NOTE.

Preparation of Sulfurous Acid.—The cheapest and most convenient method of preparing small amounts of sulfurous acid for the laboratory consists in warming fuming sulfuric acid, containing 30% SO_3, with sulfur. The acid need not be pure and the evolution is slow and regular provided only lump sulfur in not too large amount be used. The sulfur dissolves forming a blue solution from which on warming SO_2 is given off mixed with some SO_3. If sulfuric acid is objectionable the resulting solution must be boiled and the gas again absorbed.

Evolution of SO_2 ceases when the SO_3 has been acted on and the sulfur melts. If the acid remaining is allowed to cool, it contains only a small amount of dissolved sulfur and is still fit for most uses. Now that copper has risen so enormously in price the saving effected is considerable.

EDWARD HART.

[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY, U. S. DEPT. AGRICULTURE.]

THE REACTIONS OF BOTH THE IONS AND THE MOLECULES OF ACIDS, BASES AND SALTS; THE INVERSION OF MENTHONE BY SODIUM, POTASSIUM AND LITHIUM ETHYLATES.

BY W. A. GRUSE[1] AND S. F. ACREE.[2]

Received December 13, 1916.

Menthone occurs in Russian and American peppermint oils, as a rather important constituent of oils from pennyroyal and buchu has been found in geranium oil and occurs in other less well-known oils. It has also been described as a constituent of pine oil. Its constitution has been thoroughly established and the substance has been the subject of interesting investigations. The immediate practical object of this work was to try to develop a method for the detection and quantitative estimation of menthone in pine oils, and to learn something of the mechanism of a series of analogous condensation reactions with which we are working. Happily both of these objects have been realized and will be reported in other articles.

The inversion of menthone has been studied chemically by Beckmann, and from a more purely physical standpoint by Tubandt,[3] who, in the first of three papers on the subject, reached the following conclusions: (1) The inversion of menthone is a monomolecular, reversible reaction, effected by acids and bases. (2) The equilibrium point between *d*- and *l*-menthone is independent of the nature and concentration of the catalyser and of

---

[1] Research Fellow, Forest Products Laboratory, Madison, Wisconsin.

[2] In charge, Section of Derived Products, Forest Products Laboratory, Madison, Wisconsin.

[3] *Ann.*, **339**, 41 (1904); **354**, 259 (1907); **377**, 284 (1910).

the amount of menthone present; the equilibrium point attained by starting with either *d*- or *l*-menthone is the same. (3) The velocity of inversion in absolute ethyl alcohol, using sodium ethylate as catalyser in concentrations greater than 0.005 *N*, is proportional to the concentration of the catalyzer. In solutions more dilute than 0.005 *N*, the velocity drops, ceasing to be proportional to the concentration of the catalyzer. (4) Neutral salts do not affect the velocity of inversion by sodium ethylate, nor do water or indifferent organic substances, so long as they are not added in such quantities as to change the nature of the solvent.

The present work has involved the study of the inversion of *l*-menthone by sodium, potassium and lithium ethylates at 25° in absolute ethyl alcohol in very dilute solutions, to avoid the "abnormal salt or solvent effects" observed in concentrated solutions. The suggestion was made by one of us[1] in 1912, in a discussion of Tubandt's work, that if the ethylate ion is reactive in the inversion, the constant expressing this activity should be the same, whether calculated from the velocities experimentally obtained with sodium, potassium or lithium ethylates. The theory is verified in the work now reported.

Experimental.

For the especially large and accurate polarimeter used in this work we are indebted to Professor Kahlenberg, of the University of Wisconsin. It is of the largest type made by Schmidt and Haensch, and can be read directly to thousandths of a circular degree. Illumination was provided by a Type Y Cooper-Hewitt mercury quartz lamp, used in connection with a Mercury Green Line Wratten Filter No. 77, presented by Dr. Kenneth Mees, of the Eastman Kodak Company; by this arrangement, the 546.1 line of the mercury spectrum was obtained practically pure. With this illumination, it was found possible to reproduce readings on the polarimeter, under the best conditions, to ±0.001°.

