

or by electrolytic decomposition of the salts in a three-compartment cell. Final purifications were by crystallization from fuming nitric acid or by esterification with diazomethane followed by distillation in the small molecular still. The ultimate composition and equivalent weight of the acids recovered from the tetrahydronaphthalene oxidation were in satisfactory agreement with the theoretical values for *o*-phthalic acid. The products recovered from the pyrene oxidation and purified by crystallization from fuming nitric acid gave values of ultimate composition and equivalent weight corresponding to a mixture of tetra- and tricarboxylic acids, presumably phrenitic and hemimellitic acids. The products recovered from the naphthacene oxidation by a similar procedure, judged by ultimate composition and equivalent weight, consisted of a mixture of a di- and a tetracarboxylic acid, presumably *o*-phthalic and pyromellitic acids, and with the dicarboxylic acid predominating.

Summary

Apparatus has been devised and analytical methods have been worked out for following quantitatively the rate of reaction of condensed cyclic compounds with alkaline permanganate, for determining the carbon balances in the process, and for recovering and characterizing the soluble products of the oxidations. The semi-micro apparatus and methods used permitted the work to be done on samples of 500 to 800 mg. The following substances were studied: tetrahydronaphthalene, dodecahydrotriphenylene, triphenylene, decacyclene, trisdecahydrodecacyclene, naphthacene, pyrene, diphenylene oxide and

carbazole. For comparison, a sample of a typical bituminous coal was investigated under identical conditions.

Under the conditions of this oxidation tetrahydronaphthalene oxidized most rapidly; bituminous coal, pyrene and naphthacene were next; then followed the heterocyclic compounds, diphenylene oxide and carbazole; the completely aromatic compounds—decacyclene and triphenylene—were less reactive, and the nearly saturated structures were least reactive of all. A qualitative correlation between the rates of oxidation and "double bond character" of certain polycyclic hydrocarbons was found. On the basis of this evidence the bituminous coal possesses a high "double bond character." Satisfactory first order relations with respect to alkaline permanganate were found in the reactions with tetrahydronaphthalene, pyrene, naphthacene and triphenylene, showing that with these compounds the reaction with the oxidant is the rate controlling factor. Significantly higher rates of oxidation were found than have been previously reported for some of the same compounds. This may be ascribed to the excess permanganate present in the early stages of the reaction.

Only with tetrahydronaphthalene, pyrene and naphthacene did the fraction of the carbon recovered as organic acids approach that postulated from theoretical equations.

The results of this investigation are in accord with the view that bituminous coals are condensed cyclic structures of "high double bond character."

PITTSBURGH, PA.

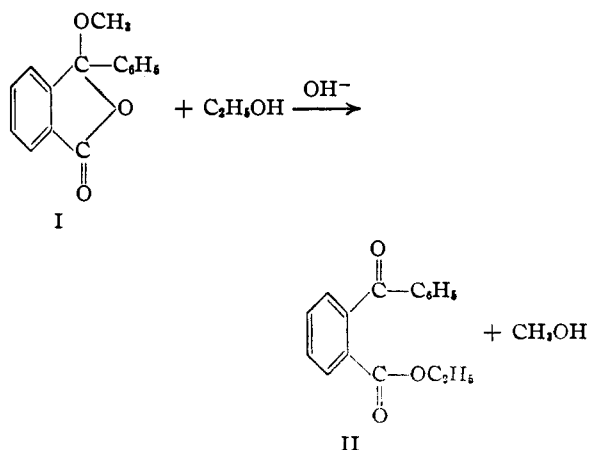
RECEIVED SEPTEMBER 14, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Kinetics of the Base-Catalyzed Reaction of Pseudo *l*-Menthyl *l*-*o*-Benzoylbenzoate with Methanol¹

BY JOHN R. SCHAEFGEN,² FRANK H. VERHOEK AND MELVIN S. NEWMAN

Pseudo methyl *o*-benzoylbenzoate (I) has been found to react with great rapidity with aqueous methanol in the presence of a small quantity of sodium hydroxide to yield its normal isomer, and with alkaline aqueous ethanol to yield normal ethyl *o*-benzoylbenzoate (II).³ This reaction therefore involves both a change from a pseudo, or lactol ether, structure to a keto ester structure and an ester interchange with the solvent. The rapidity with which this reaction took



(1) Presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, September, 1944. The material in this paper is contained in the Ph.D. thesis of J. R. S., The Ohio State University, March, 1944.

