

2. Suitable laboratory preparative methods for divinyl ether which involve only ordinary laboratory glass-ware and simple laboratory methods have been developed.

## REFERENCES.

- (1) Cretcher and Pittenger, *J. A. C. S.*, 47, 164, 1174 (1925).
- (2) Hibbert, Perry and Taylor, *Ibid.*, 51, 1551 (1929).
- (3) Ruigh and Major, *Ibid.*, 53, 2663 (1931).

## THE HYDROLYSIS OF MENTHYL ACETATE AND ACETYLIZED PEPPERMINT OIL.\*

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## INTRODUCTION.

In the routine examination of commercial samples of peppermint oil several questions arose concerning the kinetics of the reaction in which the acetylated oil is hydrolyzed with an alcoholic solution of potassium hydroxide. Some work has been done on the determination of the reaction velocity between menthyl acetate and potassium hydroxide (1), but apparently no investigation has been made of the reaction rate between acetylated peppermint oil and potassium hydroxide. The complexity of the constitution of peppermint oil might lead to the immediate assumption that the reaction between acetylated oil and potassium hydroxide could not be of the second order. Observations, however, showed that the reaction rates of the hydrolysis of acetylated peppermint oil and of pure menthyl acetate agree well enough to assume that the reaction of the acetylated oil is of the second order. It must be remembered that some samples of oil will show larger amounts of a constituent, probably resinified material, which may react with potassium hydroxide to change the value of the velocity constant.

This work represents the first of a series of experiments to determine the reaction rates of the hydrolysis of acetylated peppermint oil and of menthyl acetate by potassium hydroxide in alcoholic solution at various temperatures. For the work included in this report temperatures of 25° C., 30° C. and 35° C. were used. The purpose of the menthyl acetate was to provide a standard of comparison.

## REAGENTS AND EXPERIMENTAL PROCEDURE.

*Peppermint Oil.*—The peppermint oil used in this work was a composite sample collected during the latter part of the 1934 season. Analysis of the oil gave the following constants: Optical rotation,  $-22.6_{\text{D}}^{27^{\circ}}$ ; esters, 9.66%; total menthol, 50.23%. From this sample a sufficient quantity of acetylated oil was prepared according to the procedure of the U. S. P. X in the monograph for peppermint oil.

*Menthyl Acetate.*—Menthol, U. S. P. X, was refluxed with fused sodium acetate and an excess of acetic anhydride, C.P., for one hour. After washing with sodium carbonate T.S. to remove excess acetic anhydride, and drying over fused calcium chloride, the product was distilled under reduced pressure. The following constants were obtained: B. p. 81.5–82.5° 4 mm.; optical rotation,  $-72.9_{\text{D}}^{27^{\circ}}$ .

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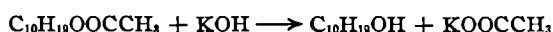
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*Alcohol, Aldehyde-Free.*—Ethyl alcohol, 95% by volume, was purified according to the method of the U. S. P. X.

Approximately 25 cc. of acetylated peppermint oil or menthyl acetate, accurately weighed, was placed in a 250-cc. volumetric flask and dissolved in aldehyde-free alcohol to the mark. This flask was placed in a thermostat having a temperature control sensitive to within 0.02 degree. In another volumetric flask, 250 cc. of standard alcoholic potassium hydroxide solution was placed and brought to the desired temperature in the thermostat. When both solutions had reached the same temperature, they were quickly poured into a 500-cc. flask and thoroughly mixed. A 10-cc. sample was withdrawn immediately and pipetted directly into an excess of standard acid in order to stop the reaction. The residual acid was then titrated with standard alcoholic potassium hydroxide solution, using a microburette graduated to 0.01 cc. At various intervals of time, 10-cc. portions were withdrawn from the reaction flask in the thermostat and similarly treated with acid and alkali. Phenolphthalein T.S. was used as the indicator.