The polarimeter tubes, which were used as reaction vessels, were made of silver-plated copper, seven dm. in length, and during the reaction were kept in a carefully regulated constant temperature bath, the arrangement being such that the tubes could be read through the end walls of the bath. Temperature control was well within 0.005°.

The entire apparatus is illustrated in Figs. 1, 2, and 3. In Figs. 1 and 2 the bath 1 rests in a framework, 2, which moves on rollers, 3, on a small iron track to allow each of the four polarimeter tubes A to be read in turn. The water is stirred downward under the false bottom 4 by the electric motor 5 and is cooled by the water coil 6 and heated by the electric light 7, which is regulated electrically. The caps K close the tubes H when readings are not taken and give better temperature regulation. The joint 8 has mica insulation to prevent electrical leaks from the motor to the bath.

---

[1] *Am. Chem. J.*, **48**, 359 (1912).

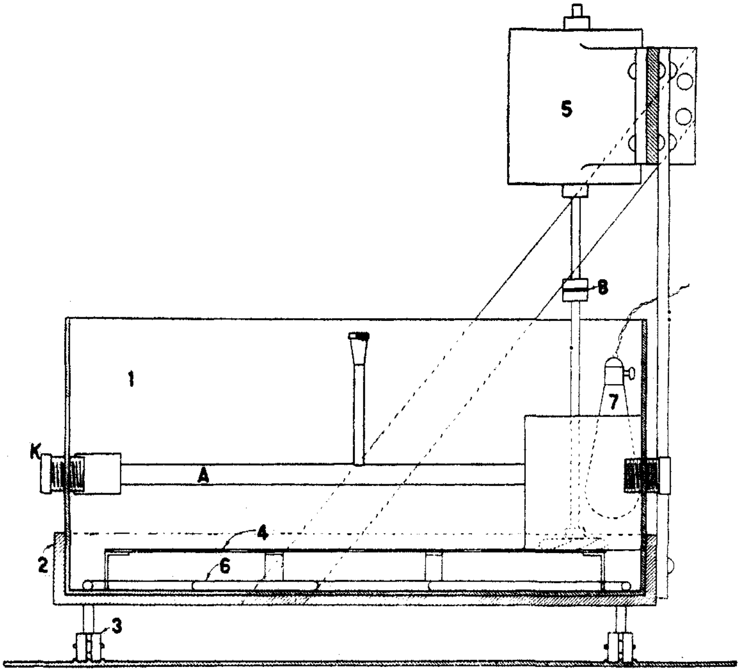

Fig. 1.

The copper polarimeter tubes A in Fig. 3 are silver plated and are held in position by the sliding collar F and the tube H. The collar B is sweated

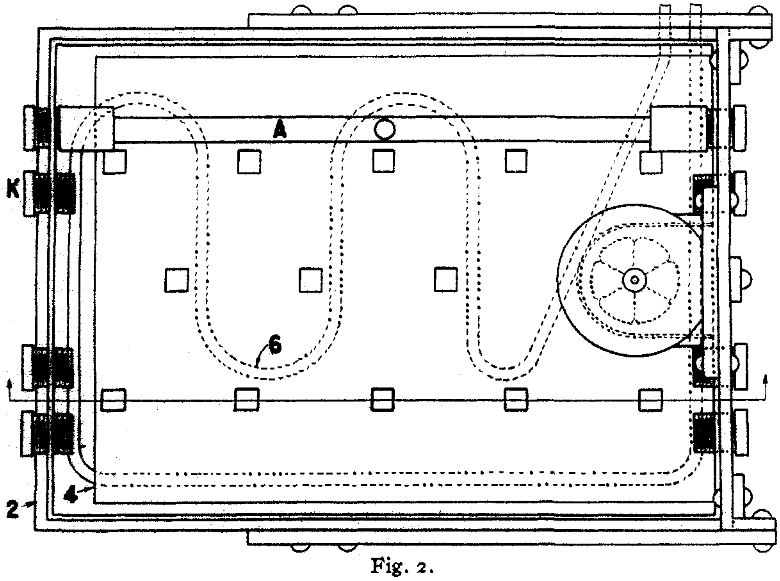

Fig. 2.

on the tube A and holds in place a small silver ring, S, sweated on the end of A. This silver ring is turned plane to fit the plane glass discs. It is very important to have the rubber washer D rest on the glass disc G exactly over the end of the tube A, as illustrated in Fig. 3, in order to prevent a distortion of the glass discs and uncertainties in measuring the optical rotation. The washer E is of considerable assistance in keeping water from coming in contact with the glass plates. The cap L covering the side tube T is kept under the water during the reaction.