(2) Present address: Goodyear Tire and Rubber Co., Akron, Ohio.

(3) McCleary, Ph.D. Dissertation, 1940, The Ohio State University.

place,⁴ and the lack of quantitative rate studies on ester interchange in basic solution stimulated this investigation.

For the quantitative study of the reaction, pseudo *l*-menthyl *l*-*o*-benzoylbenzoate was used. In the synthesis of this ester the carbonyl carbon of *o*-benzoylbenzoic acid becomes asymmetric and there are obtained two diastereoisomeric pseudo esters. The *l*-menthyl *l*-*o*-benzoylbenzoate, so named because of its large levorotation ($[\alpha]^{25}_D - 186^\circ$), crystallized readily from alcoholic solutions, whereas its isomer could not be isolated in a pure state. In the interchange reaction the asymmetric center formed in the synthesis of the ester is destroyed and *l*-menthol ($[\alpha]^{25}_D - 49^\circ$) is produced. Because of the large difference in optical rotatory power of the *l*-ester and of menthol, the reaction could be readily followed polarimetrically.

The rate of the interchange, using sodium methylate and amines as catalysts, was measured at 15, 25 and 35°. The effect on the reaction rate of salts, and of small amounts of water was determined.

Considerable difficulty was encountered in the preparation of the menthyl esters, both normal and pseudo. Ordinarily, high yields of normal ester result from acid catalyzed esterification⁵ and from the reaction of the acid chloride with the alcohol⁵; whereas pseudo esters are produced if the acid chloride-alcohol reaction mixture is added to an excess of sodium carbonate solution,⁵ or if the same reaction is carried out in the presence of pyridine.⁶ In the case of *l*-menthol, the normal ester was formed in poor yield by acid catalyzed esterification, and other methods, such as direct heating of the acid and menthol, or reaction of the acid chloride with menthol (with or without pyridine) yielded pseudo esters. An unexplainably poor yield was obtained in the reaction of the acid chloride and alcohol in the presence of pyridine. In order to determine whether this behavior was characteristic of secondary or of cyclic secondary alcohols, the isopropyl and cyclohexyl esters were prepared. However, these alcohols gave both normal and pseudo esters in the usual way.^{5,6}

Experimental

A. Preparation of the Esters.—Treatment of the acid chloride obtained from 100 g. of *o*-benzoylbenzoic acid and 38 cc. of thionyl chloride with a benzene solution of 67 g. of *l*-menthol in the presence of 67 g. of anhydrous sodium carbonate yielded 136 g. (90%) of *l*-menthyl esters (mostly pseudo types). If pyridine was used instead of sodium carbonate, the yield was low (30%). Refluxing a solution of the acid chloride and *l*-menthol in ether-benzene for twenty-four hours, or heating of the free acid with excess *l*-menthol at 150° for three hours (followed by vacuum distillation), each gave over 90% yields of *l*-menthyl esters (mostly pseudo types in each case).

(4) For example, the conversion of pseudo methyl *o*-benzoylbenzoate to the normal methyl ester was 80% complete in three minutes at room temperature when 0.064 molar potassium hydroxide was used.

(5) Meyer, *Monatsh.*, **25**, 475 (1904); **34**, 69-93 (1913).

(6) Newman and McCleary, *THIS JOURNAL*, **63**, 1537 (1941).

Fractional crystallization at room temperature⁷ of the ester mixture from ethanol gave 38 g. (25%) of pure pseudo *l*-menthyl *l*-*o*-benzoylbenzoate, m. p. 116-117°.

*Anal.*⁸ Calcd. for $C_{24}H_{28}O_3$: C, 79.1; H, 7.8; saponification equivalent, 364. Found: C, 79.2, 79.2; H, 8.0, 8.2; saponification equivalent, 370. Specific rot. -191° (25°, c 1.6, benzene, D line); -186° (25°, c 2.1, methanol, D line).

