

2.0	...	0.982	-19.4	1.507	96
3.2	...	0.978	-18.0	1.506	96
2.0	...	0.978	-20.0	1.505	..
0.8	...	0.982	-20.8	1.507	..

## Non-Official Varieties of Sandalwood.

2.4 <sup>1</sup>	8.4	0.983	-12.4	1.504	96
5.0 <sup>1</sup>	8.8	0.960	- 9.3	1.509	94
3.5 <sup>1</sup>	5.0	0.983	-13.2	1.504	96
1.2 <sup>2</sup>	...	0.954	0.0	1.505	..
2.0 <sup>2</sup>	...	0.954	- 9.7	1.504	..
5.0 <sup>2</sup>	...	0.978	-14.5	1.504	96
6.0 <sup>2</sup>	...	0.975	-14.4	1.504	..
2.5 <sup>3</sup>	...	0.954	-38.0	1.507	87
2.0 <sup>4</sup>	...	0.943	+12.1	1.500	49

\* Cc. per 100 Gm. of sandalwood.

\*\* Reported in angular degrees on the basis of a 100-mm. tube.

<sup>1</sup> Australian Sandalwood.

<sup>2</sup> From New Caledonia Islands.

<sup>3</sup> African Sandalwood.

<sup>4</sup> Amyris Species.

## CONCLUSIONS.

1. The yield of volatile oil in authentic sandalwood was found to vary considerably, being least in sandalwood chips, the amount in some instances falling below one per cent. This low yield in volatile oil in the chips is probably due, for the most part, to the inclusion of a larger proportion of sap wood.

2. The specific gravity of the volatile oil is sometimes outside the Pharmacopœial limits (0.965 to 0.980 at 25° C.), values both above and below the specifications being noted. The optical rotation in the case of some specimens falls outside the official limits (-15° to -20° in a 100-mm. tube at 25° C.), value as high as -22.50 being observed. The refractive index for the volatile oils from both the official and non-official varieties of sandalwood are essentially identical, the entire range lying between 1.500 and 1.509.

3. The specific gravity and refractive index are of little value for the detection of non-official varieties of sandalwood. The optical rotation, on the other hand, is particularly important. In the case of the volatile oils from the nine non-official samples reported not one possessed the optical rotation within the official limits, or within the limits of the volatile oils from the authentic sandalwoods.

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

BY LAWRENCE H. BALDINGER.<sup>1</sup>

## INTRODUCTION.

In the analysis of peppermint oil the United States Pharmacopœia directs that 50 cc. of half-normal alcoholic potassium hydroxide be used to hydrolyze the weighed sample of acetylated oil. Provided an excess of base is assured, it should

\* Scientific Section, A. Ph. A., New York meeting, 1937.

<sup>1</sup> Department of Pharmacy, University of Notre Dame, Notre Dame, Indiana.

be possible to use a smaller quantity of the hydroxide solution for the hydrolysis. In order to test the validity of this assumption and to supplement semi-quantitatively the determination of the reaction velocities between menthyl acetate and acetylyzed peppermint oil and potassium hydroxide the following experiments were performed:

Accurately weighed 5-cc. samples of acetylyzed peppermint oil were treated with alcoholic potassium hydroxide solution, one with 30 cc., the next with 35 cc., up to 50 cc. The flasks were placed in a water-bath, thermostatically controlled to a desired temperature within 0.2° C. The contents of the flasks, after being kept at the desired temperature for one hour, were titrated with half-normal sulfuric acid immediately after being taken from the bath. Phenolphthalein was used as the indicator. From the data obtained the percentage of menthol in each 5-cc. portion was calculated using the formula of the U. S. P. monograph for oil of peppermint. Assuming that the hydrolysis of the acetylyzed oil was complete at steam-bath temperatures, the percentage of menthol obtained in a series of experiments at that temperature was used as a basis upon which to calculate the per cent hydrolysis taking place at the different temperatures which were used. See Tables I and II.

From these results it may be roughly concluded that steam-bath temperature is necessary for complete hydrolysis of the oil, and that a volume of alcoholic potassium hydroxide less than 50 cc. may give erratic results. The lower percentages obtained when using smaller portions of potassium hydroxide may be due to the reading error involved in the back titration of the excess alkali with acid.

TABLE I.—PER CENT OF MENTHOL IN PEPPERMINT OIL.