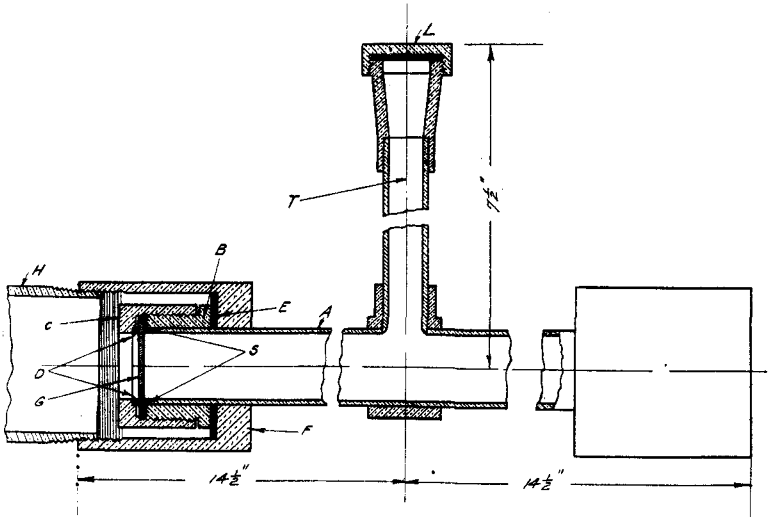

Fig. 3.

Absolute ethyl alcohol was used as solvent, and refined pycnometric determinations of its specific gravity showed that the average water content of the various samples employed was 0.029%. In the course of these determinations, psychrometric measurements of the moisture content of the air were made, and as the result of a long series of such measurements, the writers have become convinced that the figure ordinarily assumed for the weight of 1 cc. of air, 1.2 mg., as used for the correction of weighings to vacuo, is too high, and that the value 1.15 mg. per cc. is much nearer the truth under ordinary laboratory conditions.

The values of K_V, the reaction velocity at a given concentration, have been calculated by the use of the equation

$$K_V = \frac{1}{t} \log \frac{R_o - R_\infty}{R_o - R_t}.$$

Two sample[1] tables A and B for different ethylates at different dilutions, are given to show the constancy attained. Each value of K_V used in cal-

---

[1] For the complete data for the 30 tables obtained see Gruse, Dissertation, University of Wisconsin, 1916.

culating K_N in the subsequent tables is the average of a series of such constants for the different time periods, *t*.

All solutions, when finally made up for use, contained 1.6 per cent of menthone. The reason for choosing such a concentration is discussed in the following pages.

TABLE A.—THE INVERSION OF A 1.6% SOLUTION OF *l*-MENTHONE BY *N*/64 POTASSIUM ETHYLATE AT 25°.

A = 2.776°.

T.	x.	A — x.	K_V.
0	...	...	.....
3	0.185	2.591	(0.0100)
6	0.329	2.447	0.00913
10	0.511	2.265	0.00884
15	0.719	2.057	0.00868
21	0.953	1.823	0.00870
27	1.173	1.603	0.00883
33	1.370	1.406	0.00895
40	1.537	1.239	0.00876
50	1.760	1.016	0.00873
60	1.935	0.841	0.00864
75	2.182	0.594	0.00893
90	2.340	0.436	0.00893
∞	2.776	...	.....

Average K_V = 0.00882

$VK_V = K_N$ = 0.564

TABLE B.—THE INVERSION OF A 1.6% SOLUTION OF *l*-MENTHONE BY *N*/512 SODIUM ETHYLATE AT 25°.

A = 3.677°.