Chromatographic absorption on activated carbon (Darco G-60) from petroleum ether (b. p. 35-52°), followed by elution with mixtures of petroleum ether and acetone, also effected a separation of the ester mixture. The material used for the kinetic run on the *d*-ester (see Table I) was taken from a chromatogram fraction rich in *l*-menthyl *d*-*o*-benzoylbenzoate, m. p. 62-77°, $[\alpha]^{25}_D + 71^\circ$ (methanol). Further purification of this ester was not attempted.

The normal *l*-menthyl ester was prepared in 25% yield by refluxing a benzene solution of equimolar quantities of *o*-benzoylbenzoic acid and *l*-menthol for ten hours using *p*-toluenesulfonic acid as a catalyst. The product failed to crystallize, and decomposed extensively when distilled at 1 mm. pressure; hence isolation in a state of high purity was not accomplished.

Normal isopropyl *o*-benzoylbenzoate,⁹ m. p. 66-67.2°, was prepared from the acid chloride and excess isopropyl alcohol (97% esterification). Pseudo isopropyl *o*-benzoylbenzoate,⁹ m. p. 67-68.4°, was prepared by the method of Newman and McCleary (92% esterification).

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 76.1; H, 6.0. Found for normal ester: C, 76.3; H, 6.1; for pseudo ester: C, 76.0; H, 5.9.

Normal cyclohexyl *o*-benzoylbenzoate¹⁰ was prepared by Fischer esterification (90% conversion to ester). The viscous oily product failed to crystallize even after vacuum distillation. Pseudo cyclohexyl *o*-benzoylbenzoate, m. p. 106-106.8°, was prepared by the method of Newman and McCleary (quantitative esterification). It crystallized only after vacuum distillation.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.9; H, 6.5. Found for normal ester: C, 78.5; H, 6.5; for pseudo ester: C, 78.3; H, 6.5.

The esters were characterized as normal or pseudo by their ultraviolet absorption spectra,¹¹ which were taken in ethanolic solution in fused silica cells in a Beckmann Spectrophotometer. The curves for the pseudo esters showed a maximum at 280 $m\mu$ and a minimum at 255 $m\mu$ with a sharp decrease in absorption at 300 to 310 $m\mu$. The curves for the normal esters showed points of inflection only, and absorbed up to about 380 $m\mu$. The values of $\log \epsilon$ for the pseudo esters at 280 and at 255 $m\mu$ are as follows: isopropyl, 3.04, 2.81; cyclohexyl, 2.98, 2.27; *l*-menthyl (*l*-*o*-benzoylbenzoate), 3.06, 2.81.

B. Materials: Esters.—The levorotatory *l*-menthyl ester, m. p. 116-117°, prepared as in A, was crystallized to constant melting point and dried at 100° *in vacuo*. *l*-Menthyl benzoate, m. p. 53.8-54.8°, prepared from the acid chloride and *l*-menthol, was crystallized to constant melting point and dried *in vacuo*.

Methanol.—A c. p. acetone-free product was dried over and distilled from magnesium methylate by the method of Lund and Bjerrum,¹² giving a product with a d^{20}_4 , 0.79128.

Bases.—Sodium methylate solutions were prepared by dropping oxide-free reagent grade sodium into anhydrous

(7) Crystallization at the temperature of the ice-chest effected no appreciable separation.

(8) Analyses by J. Varner and J. Curtis of this Laboratory.

(9) Gleason and Dougherty, *THIS JOURNAL*, **51**, 310 (1929), reported an isopropyl *o*-benzoylbenzoate but gave no analysis, melting point, or indication of its normal or pseudo nature.

(10) *Chem. Zentr.*, **109**, I, 181 (1938), U. S. Patent 2,094,453, states that an oily cyclohexyl *o*-benzoylbenzoate was prepared. No analysis was given.

(11) Hantzsch and Schweite, *Ber.*, **49**, 213 (1916); Che-Kin Lin, *Compt. rend.*, **207**, 733 (1938); Brode, Lord and Newman, forthcoming publication.

(12) Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

methanol. For butylamine, piperidine, and triethylamine, the purest Eastman Kodak Co. product was fractionally distilled from barium oxide through a column packed with glass helices. The middle constant boiling fractions were retained. A C. P. grade of aniline was distilled through a Vigreux column and the intermediate constant boiling fraction was retained. All amine solutions were standardized by titration and stored in sealed flasks.

