accurate than the others.

Activation energies were calculated from the Arrhenius equation for the intervals 30.0–40.0° and 40.0–50.0°. The values for activation energies given in Table III are the mean of those ob-

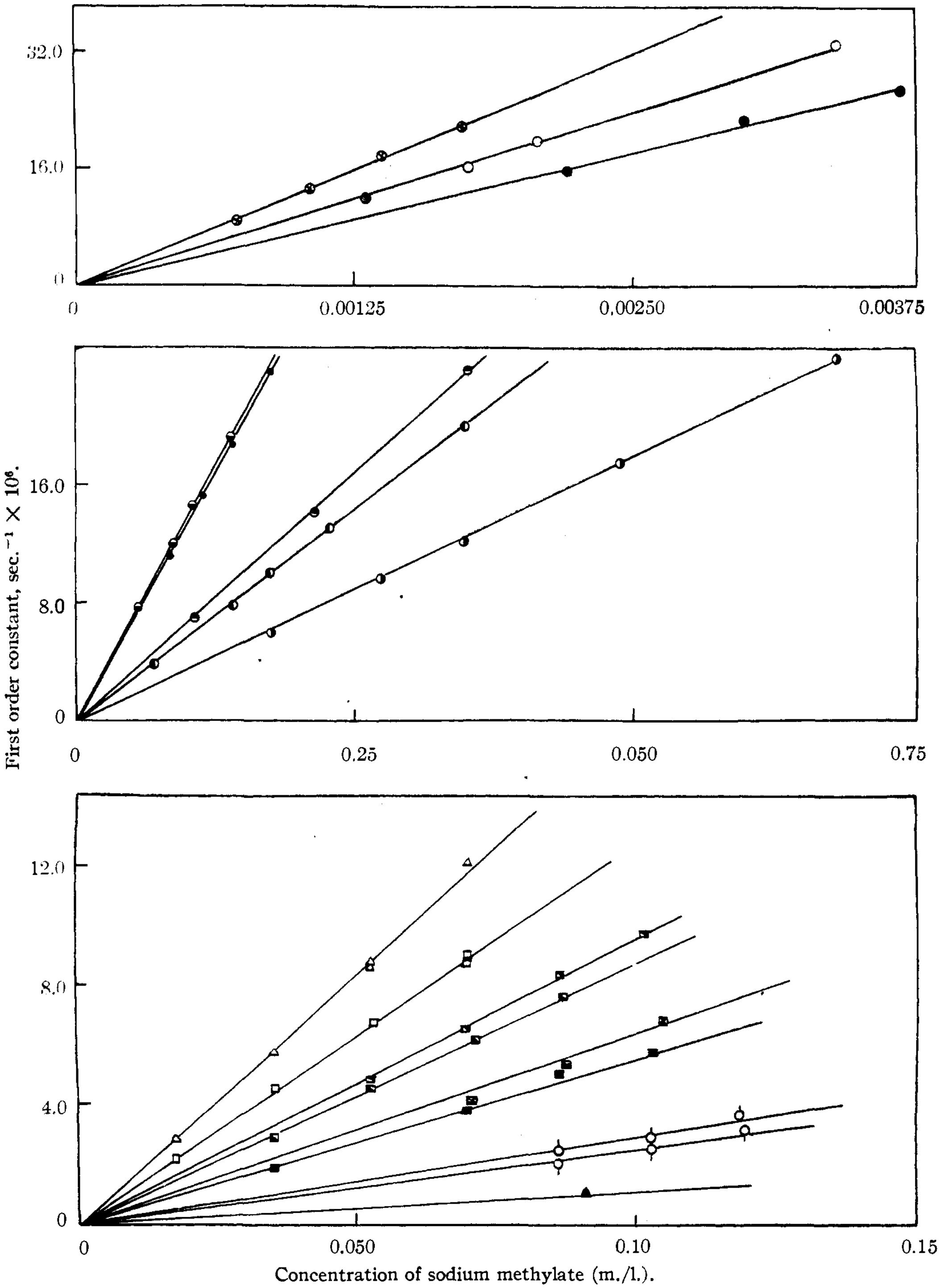

Fig. 2.—First-order rate constants for ester interchange of substituted l-menthyl benzoates in methanol as a function of the concentration of sodium methylate:

Top
⊗, p-NO$_2$
○, m-NO$_2$
●, p-CN

Middle
⊖, m-Cl
•, m-Br
◓, p-Br
◐, p-Cl
◑, o-NO$_2$

△, m-OCH$_3$
□, H
⌊, m-CH$_3$
◪, o-Cl
⊠, o-Br

■, p-CH$_3$
ȯ, p-OCH$_3$
♀, o-OCH$_3$
▲, o-CH$_3$

TABLE III

RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE BASIC METHANOLYSIS OF SUBSTITUTED *l*-MENTHYL BENZOATES

Substituent	$k^{30.0} \times 10^4$, sec.$^{-1}$	$k^{40.0} \times 10^4$, sec.$^{-1}$	Rel. rate$^{40.0}$	$k^{50.0} \times 10^4$, sec.$^{-1}$	E	$\log_{10} PZ$	$k^{40.0}_{(\text{eq. 1})} \times 10^4$ sec.$^{-1}$	E (eq. 2) cal.
				ortho Substituents				
-H	0.519	1.294^a	1.000	3.15	17,510 cal.	8.33	....	....
-OCH$_3$	.....	0.248^a	0.192	0.611	17,980	7.94	....	....
-CH$_3$	0.0383	0.0998^a	0.0771	0.248	18,160	7.80	....	....
-Cl	0.368	0.891^a	0.689	2.12	17,060	7.86	....	....
-Br	(0.208)	(0.659)^a	0.51	(1.592)	......	..	....	....
-NO$_2$	1.455	3.57	2.77	8.25	16,890	8.34	....	....
				meta Substituents				
-H	0.519	1.294^a	1.000	3.15	17,510	8.33	1.45	(17,600)
-OCH$_3$	0.685	1.704^a	1.317	4.07	17,360	8.34	2.83, 1.83^b	17,460^b
-CH$_3$	0.388	0.972^a	0.751	2.40	17,740	8.37	0.972	17,860
-Cl	5.81	13.50	10.59	30.9	16,380	8.55	12.7	16,260
-Br	5.75	13.45^a	10.47	30.6	16,380	8.56	14.1	16,190
-NO$_2$	41.8	93.1	72.1	201	15,300	8.65	90.9	15,040
				para Substituents				
-H	0.519	1.294^a	1.000	3.15	17,510	8.33	1.45	17,600
-OCH$_3$	0.1119	0.296^a	0.229	0.760	18,660	8.48	0.304	18,580
-CH$_3$	0.218	0.560^a	0.433	1.386	18,030	8.33	0.542	18,230
-Cl	2.36	5.74	4.42	13.27	16,760	8.46	5.32	16,800
-Br	2.83	6.72	5.21	15.70	16,700	8.48	5.62, 6.60^c	16,670^c
-CN	(32.0)	(73.3)	(56.8)	(100.1)	(15,700)	(8.82)	64.6	15,240
-NO$_2$	58.9	127.4	99.2	270	14,810	8.45	135	14,790

^{a} Temp. -39.9 ± 0.05°. ^{b} Calculated using $\sigma_{m\text{-OCH}_3} = +0.00 +0.40$. ^{c} Calculated using $\sigma_{p\text{-Br}} = +0.260$.

tained for the two ten-degree intervals.[11] The average deviation of the mean activation energy from those obtained from the two intervals was ±100 cal.; the maximum deviation was ±220 cal.

Log$_{10}$ PZ factors for each ester were calculated using the mean activation energy and the corresponding rate constant at 40°. These values are given in Table III.

Discussion

Kinetics.—The agreement of the equilibrium rotation with that calculated for *l*-menthol indicates that (1) the reaction in each case was forced to completion by the large excess of methanol; (2) no appreciable amounts of methyl menthyl ether or olefin were formed and (3) alkyl-oxygen fission did not occur in the methanolysis of any of the esters studied.

Experiments in which the initial concentration of ester or sodium methylate was varied gave the following results: (1) the first order constants (and specific rate constants) are independent of the initial ester concentration (see Table II and Fig. 1); (2) the first order velocity constant in each case is directly proportional to the sodium methylate concentration (see Fig. 2).[12]

For the *l*-menthyl *p*-cyanobenzoate experiments, plots of log $(\alpha_\infty - \alpha)$ *vs.* time gave straight lines only to 25 to 40% of completion. Similar plots for the *l*-menthyl *p*-nitrobenzoate experiments gave straight lines up to approximately 60% of completion. Beyond these respective ranges the points lie above the straight lines (rate decreases) drawn through the initial portions of the curves which were used to obtain the rate constants. The rate constants for *l*-menthyl *p*-cyanobenzoate are given in parentheses in Table III because of their approximate nature.