T.	x.	A — x.	K_V.
0	...	...	.....
20	0.180	3.497	(0.00108)
40	0.323	3.354	0.00100
70	0.561	3.116	0.00102
80	0.625	3.052	0.00101
166	1.177	2.500	0.00101
195	1.313	2.364	0.00098
225	1.472	2.205	0.00099
270	1.687	1.990	0.00099
315	1.897	1.798	0.00099
360	2.041	1.636	0.00098
405	2.207	1.470	0.00098
450	2.331	1.346	0.00097
∞	3.677	...	.....

Average K_V = 0.00099

$VK_V = K_N$ = 0.507

In Tables I, II and III are given the molar velocity constants, K_N for sodium, potassium and lithium ethylates, resulting from the multiplication of the reaction velocity at any concentration, K_V, by the value of the dilution V;

$$K_N = K_V V$$

The purpose of this multiplication is to make possible the comparison, at unimolecular concentration, of solutions of different dilution, and consequently of different degree of ionization. In the same tables are given the figures for the ionization of sodium, potassium and lithium ethylates at the dilutions employed. They were taken from the data of Robertson and one of us,[1] and were determined by the conductivity method. As these conductivity measurements were made in pure ethyl alcohol it does not follow that they are identical with the values which would be found in the presence of the menthone. This substance and the alkyl halides studied in other reactions, might change the physical properties of the solutions and combine partially with the ethylate. Although detailed studies along these lines are in contemplation, for lack of time they have not been completed. We have, however, in several cases, including the present study, assured ourselves that the molecular conductivity is not changed over about 2 per cent. If it is the same for all concentrations it is obvious that the value of α will not be altered. The final corrections in K_i, K_m and K_N will be made when the necessary data can be collected.

In Table IV are given the constants for sodium, potassium and lithium ethylates expressing the catalytic activity of the ethylate ion and of the non-ionized molecule of the metallic ethylate in the inversion reaction. These constants are calculated by the use of the equation $K_N = K_i\alpha + K_m(1-\alpha)$, derived by one of us.[2] It will be observed that for these tables, two averages are given, "Average" and "Average*." The first is the mean of all values of K_i or K_m, and in the second those values which have been starred in the column above have been omitted, because of the greater errors involved in them.[3] The largest difference between the two averages is four per cent., occurring in one case, andas the starred constants can be traced to doubtful values of K_N or α, or to errors arising from the form of the equation, the second average has been used for the evaluation of "K_N calculated" and for the comparison of K_i and K_m for the different ethylates.

In Tables I, II and III are given the values of "K_N calculated," and the percentage deviation, called "Per cent. Error," which the values of "K_N found" for all three ethylates show from the calculated figures. The "K_N calculated" is obtained by the use of the equation $K_N = K_i\alpha + K_m(1-\alpha)$. The values of α and $1-\alpha$ correspond to the dilution in question, and the values of K_i and K_m are the second averaged figures of the series, resulting from the intercomparison of K_N and α for chosen dilutions. In the last two columns are given the per cent. of the reaction due to the ethyl-

---

[1] *J. Phys. Chem.*, **19**, 381 (1915); *Phys. Rev. N. S.*, **6**, 61 (1915).

[2] *Am. Chem. J.*, **48**, 359 (1912).

[3] For a full discussion see Robertson and Acree, *Ibid.*, **49**, 482 (1913).

ate ions, $K_i\alpha/K_N$, and that due to the nonionized molecules of the metallic ethylate, $K_m(1—\alpha)/K_N$.

TABLE I.—EXPERIMENTAL VALUES OF K_N FOR SODIUM ETHYLATE AND MENTHONE AND FOR THE IONIZATION OF SODIUM ETHYLATE IN ABSOLUTE ALCOHOL AT 25°.

V.	α.	$1-\alpha$.	K_N.	K_N average.	K_N calculated.	Per cent. error.	% of reaction due to ions: $K_i\alpha/K_N$.	% of reaction due to molecules: $K_m(1—\alpha)/K_N$.
32	0.577	0.423	0.566 0.580	0.574	0.582	—1.39	0.50	0.50
64	0.678	0.322	0.559 0.571	0.565	0.563	+0.36	0.60	0.40
128	0.772	0.228	0.573 0.564	0.569	0.545	+4.22	0.71	0.29
256	0.871	0.129	0.538 0.532	0.535	0.526	+1.67	0.83	0.17
512	0.945	0.055	0.507 0.502	0.504	0.511	—1.38	0.93	0.07

TABLE II.—EXPERIMENTAL VALUES OF K_N FOR POTASSIUM ETHYLATE AND MENTHONE AND FOR THE IONIZATION OF POTASSIUM ETHYLATE IN ABSOLUTE ALCOHOL AT 25°.