Temperature.	Cubic Centimeters of Alcoholic Potassium Hydroxide Solution Originally Added to Samples of Acetylyzed Peppermint Oil.				
	30.	35.	40.	45.	50.
25° C.	20.96	22.22	22.36	23.43	23.82
30° C.	27.76	32.85	31.62	28.67	29.06
35° C.	30.34	32.03	33.56	33.59	34.46
40° C.	34.39	38.98	39.16	40.30	40.50
45° C.	34.99	36.39	40.17	42.11	42.86
100° C.	47.60	48.57	48.51	49.26	49.31
Steam-bath					

TABLE II.—PERCENTAGE HYDROLYSIS OF ACETYLYZED PEPPERMINT OIL.

Temperature.	Cubic Centimeters of Alcoholic Potassium Hydroxide Solution Originally Added to Samples of Acetylyzed Peppermint Oil.				
	30.	35.	40.	45.	45.
25° C.	43.07	45.65	45.94	48.14	48.94
30° C.	57.04	67.50	64.97	58.91	59.71
35° C.	62.34	65.81	68.95	69.02	70.80
40° C.	70.66	80.09	80.46	82.80	83.21
45° C.	71.89	74.46	82.54	86.52	88.06

In a previous publication (1) the reaction rates of the hydrolysis of acetylyzed peppermint oil and of pure menthyl acetate at 25° C., 30° C. and 35° C. were reported. This paper is a report of further work on the problem using temperatures of 40° C., 45° C. and 50° C.

#### REAGENTS AND EXPERIMENTAL DATA.

The peppermint oil used in this work had the following constants: Optical rotation,  $-21.8_{D}^{27}$ ; esters, 9.46%; total menthol, 51.65%. The other reagents,

the experimental procedure and the theoretical discussion are the same as reported previously (*loc. cit.*). See Tables III and IV.

TABLE III.—HYDROLYSIS OF MENTHYL ACETATE.

<i>t</i> (Minutes).	40° C.		45° C.		50° C.	
	<i>k</i> ·10 <sup>2</sup> .	% Hydrolysis.	<i>k</i> ·10 <sup>2</sup> .	% Hydrolysis.	<i>k</i> ·10 <sup>2</sup> .	% Hydrolysis.
0						
15	8.63	25.3	11.82	33.3	18.65	44.4
30	9.59	43.8	12.58	52.8	18.89	63.6
45	9.33	54.2	10.61	59.3	18.13	73.0
60	9.50	62.5	11.25	68.5	19.42	81.0
75	10.31	70.5	11.95	75.6	17.95	83.9
90	9.69	73.4	9.27	75.9	19.91	88.8
105	10.06	77.9	12.03	82.8	18.31	89.8
120	10.07	80.8	13.63	87.5	19.30	92.4
135	10.53	84.0	12.92	88.6	19.02	93.6
150	10.96	86.8	12.58	89.7	21.85	95.9
170	10.94	88.6	12.30	91.2	20.27	96.3
190	10.40	89.5	12.78	93.0	20.65	97.2
210	10.36	92.1	13.93	95.0	20.41	97.3
240	...	..	13.32	95.8	19.81	98.2
270	...	..	12.85	96.4	...	..
Av. 10.1			Av. 12.47		Av. 19.47	

TABLE IV.—HYDROLYSIS OF ACETYLATED PEPPERMINT OIL.

<i>t</i> (Minutes).	40° C.		45° C.		50° C.	
	<i>k</i> ·10 <sup>2</sup> .	% Hydrolysis.	<i>k</i> ·10 <sup>2</sup> .	% Hydrolysis.	<i>k</i> ·10 <sup>2</sup> .	% Hydrolysis.
0	..	..	...	..	...	..
10	..	..	...	..	18.78	36.5
15	..	..	11.07	30.8	...	..
20	..	..	...	..	17.28	54.5
30	..	..	11.92	52.4	16.10	65.1
40	..	..	...	..	16.28	74.4
45	8.93	57.3	11.95	65.4	...	..
50	..	..	...	..	15.63	79.6
60	8.62	65.4	12.75	76.2	16.11	85.1
75	9.23	74.6	11.03	78.5	16.84	90.8
90	8.77	78.2	9.89	80.5	14.04	90.8
105	8.19	80.5	9.70	83.9	...	..
120	8.38	84.6	...	..	14.09	95.36
135	8.41	87.4	...	..	...	..
150	8.58	90.1	9.77	91.8	...	..
170	7.79	90.5	11.11	95.5	...	..
190	7.56	92.0	10.15	95.5	...	..
230	..	..	9.53	97.0	...	..
250	7.89	96.3	10.77	98.5	...	..
270	..	..	9.97	98.5	...	..
Av. 8.40			Av. 10.5		Av. 16.28	