The abnormal behavior of these two esters may be accounted for on the basis of slow side reactions which involve the consumption of sodium methylate. King[13] found that the first order constants for the methanolysis of some aralkyl *p*-nitrobenzoates decreased markedly and regularly with time. The exact nature of these side reactions was not investigated.

At 40° for experiments with *l*-menthyl benzoate under comparable conditions, the first order constants obtained from the initial slopes of the plots of log $(\alpha_\infty - \alpha)$ *vs.* time were essentially the same in the absence or presence of water up to 1 molar (see Table II). In the presence of water, however, there was an upward curvature of the points in the latter part of the reaction, which was more noticeable the greater the amount of water added, and the higher the temperature. In a solution 5.27 molar in water the initial rate was about 20% lower than in anhydrous methanol at equivalent

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(11) Activation energy (and log PZ) for the ortho bromo ester is not given because of the large difference in the values obtained for the two ten-degree intervals. No reason for this difference could be given.

(12) Attempts were also made to carry out experiments in pyridine at such concentrations of methanol that it could be established whether or not the rate is also first order with respect to methanol under these conditions. However, the rapid precipitation of sodium methoxide and the darkening of the solutions interfered.

(13) King, THIS JOURNAL, **61**, 2383 (1939).

alkali concentration. At 50° there was very rapid departure from linearity even for a solution 0.05 molar in water. The addition of water probably causes hydrolysis resulting in a continuous loss of alkali.

The addition of sodium chloride (see Table II) had no appreciable effect on the rate of methanolysis of *l*-menthyl *p*-methoxybenzoate.

Effect of Substituents.—The results given in Table III show that for substitution in the *meta* and *para* positions, the greater the electron withdrawing power of the substituent the greater is the specific rate constant and the lower the activation energy; the greater the electron donating power of the substituent the lower the rate constant and the greater the activation energy. Further, for these substituents the activation energy alone accounts for variations in rate, as the $\log_{10} PZ$ factor is nearly constant (average value, 8.45). The $\log_{10}PZ$ factor for the *m*-NO_2 ester appears to be significantly higher than the average.

ortho Substituents, in contrast to the *meta* and *para* substituents, retard reaction regardless of their nature and changes in both activation energy and $\log_{10} PZ$ factor are found.[14]

Substituent and Reaction Constants.—Hammett[15] has shown that the rates (and equilibria) of many reactions of meta and para substituted benzene derivatives follow the relation

$$\log k_0 - \log k' = \sigma\rho \qquad (1)$$

where k = rate constant of substituted derivative
k_0 = rate constant of unsubstituted derivative
σ = substituent constant
ρ = reaction constant.

By plotting $\log k^{40}$ values from Table III against the substituent constants given by Hammett, the slope of the resulting best straight line gave a value for the reaction constant, ρ, of $+2.530$ and from the intercept $\log k_0 = -3.837$. Using these values the rate constants for the *meta* and *para* derivatives studied were calculated from equation (1) and tabulated in Table III.

In calculating $\log k^{40}$ for the *p*-cyano derivative, a value of $+ 0.66$ was used for the substituent constant.[16] The value given by Hammett for this substituent applies only to reactions of derivatives of aniline and phenol.[15] Better agreement is also obtained between observed and calculated rate constants not only for the basic methanolysis but also for the basic hydrolysis of ethyl and methyl benzoates by using, in place of the values given by Hammett, $\sigma_{m\text{-OCH}_3} = +\ 0.040$, and $\sigma_{p\text{-Br}} = +\ 0.260$.

Activation energies for reactions of a series of *meta* and *para* substituted benzene derivatives for which entropies of activation are essentially constant can be calculated from the relation

$$E = -(2.303\ RT)\sigma\rho + E_0 \qquad (2)$$

where E = activation energy for *m*- or *p*-substituted derivative
E_0 = activation energy for unsubstituted derivative
σ and ρ are same as for eq. 1
R is gas constant in calories per mole
T is absolute temperature

Using a value of $E_0 = 17{,}610$, activation energies for the present series were calculated and are tabulated in Table III.

Equation (2), which was obtained in its essentials by Hinshelwood, Laidler and Timm,[17a] and Hammett[17b] is useful for calculating reasonably accurate activation energies for any reaction series for which the substituent constants, σ, are known, the reaction constant, ρ, has been determined[18] and for which the PZ factors may be assumed essentially constant. Only the activation energy for any one of the substituted (or unsubstituted) derivatives is needed. It follows from equation (2) that ρ is an inverse function of the absolute temperature, as Hammett has shown.[19]

A comparison (Table III) of experimental values of rate constants and activation energies with those obtained from equations (1) and (2) shows the calculated activation energies (average deviation, 100 cal., omitting *p*-CN) to be within experimental error, and the rate constants (average deviation 6%, omitting *m*-OCH_3) nearly so. A noticeable exception is the *m*-methoxy substituent.