V.	α.	$1-\alpha$.	K_N.	K_N average.	K_N calculated.	Per cent. error.	% of reaction due to ions: $K_i\alpha/K_N$.	% of reaction due to molecules: $K_m(1—\alpha)/K_N$.
32	0.579	0.421	0.576 0.563	0.569	0.585	—2.81	0.50	0.50
64	0.674	0.326	0.564 0.580	0.572	0.566	+1.05	0.60	0.40
128	0.767	0.233	0.549 0.552	0.550	0.548	+0.37	0.70	0.30
256	0.854	0.146	0.540 0.527	0.533	0.530	+0.57	0.81	0.19
512	0.923	0.077	0.491 0.491	0.491	0.516	—5.09	0.90	0.10

TABLE III.—EXPERIMENTAL VALUES OF K_N FOR LITHIUM ETHYLATE AND MENTHONE AND FOR THE IONIZATION OF LITHIUM ETHYLATE IN ABSOLUTE ALCOHOL AT 25°.

V.	α	$1-\alpha$.	K_N.	K_N average.	K_N calculated.	Per cent. error.	% of reaction due to ions: $K_i\alpha/K_N$.	% of reaction due to molecules: $K_m(1—\alpha)/K_N$.
32	0.455	0.545	0.474 0.493	0.483	0.486	—0.62	0.47	0.53
64	0.562	0.438	0.492 0.492	0.492	0.488	+0.81	0.58	0.42
128	0.677	0.323	0.474 0.476	0.475	0.490	—3.15	0.69	0.31
256	0.786	0.214	0.486 0.489	0.487	0.492	—1.03	0.80	0.20
512	0.885	0.115	0.491 0.491	0.491	0.494	—0.61	0.89	0.11

TABLE IV.—K_i AND K_m FOUND FOR SODIUM, POTASSIUM AND LITHIUM ETHYLATES, RESPECTIVELY, WITH MENTHONE AT 25°.

		$NaOC_2H_5$.		KOC_2H_5.		$LiOC_2H_5$.	
		K_i.	K_m.	K_i.	K_m.	K_i.	K_m.
V = 32	V = 64	0.535	0.625	0.583*	0.550*	0.529	0.444
V = 32	V = 128	0.563*	0.589	0.521	0.624	0.463	0.500
V = 32	V = 256	0.511	0.650	0.514	0.645	0.492	0.476
V = 32	V = 512	0.553*	0.767	0.473	0.700	0.493	0.474
V = 64	V = 128	0.578*	0.536*	0.494	0.730	0.427*	0.574*
V = 64	V = 256	0.516	0.669	0.501	0.719	0.483	0.499
V = 64	V = 512	0.492	0.720	0.466*	0.791	0.492	0.493
V = 128	V = 256	0.491	0.834	0.505	0.700	0.513	0.394*
V = 128	V = 512	0.483	0.863*	0.462	0.840*	0.500	0.422*
V = 256	V = 512	0.481	0.901*	0.444*	1.052*	0.500	0.463
Average		0.520	0.715	0.515	0.734	0.489	0.474
Average*		0.501	0.693	0.501	0.701	0.496	0.478

Discussion of Results.