Salts.—Anilinium and butylammonium benzenesulfonate were prepared by mixing ethyl acetate solutions of acid and base. The salts were recrystallized to constant melting point from ethyl acetate-ethanol mixtures, and dried at 100° *in vacuo*. Piperidinium ion was prepared in solution by adding an excess of piperidine to a solution of anilinium benzenesulfonate. A solution of butylammonium ion was made up by weight from the benzenesulfonate salt.

C. Apparatus and Procedure.—Methanolic solutions of base and of ester¹³ were added to separate arms of an inverted Y reaction tube, and then brought to the temperature desired by use of a thermostat. The Y tube was tilted to mix the solutions at zero time, and the contents were then poured into a four-decimeter jacketed polarimeter tube through which water from a thermostat was being pumped. The rotations were taken with a Schmidt and Haensch polarimeter reading accurately to $\pm 0.03^\circ$. The temperature control in the polarimeter tubes was accurate to $\pm 0.05^\circ$. The thermostat bath was cooled by circulating the thermostat liquid (water) through a coil immersed in ice water. The flow of water was controlled by a solenoid valve connected through a relay system. While readings were not actually being taken, the jacketed polarimeter tubes were enclosed in an air-bath, which varied $\pm 2^\circ$ from the temperature of the thermostat.

Data and Discussion

For each catalyst and temperature first-order graphs of the logarithm of the final rotation minus the observed rotation plotted against the time were prepared. For sodium methylate, triethylamine, and piperidine as catalysts, the curves were straight lines to 95% completion. The curves for butylamine deviated appreciably from a straight line. Titration of aliquot portions of the reaction mixture at given time intervals in experiments with butylamine showed that the base was being slowly used up. It is thought that the amine slowly reacts with the ester to form the amide, causing a decrease in base concentration and a deviation from linearity on the first-order graph. For those cases in which deviation from a straight line was observed, the slopes of the initial portions of the curves were used in estimating the velocity constants.

Experiments in which either the base concentration or the initial ester concentration was varied gave the following results: (1) the first-order velocity constant was found to be independent of the initial ester concentration (see Table I); (2) the first-order velocity constant was shown to be directly proportional to the sodium methylate concentration (see Fig. 1); (3) the first-order velocity constant in the case of the amines was found to be directly proportional to the concentration of methylate ion in equilibrium with the amines (see Fig. 2).

The addition of salts had no effect when sodium methylate was the catalyst, but in the amine

TABLE I
CATALYSIS BY SODIUM METHYLATE

Ester, m./l.	NaOCH ₃ , m./l.	k, min. ⁻¹
	15.00 \pm 0.05°	
0.0451	0.0379	0.103
.0451	.0380	.105
	25.06 \pm 0.05°	
0.0668	0.00447	0.0216
.0407	.00876	.0465
.0474	.00891	.0442
.0739	.00898	.0458
.0467	.0135	.0683
.0535	.0174	.0921
.0481	.0251	.133
.0480	.0251	.129 ^a
.025	.0259	.0964 ^b
.0475	.0307	.165
.0539	.0380	9.06 $\times 10^{-8}$ ^c
.0482	.0395	.208
.0482	.0509	.270
	35.02 \pm 0.05°	
0.0525	0.00945	.0903
.0476	.0172	.165
.0491	.0261	.251
.0466	.0306	.292
.0465	.0306	.286 ^d
.0466	.0308	.288 ^d
.0458	.0416	.401

^a Solution 2.14 *m* in H₂O. ^b Experiment with *d*-pseudo ester. ^c Experiment using menthyl benzoate, a normal ester. Note that the reaction is much slower. ^d Solution 0.0391 *m* in NaCl. ^e Solution 0.0390 *m* in NaCl.