Ortho Effect.—Except for the ortho nitro group, the differences between the activation energies for corresponding *para* and *ortho* substituents are not large while in each case the log PZ factor is noticeably less for an ortho than for the corresponding *para* substituent (see Table III). Accordingly, it appears reasonable to assume as an approximation that the resonance and inductive effects of a substituent are the same in the para and ortho positions. The departure of the ratio of rate constants for corresponding para and ortho substituents, k_p/k_o, from unity must then give at least a qualitative measure of the *ortho* effect. In Table IV the k_p/k_o ratios are given for the present series as well as those calculated from the literature data[20,21] on the hydrolysis of substituted ethyl benzoates. For each series the order of increasing k_p/k_o ratios is $OCH_3 < Cl, CH_3 < Br < NO_2$.

Although the ortho effect is known to be very specific, even varying with solvent in certain cases,[22] it seems apparent from the above treat-

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[14] See more specific discussion under "*ortho* effect."

[15] Hammett, ref. 4, pp. 184–192.

[16] This is close to the values obtained from other sources by Kilpatrick and Eanes, THIS JOURNAL, **65**, 589 (1943), and John D. Roberts, Mass. Inst. Tech., private communication.

[17] (a) Hinshelwood, Laidler and Timm, *J. Chem. Soc.*, 848 (1938); (b) Hammett, ref. 4, p. 197, footnote 40. The authors are indebted to Prof. Hammett for these references.

[18] Hammett, ref. 4, pp. 187–191.

[19] Hammett, THIS JOURNAL, **59**, 96 (1937).

[20] Tommila, *Ann. Acad. Sci. Fennicae*, Ser. A57, No. 13, 3–34 (1941).

[21] Evans, Gordon and Watson, *J. Chem. Soc.*, 1430 (1937); Ingold and Nathan, *ibid.*, 222 (1936).

[22] Hammett, ref. 4, p. 207.

TABLE IV

Ortho EFFECT k_p/k_o RATIOS OF RATE CONSTANTS FOR CORRESPONDING *Para* AND *Ortho* SUBSTITUENTS

Substituent	I Basic methanolysis of *l*-menthyl benzoates in methanol k_p/k_o[40]	II Basic hydrolysis of ethyl benzoates in 60% (vol.) aq. acetone[21] k_p/k_o[25]	III Basic hydrolysis of ethyl benzoates in 85% (vol.) aq. ethanol[21] k_p/k_o[25]
OCH_3	1.2	0.52[a]	..
CH_3	5.7	3.4	3.2
Cl	6.4	2.7	1.7
Br	10.2	4.7	..
NO_2	36.0	14.6	13.3

[a] Data for OC_2H_5. The ratio for OCH_3 is probably not greatly different from this.

ment that both basic ester interchange and hydrolysis of *ortho* substituted benzoates is increasingly retarded by *ortho* substituents (any one of those discussed here) with increasing steric requirements. With regard to the relative effects of groups participating in the *ortho* effect, two orders have been noted in studies of the rates of racemization of optically active biphenyl derivatives. The order of effectiveness of substituents (X) in retarding the racemization of 2-X-2'-nitro-6'-carboxybiphenyls and 2-X-5-methyl-2'-nitro-6'-carboxybiphenyls is $OCH_3 < NO_2 < Cl < CH_3 < Br$.[23a] However, in 2-nitro-6-carboxy-2'-methoxy-3'-X-biphenyls the order is $OCH_3 < Cl < CH_3 < Br < NO_2$.[23b] It is the latter order that corresponds with the ortho effect in basic interchange and hydrolysis of *ortho* substituted benzoates.

Comparison of Basic Ester Interchange and Ester Hydrolysis.—The kinetics of the basic ester interchange reaction studied here are similar to those for basic ester hydrolysis, that is, both are first order with respect to the concentrations of ester and to methoxide ion and hydroxide ion, respectively. Both reactions involve exclusively acyl-oxygen fission. The reaction rates and activation energies for meta and para substituents follow the same qualitative and quantitative relationships. The reaction constants, ρ, are of closely similar magnitude, for example, $+2.530$ for the present basic ester interchange series; $+2.373$ for the basic hydrolysis of ethyl benzoates in 56 weight per cent. aqueous acetone at 25°[24]; $+2.305$ for methyl benzoates under the same conditions[25]; and $+2.498$ for ethyl benzoates in 87.8 weight per cent. aqueous ethanol at 30°.[15] Finally, the order of the *ortho* effect of substituents is the same for these two types of reactions.