In the solution of menthone and alkali metal ethylate, for example, we have nonionized molecules of ethylate, ethylate ions and alkali metal ions. The influence of each of these three substances on the menthone can be expressed by the equation

$$K_V = K_i C_{OC_2H_5} + K_i' C_{Na} + K_m C_{NaOC_2H_5}$$

provided that the dilutions are so dilute that there is no "abnormal" salt or solvent effect. The present work in these very dilute or ideal solutions was undertaken in order to avoid these abnormal effects. When no other sodium (potassium, lithium) salt is added $C_{OC_2H_5}$ and C_{Na} are equal and the equation becomes $K_N = (K_i + K_i')\alpha + K_m(1 - \alpha)$. Now experiments with many analogous reactions have shown that K_i' for sodium, potassium and lithium ions is small and negligible and that the K_i calculated really represents practically only the activity of the ethylate ion. If the K_i' were the same and small for each cation the values calculated for K_i for the ethylate ion would be the same for all three ethylates. If the value for K_i' were large and different the values for K_i given in the preceding tables would be *different*, especially in the presence of added salts of alkali metal. These neutral salts, because of the cations, should also cause the inversion of menthone even though no ethylate were present. The experiments of Tubandt with added sodium iodide and sodium acetate indicate that the effect of the cation is negligible, but in order that the point might be settled definitely, two experiments were made in which the optical rotation of *N*/64 solutions of sodium and lithium bromides, respectively, containing 1.6% of menthone, was observed over a period of a week. As the following table of polarimetric readings shows, any inversion which might have taken place was so small as to be within the error of reading.

	LiBr.	NaBr.
First day	326.461°	326.461°
Three hours later	326.489°	326.480°
Second day	326.478°	326.480°
Fourth day	326.480°	326.495°
Eighth day	326.482°	326.471°

As a result of these experiments, it is evident that K_i', if it has a real value, is so small as not to be measureable, and that the K_i calculated may be considered to represent the activity of the ethylate ion only.

Since the molecule of a metallic ethylate ionizes according to the equation

$$MOC_2H_5 \rightleftarrows \overset{+}{M} + \overset{-}{O}C_2H_5$$

and the negative ion is the same, no matter what the nature of the positiv ion, it follows that, in any of its reactions, the activity of the ethylate ion should be the same, no matter whether it be derived by the ionization of sodium, potassium, or lithium ethylate. For the influence of the ethylate ion in the inversion of menthone as here presented, we find the value of K_i to be

	K_i average.	K_i average*.
KOC_2H_5	0.515	0.501
$NaOC_2H_5$	0.520	0.501
$LiOC_2H_5$	0.489	0.496

The values of K_i given under "Average" are sufficiently close to bear out the requirements of the theory, and those under "Average*" show an excellent agreement. The significance of the two averages has been explained above.

A study of the data given for K_N in Tables I, II and III will show three striking facts. First, the constants obtained for sodium and potassium ethylates are very close in value, dilution for dilution, while those for lithium ethylate differ markedly from them; second, the molar constants, K_N, for sodium and potassium ethylates drop off with dilution beyond a certain point, while those for lithium ethylate are approximately constant from first to last; third, at the final dilution used, $N/512$, the molar constants, K_N, for sodium and potassium ethylates have dropped off to a point where they approximate very closely the values for lithium ethylate at that dilution; in other words, the three ethylates have the same catalytic activity in very dilute solutions. A brief discussion will show that these results may be anticipated on the assumption that the reaction involves both the ions and the molecules of the catalyzer.

In the first place, reference to Table IV will show that the constants found for the reactivity of both the ethylate ion and the molecule are nearly the same for sodium and potassium ethylates, but that K_m for lithium ethylate is somewhat lower than for sodium and potassium ethylates.

	K_i.	K_m.
KOC_2H_5	0.501	0.701
$NaOC_2H_5$	0.501	0.693
$LiOC_2H_5$	0.496	0.478

From the ionization data given in Tables I, II and III, it will be seen that the figures for sodium and potassium ethylates are nearly identical at the same dilutions. Thus, it appears that all the factors governing catalytic activity, molecular constant, ionic constant, concentration of molecule and concentration of ion, are nearly the same, so that approximate identity in total constants is to be expected. For lithium ethylate, however, the constant for the activity of the molecule, K_m, is considerably lower than those for sodium and potassium ethylates; furthermore, the ionization of lithium ethylate in the more concentrated solutions is considerably less than that of sodium and potassium ethylates at the same concentrations. Since the activity of the lithium ethylate molecule is less, and its concentration higher than those for the other ethylates, lower total reactivity is to be expected.