TABLE II
CATALYSIS BY AMINES

Ester, m./l. $\times 10^3$	Amine, m./l. $\times 10^3$	Other	ρK_b	CH ₃ O ⁻ , m./l. $\times 10^4$	k, min. ⁻¹ $\times 10^4$
		Piperidine 25.06 \pm 0.05°			
4.95	0.87	...	5.06	2.70	6.21
4.91	1.60	...	5.05	3.74	9.06
5.03	1.73	H ₂ O, 0.99 <i>m</i>			9.21
5.10	1.75	...	5.05	3.90	10.1
4.95	2.46	...	5.04	4.69	12.1
4.57	3.94	...	5.02	6.09	18.1
		Piperidine 35.02 \pm 0.05°			
3.98	3.47	{ Aniline, 0.025 <i>m</i> C ₆ H ₅ NH ₂ SO ₃ C ₆ H ₅ , 0.025 <i>m</i>	4.52	0.42	2.81
4.94	0.875	...	5.06	2.72	11.5
4.95	1.69	...	5.05	3.84	17.2
4.95	2.48	...	5.04	4.70	23.7
4.72	3.95	...	5.02	6.10	30.4
4.46	3.96	C ₆ H ₅ NH ₂ , 0.032 <i>m</i>			28.6
4.52	4.01	NaCl, 0.0376 <i>m</i>	4.47	11.5	57.3
		Butylamine 35.02 \pm 0.05°			
4.49	2.90	BuNH ₂ SO ₃ C ₆ H ₅ , 0.0282 <i>m</i>	4.56	0.28	2.06
4.09	2.91	BuNH ₂ SO ₃ C ₆ H ₅ , 0.0056 <i>m</i>	4.75	0.91	3.94
3.90	2.32	BuNH ₂ SO ₃ C ₆ H ₅ , 0.0011 <i>m</i>	4.92	2.32	8.56
5.17	0.62	...	5.00	2.44	8.33
4.97	1.21	...	4.99	3.48	12.7
4.80	1.73	...	4.98	4.20	17.8
4.40	2.72	BuNH ₂ SO ₃ C ₆ H ₅ , 0.00066 <i>m</i>	4.96	4.45	18.3
4.22	2.90	...	4.97	5.50	25.8
4.25	2.90	...	4.97	5.50	26.0
		Triethylamine 35.02 \pm 0.05°			
4.72	3.82	...	5.88	2.24	9.08

(13) *l*-Menthyl *l*-o-benzoylbenzoate unless otherwise designated.

catalysis showed the secondary salt effect to be expected if the catalyst is the methylate ion.

The addition of small amounts of water was without effect on the reaction rate.