#### THEORETICAL AND ANALYTICAL DATA.

If, in the reaction between menthyl acetate and potassium hydroxide,

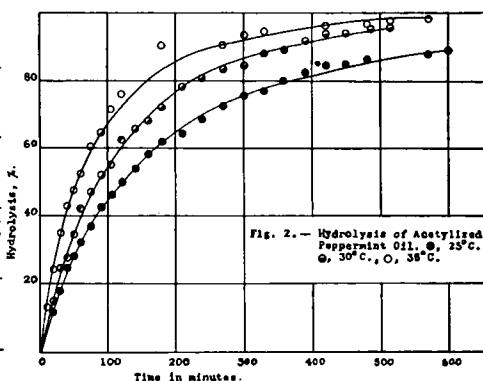
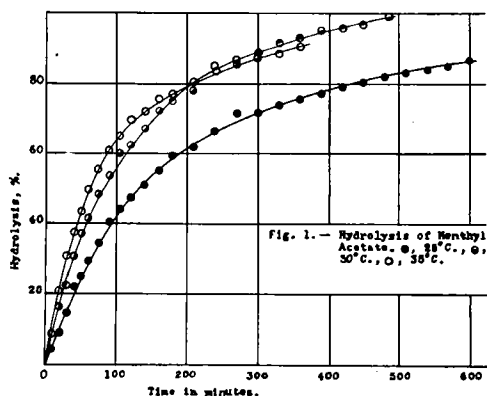


$a$  and  $b$  represent the initial molar concentrations of the two reacting substances, and  $x$  the amount transformed in the interval of time  $t$ , the velocity of the reaction will be expressed by the equation,

$$\frac{dx}{dt} = k(a - x)(b - x)$$

which, upon integration and substitution of Briggsian logarithms, becomes

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$$



In Tables I and II,  $a - x$  is expressed as the number of cubic centimeters of 0.9744  $N/2$  sulfuric acid required to titrate 10 cc. of the reaction mixture and represents the amount of potassium hydroxide present in that volume of the mixture at the time  $t$ . The term  $b - x$  is also expressed as cubic centimeters of acid of the same normality and represents the amount of menthyl acetate or acetylated peppermint oil present in 10 cc. of the reaction mixture at the time  $t$ . The term  $a - b$  is expressed as the number of equivalents of potassium hydroxide present in excess in one liter of the reaction mixture. The time  $t$  is expressed in minutes.

Using the formula,

$$\text{Per cent hydrolysis} = \left(1 - \frac{b-x}{b}\right) 100$$

the percentage of ester hydrolyzed was calculated for each experiment. See Tables I and II and Figs. 1 and 2.

TABLE I.—HYDROLYSIS OF MENTHYL ACETATE.

<i>t.</i>	25° C.			30° C.			35° C.		
	<i>a - x.</i>	<i>b - x.</i>	<i>k · 10<sup>3</sup>.</i>	<i>a - x.</i>	<i>b - x.</i>	<i>k · 10<sup>3</sup>.</i>	<i>a - x.</i>	<i>b - x.</i>	<i>k · 10<sup>3</sup>.</i>
0	5.593	4.693	...	5.545	3.895	...	5.515	4.705	...
40	4.562	3.662	2.572	4.340	2.690	3.893	3.745	2.935	5.377
50	4.400	3.500	2.493	4.089	2.439	4.069	3.455	2.642	5.548
60	4.235	3.335	2.412	3.928	2.278	3.974	3.170	2.357	5.808
75	3.970	3.070	2.483	3.672	2.022	4.039	2.903	2.090	5.735
90	3.710	2.810	2.595	3.448	1.798	4.119	2.655	1.842	5.822
105	3.530	2.630	2.582	3.212	1.562	4.358	2.450	1.637	5.925
120	3.380	2.480	2.551	3.114	1.464	4.163	2.290	1.477	5.909
140	3.190	2.290	2.542	2.924	1.274	4.244	2.135	1.322	5.802
160	3.010	2.110	2.564	2.725	1.074	4.487	1.960	1.147	5.971
180	2.810	1.910	2.669	2.608	0.958	4.322	1.890	1.077	5.683
210	2.710	1.810	2.479	2.458	0.808	4.499	1.740	0.927	5.683
240	2.500	1.604	2.551	2.267	0.617	4.915	1.620	0.807	5.683
270	2.240	1.340	2.859	2.222	0.572	4.626	1.460	0.647	6.150
300	2.230	1.330	2.596	2.109	0.459	4.859	1.400	0.587	6.002
Inf.	0.900	0.000	...	1.650	0.000	...	0.810	0.000	...

TABLE II.—HYDROLYSIS OF ACETYLATED PEPPERMINT OIL.