The second point, namely, that the constants for sodium and potassium ethylates drop off with dilution, while those for lithium ethylate remain constant, is also readily explainable by reference to the theory under discussion. As dilution progresses, the relative concentrations of the two effective components of the solution, the ions and the molecules, are changed; if the catalytic activities of these two components differ, then a change of molar constant with dilution is to be expected. If the molecule is more reactive than the ion, K_N should decrease with dilution, since the concentration of the highly reactive molecule is decreasing and that of the less reactive ion is increasing; this is what occurs in the case of the sodium and potassium ethylates. If the relations of the activities were reversed, then dilution should cause a rise in molar constant; while if the activity of the ion and the molecule is the same, then dilution should have no effect on the value of the reaction constant. The latter is the case with lithium ethylate. As can be seen from Table IV, K_i in this case is 0.496, while K_m is 0.478, and as dilution progresses, the molecule is replaced by the nearly equal reactive ion; the total constant remains practically unchanged.

The third point, that in $N/32$ solutions the sodium and potassium ethylates are nearly 20% more active than lithium ethylate whereas in solutions as dilute as $N/512$ the catalytic activities of all three ethylates are very nearly the same, will be readily understood from what has already been said. For dilution $N/512$ we have

	K_V.	K_N.
KOC_2H_5	0.00096	0.491
$NaOC_2H_5$	0.00098	0.504
$LiOC_2H_5$	0.00096	0.491

A reference to the value of α will show that all three ethylates are approximately ninety per cent. ionized at this dilution. The determining factors for the reaction velocity, which in very dilute solutions are practically only the concentration and reactivity of the ethylate ion, are very nearly the same, and the close agreement of the values obtained experimentally is in harmony with the requirements of the theory that the inversion is brought about by the simultaneous action of the ethylate ions and the molecules of the ethylate.

The comparison of the calculated and found values of K_N, given for all three ethylates in Tables I, II and III shows differences, in one case as high as five per cent., and in one other of 4%. The average deviation, considering the figures for all three ethylates, is 1.5%, which may be regarded as quite satisfactory, and certainly entirely sufficient to fulfil the requirements of the theory under discussion.

Salt Effects.

The writers wish to emphasize, as one of them has pointed out repeatedly, that the real value of K_i and K_m obtained by the use of the equation

$$K_N = K_i\alpha + K_m(1-\alpha)$$

may, in some cases, be hidden by salt effects, especially in the concentrated solutions. The normal "salt effect" was described as the change in reaction velocity due solely to the changes in α, in accordance with the above equation involving the true values of K_i and K_m, whereas the "abnormal salt effect" was thought to be due to changes in the physical properties of the solutions, especially concentrated solutions; thus, density, viscosity, solvation, dielectric constant, and all other well-known physical properties might have considerable influence on conditions in the solution. These "abnormal salt effects" become more nearly negligible as the solutions approach the "ideal," and can in all cases be expressed by some equation such as

$$K_N = [K_i\alpha + K_m(1 - \alpha)][1 + fC_{\text{salt}}],$$

in which fC_{salt} represents the "abnormal effects" of the molecules, anions or cations of the reacting substances, or of those formed or added. The measurement of reaction velocities in concentrated solutions may, therefore, involve errors which can be discovered only by the measurement of the true K_i and K_m in very dilute solutions; it is clear that the use of uncorrected data might give a positive, though small, value for K_i or K_m, when the corrected data would show K_i or K_m to be zero. If a change in the concentration of any substance present causes a change in K_N other than that calculated from the equation

$$K_N = K_i\alpha + K_m(1 - \alpha)$$

it is clear that an "abnormal salt effect" is being produced, whose value, and those of the true K_i and K_m, can be ascertained by actual measurements in very low concentrations, or by making a few measurements in more concentrated solutions and correcting by the use of the above equations containing fC_{salt}. In the study of the action of ethylates on alkyl halides, the fC_{salt} was measured for the alkyl halide, ether and sodium iodide; in a number of cases[1] it was practically zero, while in others[2] it was large enough to study accurately; in the latter, it was shown how to correct K_N, K_i and K_m for this "abnormal salt effect."