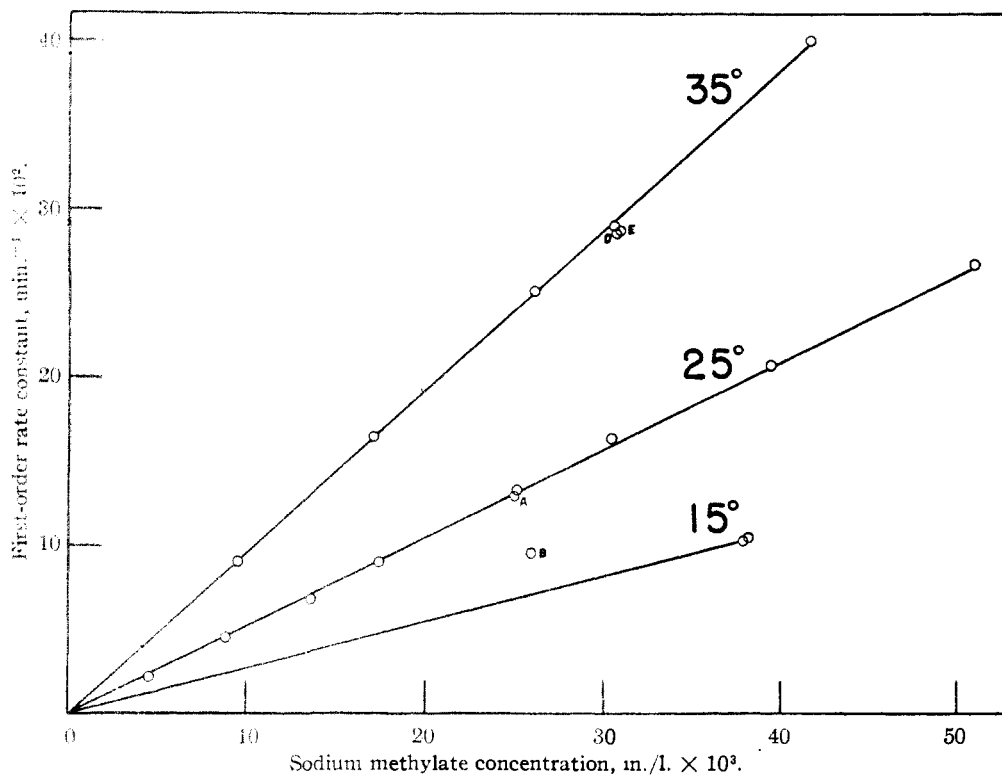


Fig. 1.—Catalysis by sodium methylate. (Letters refer to footnotes to Table I.)

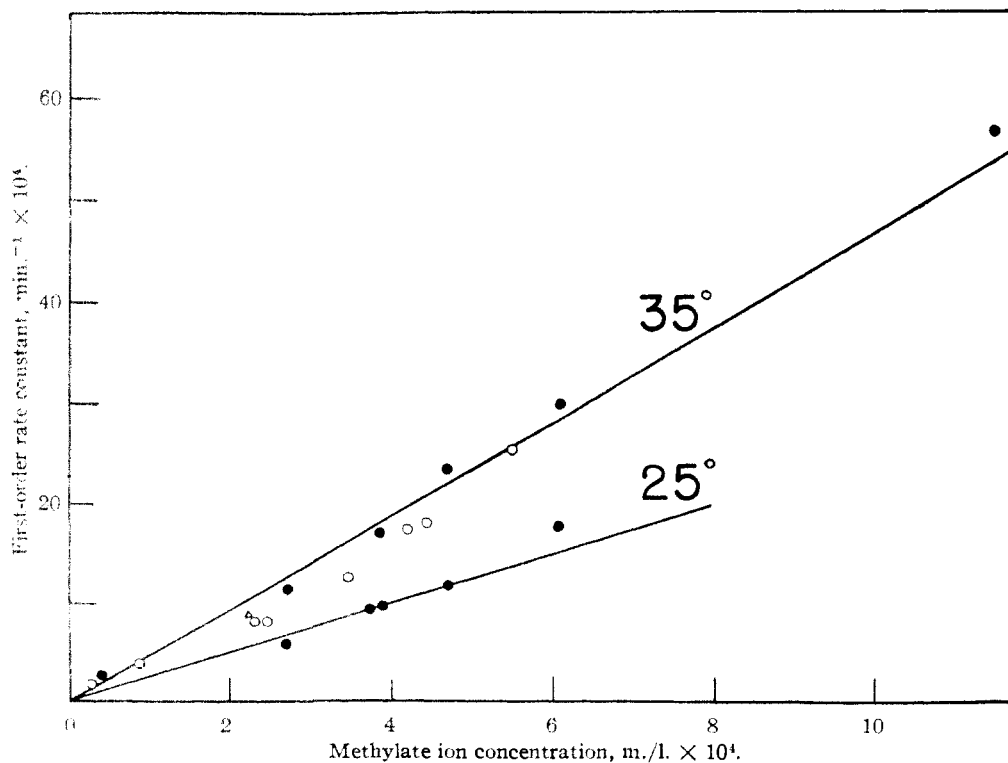


Fig. 2.—Catalysis by amines: ●, piperidine; ○, butylamine; △, triethylamine.

Table I records the data for sodium methylate catalysis; Table II those for amine catalysis. In Table II the first three columns give the composition of the solution; the fourth gives the value of the logarithmic dissociation constant of the amine appropriate to the ionic strength of the solution at equilibrium¹⁴; the fifth, the concentration of methylate ion as calculated from the values in columns 2, 3, and 4; and the sixth column, the value of the observed velocity constant.

The data of the second and third columns of Table I, and of the fifth and sixth columns of Table II are plotted in Figs. 1 and 2. These figures show that the rate of the reaction at zero base concentration approximates zero. The linearity of the curves points to specific catalysis by the methylate ion, but the proportionality constants in the equation $k = k'(\text{CH}_3\text{O}^-)$ are different for the two sets of data, the values being 5.27 (25°) and 9.59 (35°) for Fig. 1, and 2.63 (25°) and 4.72 (35°) for Fig. 2. No satisfactory explanation for this discrepancy can be obtained from the data. The deviation of the first-order curves from linearity in the case of butylamine is not great enough to account for it. The data show that there is no retardation of the reaction due to the presence of free amine, and that there is no definite trend in the values of k' with change in the ionic strength.

