lutions. Crystals, while well defined, were small. As has been indicated, the beta prime X-ray pattern is somewhat similar to that of subalpha. The distinguishing features are indicated in Table IV, a summary table of characteristic values. In brief, the chief difference is that beta prime lacks the two medium strength lines shown by subalpha for the region between 4.15 Å. and 3.65 Å.

Beta.—The beta form is obtained by slow crystallization from solvent or by transformation of alpha and beta prime forms. It was not obtained directly from the melt. The crystals from solvent are relatively large platelets with a beautiful gloss. Beta is the only truly stable crystalline form.

Acknowledgment.—The authors are grateful to the members of this Laboratory who have given valued advice and experimental assistance.

Summary

While largely confirming the work of Malkin, a reëxamination of the polymorphic behavior of 1-monostearin and 1-monopalmitin has resulted in new information which differs in important aspects from earlier findings.

These monoglycerides have four forms—subalpha, alpha, beta prime and beta. The last three have melting points increasing in the order named. Beta alone is thermodynamically stable. Beta prime has been obtained only from solvent. There is a reversible alpha–subalpha transformation about 25° below the alpha m. p. but above room temperature. All forms for a given monoglyceride have very nearly the same long spacing and appear to be tilted double-chain-length structures. The forms are readily distinguished by means of short spacings except for subalpha and beta prime, which, in spite of notable differences in thermal behavior, show only minor differences in diffraction pattern.

IVORYDALE, OHIO RECEIVED MARCH 4, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Kinetics of the Reaction between Ethylene Chlorohydrin and Hydroxyl or Alkoxyl Ions in Mixed Solvents[1,2]

BY JOHN ED STEVENS,[3] C. LAW McCABE AND J. C. WARNER

Previous investigations of the reaction between ethylene chlorohydrin and hydroxyl ion have established the following facts concerning the reaction. It is clearly second order,[4,5,6] the rate being proportional to the concentration of chlorohydrin and to the concentration of hydroxyl ion, and the side reaction with water at temperatures in the vicinity of 30° is so slow[7] that it may be neglected. There is no significant back reaction in alkaline solution[8] and the product with water as the solvent is ethylene oxide and not ethylene glycol.[9] There is a very small negative kinetic salt effect in water and in water–ethanol mixtures.[6] More recently, Porret,[10] who apparently was unaware of the work of Winstrom and Warner,[6] has reported the results of an investigation which duplicates their kinetic studies in water as solvent. His velocity constants, activation energy and kinetic salt effects are in excellent agreement with those reported by Winstrom and Warner. Porret[11] has also determined equilibrium constants for the reaction in the temperature range 0 to 50°. These results confirm the view that no correction for the back reaction needs to be made in alkaline solutions.

It was the purpose of the present investigation to study the kinetics of this reaction in a number of water–non-aqueous solvent mixtures down to low dielectric constants for the mixtures, *i. e.*, to high concentrations of the non-aqueous solvents.

Experimental

Materials and Procedure.—Previously described[6] methods for the purification of materials and the preparation of reagents were used with only minor modifications. Temperature variations in thermostats were followed by means of Beckman thermometers and absolute temperatures were established within 0.01° by use of a N.B.S. platinum resistance thermometer. The thermostat operated at 30 ± 0.005° was of the conventional type, and the one operated at 15 ± 0.01° was also of the conventional type, but was placed inside a large insulated container through which air, cooled by ice, was circulated to maintain the environment at 10 to 12°. Experiments at 0 ± 0.005° were carried out in large Dewar flasks filled with washed cracked ice and distilled water.

Standard solutions of sodium ethoxide and sodium methoxide were prepared by treating metallic sodium with the corresponding anhydrous alcohol, determining the concentration by titration and then diluting to the desired strength with the anhydrous alcohol.

Since the reaction proceeds with a decrease in hydroxyl or alkoxyl ion concentration and a corresponding increase in

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(1) Abstracted from a dissertation submitted by John Ed Stevens to the Carnegie Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Science.

(2) Presented before the Physical and Inorganic Division at the Detroit meeting of the American Chemical Society, April, 1943.

(3) Present address: Shell Development Company, Emeryville, Calif.

(4) Evans, *Z. physik. Chem.*, **7**, 335 (1891).

(5) Smith, *ibid.*, **81**, 339 (1912); **A152**, 153 (1931).

(6) Winstrom and Warner, THIS JOURNAL, **61**, 1205 (1939).

(7) Radulescu and Muresanu, *Bull. Soc. Sci. Cluj. Roumanie*, **7**, 128 (1932).

(8) Brönsted, Kilpatrick and Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

(9) British Patents 286,850 (Feb. 8, 1927); 292,066 (Jan. 11, 1927). Ushakov and Mikhailov, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 249 (1937).

(10) Porret, *Helv. Chim. Acta*, **24**, 80E (1941).