A direct comparison of data gives further information. The essentially constant $\log_{10}PZ$ factor (8.45) for the methanolysis of *meta* and *para* substituted *l*-menthyl benzoates is markedly less than that (9.75) for the hydrolysis of *meta* and *para* substituted ethyl benzoates in 85 volume per cent. aqueous ethyl alcohol[21] (the most similar solvent for which data are available for comparison). This difference in $\log_{10}PZ$ for these two reactions probably would be even greater if a comparison under similar solvent conditions were possible, for the $\log_{10}PZ$ factor for basic hydrolysis of meta and para substituted ethyl benzoates increases with decreasing water content of the alcoholic solvent.[26]

Further, in this connection, it can be seen from the data of Table IV that the actual magnitude of the ratios of the rate constants, k_p/k_o, for corresponding *para* and *ortho* substituents is in general appreciably greater for the basic methanolysis of *l*-menthyl benzoates than for the hydrolysis of ethyl benzoates.

The cause of the smaller PZ factor and the larger magnitude of the k_p/k_o ratios for the methanolysis than the hydrolysis is probably in a large part caused by the greater steric requirements and less rigidity of the *l*-menthyl component than that for an ethyl group, but also may in a smaller part be due to a similar relation between methylate ion and hydroxide ion, respectively.

The present study furnishes, consequently, more convincing experimental evidence than any previously reported in support of the often inferred analogy between basic hydrolysis and interchange of ordinary esters.

Mechanism of Basic Ester Interchange.—The present results do not differentiate between the three mechanisms for basic ester interchange of ordinary esters, which are analogous to those given by Hammett,[27] Day and Ingold,[28] and Lowry[29] for basic ester hydrolysis.

Summary

The kinetics, reaction rates, and temperature coefficients for the sodium methylate catalyzed reactions of a series of seventeen *ortho*, *meta* and *para* substituted *l*-menthyl benzoates with methanol have been investigated polarimetrically.

The sodium methylate catalyzed methanolysis of substituted *l*-menthyl benzoates (1) is first order with respect to ester and to methoxide ion; (2) does not involve alkyl-oxygen fission; (3) is accelerated by electron attracting substituents in *meta* and *para* positions, and retarded by electron donating substituents; (4) has values of $\log_{10}PZ$ which for *meta* and *para* substituents are nearly constant; (5) has rate constants and activation energies for *meta* and *para* substituents which may be calculated from Hammett's σ and

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(23a) Adams, Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, Vol. I, p. 362.

(23b) *Ibid.*, p. 368.

(24) Tommila and Hinshelwood, *J. Chem. Soc.*, 1801 (1938); Tommila, *Ann. Acad. Sci. Fennicae*, Ser. **A57**, No. 13, 3-24 (1941); No. 9, 3-12 (1941); *C. A.*, **38**, 6174 (1944).

(25) Tommila, Brehmer and Elo, *Ann. Acad. Sci. Fennicae*, Ser A, II, Ch. No. 16, 14 (1945); *C. A.*, **41**, 903 (1947).

(26) Tommila and Ketonen, *Suomen Kemistilehti*, **18B**, 24-28 (1945).

(27) Hammett, ref. 4, p. 355.

(28) Day and Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

(29) Lowry, *J. Chem. Soc.*, **127**, 1380 (1925).

p functions; (6) is retarded to an increasing extent by *ortho* substituents with increasing steric requirements.

Evidence that basic ester interchange and basic ester hydrolysis are similar is provided.

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[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE COMPANY]

The Polymorphism of Certain Behenyl Mixed Triglycerides. A New Metastable Crystalline Form of Triglycerides

BY F. L. JACKSON AND E. S. LUTTON

Previous communications have discussed the X-ray diffraction and thermal behavior of mixed saturated diacid triglycerides.[1,2,3] These compounds, like the single fatty acid triglycerides,[4] *e. g.*, tristearin, in most cases exhibit three polymorphic forms (alpha, beta prime and beta) each with a characteristic melting point. Some differ in having only two such forms, *e. g.*, 2-stearyldipalmitin with no beta form,[2] while others have four forms each with characteristic melting level, *e. g.*, 2-myristyldistearin with alpha-2, beta prime-2, beta prime-4, and beta-3 forms.[1] Glycerides have been found to show a notable individuality in degree of stability of metastable forms. In no case has the vitreous-type form of Clarkson and Malkin[5,6] been observed.