In the work here presented, not only has the concentration of the catalyzing ethylate been varied as widely as the nature of the reaction would permit, but the apparatus was so constructed that long polarimeter tubes could be used, thus making possible the employment of very dilute menthone solutions, which would, at the same time, give measureable changes in rotation. Since, throughout the present work, solutions of menthone of 1.6% concentration were used instead of the 10% solutions employed by Tubandt, any abnormalities in ionization, ionic velocities, reaction velocities, etc., brought out in the solution by such a concentration of menthone are likely to be negligible. This conclusion is supported by the fact that the values of K_i calculated from the data for sodium, potassium and lithium ethylates are identical, an indication that any "abnormal salt effect" which may exist, is small or the same for all three. Since the solutions were purposely made very dilute, we do not anticipate that the corrections will be found very large when the necessary physical constants are measured.

Preliminary experiments with added salts have indicated the occurrence of an abnormal salt effect, especially in the case of lithium bromide. As the work of Jones[3] has indicated a high degree of solvation for lithium bromide in ethyl alcohol, some such effect is to be anticipated; the question will be studied further.

Summary.

(1) The velocity of inversion of menthone by sodium, potassium and lithium ethylates in absolute ethyl alcohol at 25° has been measured at dilutions varying from $N/32$ to $N/512$.

(2) By substituting the molar velocity constants, K_N, and the corresponding values of α in the proper equations, values have been obtained for the catalytic activity of the ethylate ion and the nonionized molecule of the metallic ethylate.

(3) The constants expressing the activity of the ethylate ion have been found to be the same whether the experiment be made with sodium,

---

[1] Marshall, Harrison and Acree, *Am. Chem. J.*, **49**, 369, 385, 391, 396, 400 (1913); Joseph Chandler, Dissertation, Johns Hopkins University, 1912.

[2] Marshall and Acree, *J. Phys. Chem.*, **19**, 589 (1915); B. M. Brown, Dissertation, Johns Hopkins University, 1913.

[3] *Am. Chem. J.*, **35**, 316 (1906).

potassium or lithium ethylate; namely, $K_i = 0.501$, $K_i = 0.501$ and $K_i = 0.496$, respectively.

(4) The constants, K_m, expressing the activity of the nonionized molecule of the metallic ethylate, have been found to be very close for sodium and potassium ethylates, namely, $K_m = 0.693$ and $K_m = 0.701$, respectively, but somewhat lower for lithium ethylate, $K_m = 0.478$, which is practically the same as that found for the ethylate ion, $K_i = 0.496$ in the case of lithium ethylate.

(5) Making use of the above considerations, satisfactory explanations have been offered for the approximate equality of the velocity constants, K_N, found for sodium and potassium ethylates, as well as for the deviation of the lithium ethylate constant from this value; for the fact that the molar constants, K_N, for lithium ethylate remain unchanged with dilution, while the same values for potassium ethylate and sodium ethylate drop considerably as the concentration decreases; and for the nearly identical value assumed by the velocity constants for all three ethylates in very dilute solutions.

(6) The averaged values of the constants for the ionic and molecular activities have been substituted in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$ and these calculated values of K_N have been compared with those found experimentally. The average deviation is about 1.5 per cent.

Strong support of the theory here presented is found in unpublished work by Dr. C. N. Myers, on the formation of imido-esters from nitriles, catalysed by metallic ethylates; particularly important is the fact that the data obtained in very dilute solutions harmonized perfectly with the theory. Dr. Myers' work will be published in the near future.

MADISON, WIS.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE CORRELATION OF IONIZATION AND STRUCTURE IN UNSATURATED ACIDS.

BY C. G. DERICK AND OLIVER KAMM.[1]

Received December 23, 1916.

This research is a part of the general investigation of the correlation of ionization and atomic linking structure which has been in progress in this laboratory during the past five years. The laboratory investigation of this general problem has been concerned chiefly with the study of the effect, from the standpoint of ionization constants, of the substitution of a given atom or group of atoms into the paraffin monocarboxylic acids. In this field the probability of a correlation between the position

---

[1] A chapter from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois (Kamm, 1915). See also THIS JOURNAL, 38, 400 (1916).