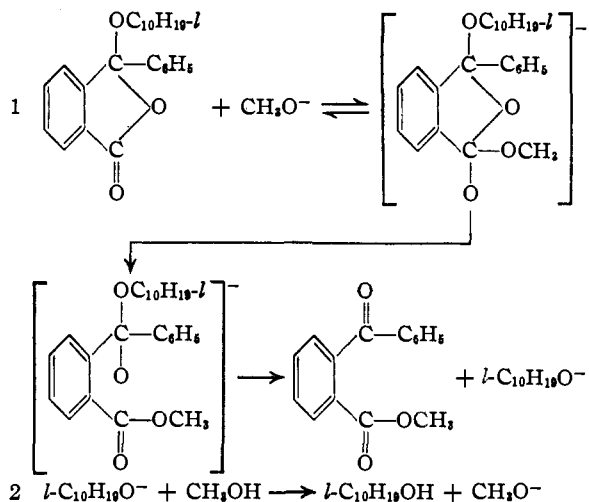
Using the values of k' obtained from the slopes of the lines in Figs. 1 and 2, the energy of activation is calculated to be 11,100 cal. for the data of Fig. 1 and 10,800 cal. for the data of Fig. 2.

The average rotation at the end of the reaction is that of pure *l*-menthol at the same concentration. Therefore, in the ester interchange, no change in the configuration at the asymmetric carbon atom attached to the alcoholic oxygen has

(14) Schaeffgen, Newman and Verhoek, *THIS JOURNAL*, **66**, 1847 (1944).

taken place, and it may be concluded that fission of the pseudo-ester takes place at the bond between the alcoholic oxygen and the carbonyl carbon of the acid.¹⁵

The following mechanism is postulated for the reaction, equation (1) being rate determining:



Summary

The reaction of pseudo *l*-menthyl *l*-*o*-benzoylbenzoate with methanol in the presence of methylate ion to form normal methyl *o*-benzoylbenzoate has been shown to be a pseudo first-order reaction, specifically catalyzed by methylate ion. The activation energy is 11,000 cal. There is no detectable primary salt effect. Fission of the pseudo-ester takes place at the bond between the alcoholic oxygen and the carbonyl carbon of the acid. A mechanism consistent with the facts has been postulated.

(15) Cf. Holmberg, *Ber.*, **45**, 2997 (1912).

COLUMBUS, OHIO

RECEIVED OCTOBER 25, 1944

[CONTRIBUTION FROM THE BUREAU OF MINES, PACIFIC EXPERIMENT STATION, U. S. DEPARTMENT OF THE INTERIOR]

Heats of Formation of $\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3$, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, and $\text{KAl}(\text{SO}_4)_2$ ¹

BY FRANK E. YOUNG²

The heats of formation of several metallurgically important compounds of aluminum are being determined at the Pacific Experiment Station of the Bureau of Mines. A previous paper³ described determinations of the heats of formation of aluminum nitrate hexahydrate and enneahydrate. New determinations of the heats of formation of anhydrous and hexahydrated aluminum sulfate and anhydrous and dodecahydrated potassium aluminum sulfate are reported in the present

paper. The only previously available value of the heat of formation of anhydrous aluminum sulfate is an estimate, and those of the other compounds are based upon data antedating modern thermochemical methods. Such data frequently are found to be unreliable.

Materials

Aluminum sulfate hexahydrate was prepared by heating recrystallized J. T. Baker aluminum sulfate octadecahydrate (containing a maximum of 0.20% alkali salts before recrystallization) in a stream of dry air to 100° in five and one-half hours, followed by twenty-one hours at 120°. Analysis showed a composition corresponding to $\text{Al}_2(\text{SO}_4)_3 \cdot 4.54\text{H}_2\text{O}$. The water content was adjusted by

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

(2) Chemist, Pacific Experiment Station, Bureau of Mines.

(3) Young, *THIS JOURNAL*, **66**, 777 (1944).