In the present paper there are discussed the X-ray diffraction and thermal characteristics of the new diacid triglycerides, 2-behenyldipalmitin ($PC_{22}P$), 2-behenyldistearin ($SC_{22}S$), 1-palmityldibehenin ($PC_{22}C_{22}$), and 1-stearyldibehenin ($SC_{22}C_{22}$). These glycerides are of practical interest in that some probably occur in hydrogenated rapeseed and mustard seed oils.

TABLE I

ANALYTICAL CONSTANTS OF STARTING MATERIALS AND PRODUCTS

	I. V.		Saponification value		Hydroxyl value		% Monoglyceride[10]	M. p., °C.		
	Calcd.	Found	Calcd.	Found	Calcd.	Found		Found	Lit.	Ref.
Erucic acid	74.5	74.5						33.4	33.5	10
Behenic acid	0	0.2						80.2	80.0	10
1-Monopalmitin	0	0	169.6	169			98.4	76.5	77.0	7
1-Monostearin	0	0.1	156.4	156.3			101.9	81.5	81.5	7
1,3-Dipalmitin	0	0	197.3	197.4	98	99	0.5	72.4	72.9	11
1,3-Distearin	0	0.1	179.7	179.4	90	92	0.4	78.2	78.2	11
$PC_{22}P$			188.8	190.6				66.6		
$SC_{22}S$			177.7	177.3				70.6		
$PC_{22}C_{22}$			172.5	172.3				66.1		
$SC_{22}C_{22}$			167.7	167.8				73.5		

The polymorphism of these behenyl-containing glycerides is similar in type to that reported for shorter chain compounds. However, the behenyl compounds all show rather high beta prime stability, $PC_{22}C_{22}$ exhibiting no beta form at all. The beta forms of the symmetrical compounds are beta-3, that of $SC_{22}C_{22}$ is beta-2.

A feature of considerable interest is the new sub-alpha form clearly manifested by the unsymmetrical behenyl glycerides at low temperatures (−50°). At higher temperatures, it transforms reversibly to alpha; it appears to be analogous to the sub-alpha form of monoglycerides.[7]

Experimental

The four mixed triglycerides were made by treating the corresponding mono- and diglycerides with an excess of behenyl chloride in the presence of pyridine according to established methods. The mono- and diglycerides were prepared by directed rearrangement according to the method of Eckey.[8] The behenyl chloride was prepared by treating an excess of oxalyl chloride with behenic acid, which had been obtained by complete hydrogenation of carefully purified erucic acid ($\Delta^{13:14}$-docosenoic acid).[9] Constants for the starting materials and the final products are given in Table I.

Final purification of the glycerides was accomplished by four to six crystallizations from Skellysolve B or Skellysolve B–ethyl ether mixtures.

The polymorphism of the glycerides was studied by X-ray and melting point techniques described previously.[4] A General Electric XRD unit was used to obtain flat film patterns using a 0.025" pinhole. The film distances were 5.0 cm. for most short spacing determinations, and 10.0 cm. for detailed short spacing and for long spacing patterns. Detailed X-ray data are reported in Table II. For identification purposes and quick reference, the characteristic thermal and X-ray data for the various poly-

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[1] Jackson and Lutton, THIS JOURNAL, **71**, 1976 (1949).

[2] Lutton, Jackson and Quimby, *ibid.*, **70**, 2441 (1948).

[3] Lutton, *ibid.*, **70**, 248 (1948).

[4] Lutton, *ibid.*, **67**, 524 (1945).

[5] Clarkson and Malkin, *J. Chem. Soc.*, 666 (1934).

[6] Clarkson and Malkin, *ibid.*, 985 (1948).

[7] Lutton and Jackson, THIS JOURNAL, **70**, 2445 (1948).

[8] Eckey and Formo, *J. Am. Oil Chem. Soc.*, **26**, 207 (1949).

[9] Handschumacher and Linteris, *ibid.*, **24**, 143 (1947).

[10] Ralston, "Fatty Acids and Their Derivatives," John Wiley & Sons, Inc., New York, N. Y., 1948.

[11] Baur, *et al.*, THIS JOURNAL, **71**, 3363 (1949).