<i>t.</i>	25° C.			30° C.			35° C.		
	<i>a - x.</i>	<i>b - x.</i>	<i>k · 10<sup>3</sup>.</i>	<i>a - x.</i>	<i>b - x.</i>	<i>k · 10<sup>3</sup>.</i>	<i>a - x.</i>	<i>b - x.</i>	<i>k · 10<sup>3</sup>.</i>
0	5.513	2.473	...	5.471	2.346	...	5.426	2.391	...
40	4.909	1.869	2.768	4.719	1.594	3.957	4.406	1.371	5.882
50	4.819	1.779	2.631	4.562	1.437	4.054	4.290	1.255	5.540
60	4.714	1.674	2.631	4.384	1.259	4.390	4.169	1.134	5.437
75	4.597	1.557	2.529	4.268	1.143	4.124	3.985	0.950	5.539
90	4.460	1.420	2.573	4.150	1.025	4.037	3.880	0.845	5.296
105	4.370	1.330	2.495	4.078	0.953	3.799	3.710	0.675	5.698
120	4.273	1.233	2.483	3.905	0.780	4.183	3.610	0.575	5.734
140	4.180	1.140	2.400	3.831	0.706	3.964	...	...	...
160	4.073	1.033	2.406	3.772	0.647	3.763	...	...	...
180	3.985	0.945	2.391	3.678	0.553	3.826	...	...	...
210	3.920	0.880	2.226	3.538	0.413	4.071	...	...	...
240	3.820	0.780	2.215	3.480	0.355	3.931	...	...	...
270	3.720	0.680	2.254	3.414	0.289	3.948	...	...	...
300	3.640	0.600	2.152	3.395	0.270	3.690	...	...	...
Inf.	3.040	0.000	...	3.125	0.000	...	3.035	0.000	...

## CONCLUSIONS.

1. The reaction constants for the hydrolysis of menthyl acetate and of acetylated peppermint oil have been determined at 25° C., 30° C. and 35° C.

2. Until further work at different temperatures has been completed no definite conclusions can be drawn regarding the application of the van't Hoff and Arrhenius equation to the variation of the velocity constant with temperature. It has been observed in this work that the velocity of the reaction is more than doubled for a 10° rise in temperature.

## REFERENCE.

- (1) Nekrasova, *Arch. Pharm.*, 266, 595 (1928); through *C. A.*, 23, 474 (1929).

The author takes this opportunity to acknowledge the help of Mr. Robert F. Ervin in determining the constants in this work.

## A NOTE ON THE MAGNESIA MAGMA HEAVY METALS TEST.\*

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The U. S. P. XI test for heavy metals in magnesia magma is as follows:

"To 5 cc. of Magnesia Magma, add 10 cc. of diluted hydrochloric acid and 10 cc. of distilled water, mix thoroughly, and filter if necessary. Warm the solution to 50° C., add 25 cc. of freshly prepared hydrogen sulfide T.S., and allow the mixture to stand at room temperature for ten minutes. When viewed in a Nessler tube, looking downward through the column of liquid above a white surface, the solution does not show a deeper coloration than that produced by 25 cc. of distilled water, to which 0.5 cc. of lead nitrate solution, containing 0.1599 Gm. of lead nitrate in 1000 cc. of distilled water, has been added, and treated as directed in the foregoing procedure for the Magnesia Magma."

If one follows the directions for the preparation of the standard lead sulfide sol literally he would add 0.5 cc. of lead nitrate solution to 25 cc. of distilled water, followed by 10 cc. of diluted hydrochloric acid, 10 cc. more of distilled water and, after heating to 50° C., 25 cc. of hydrogen sulfide T.S. As the volume of a standard prepared in this manner is slightly over 70 cc. the analyst, realizing that something is wrong, may simply add 25 cc. of hydrogen sulfide T.S. to a mixture of 0.5 cc. of lead nitrate solution and 25 cc. of distilled water, or he may reason that 5 cc., rather than 25 cc., of distilled water is to be mixed with the lead nitrate solution and then "treated as directed in the foregoing procedure for the Magnesia Magma," *i. e.*, adding diluted hydrochloric acid, distilled water and hydrogen sulfide T.S. In consequence of the ambiguity of the official directions at least three different methods of preparing the standard solution have been used. Briefly, the outcome has been that the test is either too stringent or too lenient, for the color produced in an acidified standard is almost imperceptible and very few magmas pass the test, while the light brown color of the non-acidified standard is sufficiently pronounced to allow practically all magmas, some of which may contain excessive quantities of heavy metals, to meet the requirements.

It may be stated here that the correct procedure in preparing the standard, according to a communication from the Chairman of the Sub-Committee on Inorganic Chemicals, is to add 0.5 cc. of lead nitrate solution to 25 cc. of distilled water and, after warming to 50° C., to add 25 cc. of hydrogen sulfide T.S.

Because of the variation in color of the sulfide sol produced by the presence of acid it was decided to investigate the effect of the free acid in the magma solution upon the accuracy of the test. The quantity of free acid in the solution remaining after the neutralization of the magma is approximately 5 cc. of diluted hydrochloric

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