## DISCUSSION.

As a result of a large number of observations on a variety of chemical reactions it has been shown that in general the velocity of a reaction is doubled or trebled for an increase in temperature of ten degrees. From the data given in Table V the reaction-constant ratios over ten-degree changes have been calculated and are as

follows: Menthyl acetate,  $k_{35}/k_{25}$  (obs.) 2.25;  $k_{40}/k_{30}$  (obs.) 2.34, (calc.) 2.19;  $k_{45}/k_{35}$  (obs.) 2.16, (calc.) 2.14;  $k_{50}/k_{40}$  (obs.) 1.93, (calc.) 2.09: Acetylyzed Peppermint Oil,  $k_{35}/k_{25}$  (obs.) 2.34;  $k_{40}/k_{30}$  (obs.) 2.06, (calc.) 2.28;  $k_{45}/k_{35}$  (obs.) 1.87, (calc.) 2.22;  $k_{50}/k_{40}$  (obs.) 1.93, (calc.) 2.17. One of the several empirical expressions which have been suggested for representing the variation of the velocity constant, is that proposed by van't Hoff and verified by Arrhenius (2),  $d \ln k/dT = Q/R \cdot 1/T^2$ , where  $Q$  is a constant and  $R$  is the gas constant. Integration of this expression between the limits  $k_1, T_1$  and  $k_2, T_2$  gives the expression  $\ln k_1/k_2 = Q/R (1/T_2 - 1/T_1)$ . The Arrhenius equation may also be written  $1/k \cdot dk/dT = Q/RT^2$ , where  $1/k \cdot dk/dT$  is the temperature coefficient of the reaction per unit velocity per degree rise in temperature; the rate of increase with temperature of reaction velocity will therefore diminish with rise in temperature. The custom is to call the ratio of the velocities at two temperatures ten degrees apart the temperature coefficient; usually  $35^\circ \text{C.}$  and  $25^\circ \text{C.}$  are selected so that  $k_{35}/k_{25}$  is usually referred to as the temperature coefficient of a reaction. For this range of temperature, the Arrhenius equation becomes  $2.303 \log k_1/k_2 = Q/1.9864 (1/308 - 1/298)$  so that  $\log k_2/k_1 = Q/41,988$ .

For the hydrolysis of menthyl acetate by potassium hydroxide the value of  $Q$  is 14,768  $k_{35}/k_{25}$  is 2.248; for the hydrolysis of acetylyzed peppermint oil by potassium hydroxide, the value of  $Q$  is 15,531 and  $k_{35}/k_{25}$  is 2.344. In Table V are tabulated the reaction constants of this and previous work, also calculated values for reaction constants at those temperatures used in the experiments. The calculated values were determined using the value of  $Q$  obtained with temperature coefficient  $k_{35}/k_{25}$ .

TABLE V.—REACTION CONSTANTS, OBSERVED AND CALCULATED.

T Abs.	Menthyl Acetate, $k \cdot 10^2$ .		Acetylyzed Peppermint Oil, $k \cdot 10^2$ .	
	Obs.	Calc.	Obs.	Calc.
298	2.57	...	2.40	...
303	4.33	3.88	4.06	3.70
308	5.77	...	5.62	...
313	10.11	8.49	8.40	8.43
318	12.47	12.34	10.51	12.48
323	19.47	17.72	16.13	18.29

## CONCLUSION.

While it has been observed that the velocity of the hydrolysis reaction is approximately doubled for a ten-degree rise in temperature, the lack of agreement in the results for acetylyzed peppermint oil would appear to indicate that either counter reactions or side reactions take place between the potassium hydroxide and constituents in the oil other than the menthyl acetate. Experimental difficulties may also account for some of the results since at the higher temperatures the reaction proceeds at a much faster rate. While the problem is chiefly of theoretical interest, it is apparent from a practical point of view that a fair excess of base is necessary in such reactions and that heating of such reaction mixtures to a fairly high temperature for at least one hour will do much to insure concordant results.

## REFERENCES.

- (1) Baldinger, *Jour. A. Ph. A.*, 26, 208 (1937).
- (2) Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Company, New York, 969-970 (1931).