(11) Porret, *Helv. Chim. Acta*, **27**, 1321 (1944).

chloride ion concentration, it is obvious that the reaction may be followed by withdrawing samples at suitable time intervals, delivering them into an excess of standard acid to stop the reaction, and titrating for either excess acid or chloride. In each new solvent mixture, it was always established that these two methods of following the reaction gave results which were in agreement within the experimental error; thereafter the acid-base titration (rosolic acid indicator) was used in a majority of the experiments.

In most experiments, equal starting concentrations of ethylene chlorohydrin and carbonate-free hydroxide (or alkoxide) were used and the velocity constant was obtained from the slope of the best straight line obtained by plotting $1/c$ against time.

Kinetic Results.—Velocity constants were determined in 1,4-dioxane–water, methanol–water, ethanol–water, isopropanol–water and *t*-butanol–water mixtures at 30°. Rates were also determined at 0 and 15° in the first three of the above solvent mixtures.

Velocity constants in ethanol–water mixtures are given in Table I. The rate in 100% ethanol was determined by using sodium ethoxide and ethylene chlorohydrin as reactants in anhydrous alcohol. Table II gives the velocity constants in methanol–water and 1,4-dioxane–water mixtures including the rate constant for the reaction of sodium methoxide with ethylene chlorohydrin in 100% methanol. Table III reports the velocity constants obtained at 30° in isopropanol–water and in *t*-butanol–water mixtures. In Fig. 1, velocity constants as a function of dielectric constant[11a] at 30° are summarized for all of the solvent mixtures.

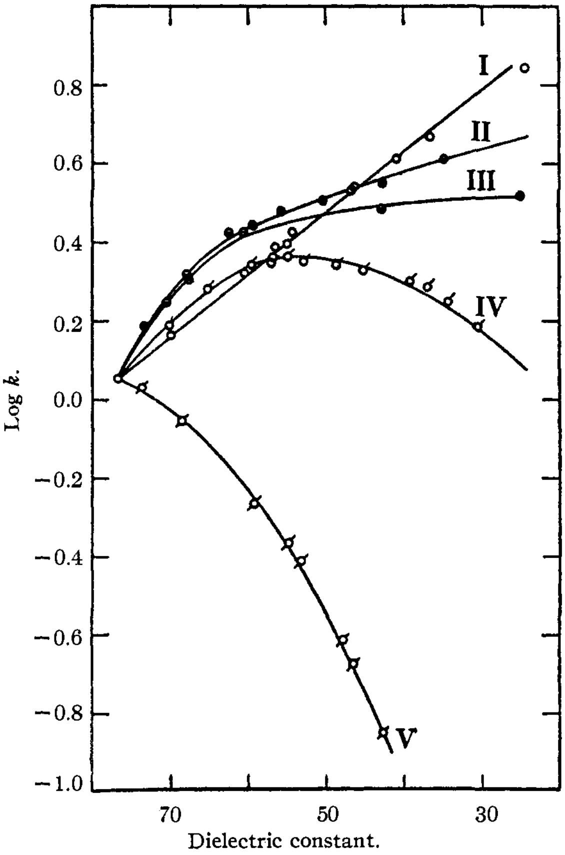

Fig. 1.—All at 30°: I, dioxane-water; II, isopropanol-water; III, *t*-butanol-water; IV, ethanol-water; V, methanol-water.

TABLE I

SUMMARY OF RESULTS IN ETHANOL-WATER MIXTURES

Wt. % ethanol	Dielectric constant	k (min.$^{-1}$)	Wt. % ethanol	Dielectric constant	k (min.$^{-1}$)
	At 30°			At 15°	
0.0	76.7	1.13	0.0	82.2	0.166
11.9	70.0	1.56	9.6	76.7	.710
20.6	65.0	1.93	20.6	70.0	.284
30.0	59.5	2.23	28.8	65.0	.349
34.3	57.0	2.27	37.6	59.4	.376
37.6	55.0	2.33	44.8	55.0	.359
40.9	53.0	2.28	54.9	48.9	.323
48.4	48.7	2.21	61.7	45.0	.302
54.9	45.0	2.17		At 0°	
65.8	39.0	2.04	0.0	88.4	.0186
69.7	36.9	1.95	18.6	76.7	.0307
75.0	34.2	1.81	20.6	75.4	.0325
83.7	30.1	1.53	36.6	65.0	.0450
100.0	23.5	0.95	37.7	64.3	.0460
			52.1	55.0	.0387
			54.9	53.2	.0378
			68.6	45.0	.0290

TABLE II

SUMMARY OF RESULTS IN METHANOL-WATER AND 1,4-DIOXANE-WATER MIXTURES

	In methanol–water			In 1,4-dioxane–water		
Temp., °C.	Wt. % methanol	Dielectric constant	k (min.$^{-1}$)	Wt. % dioxane	Dielectric constant	k (min.$^{-1}$)
30	0.0	76.7	1.13	0.0	76.7	1.13
	7.0	73.7	1.08	7.6	70.0	1.50
	18.0	68.4	0.878	18.6	60.4	2.11
	37.9	59.0	.545	22.9	56.7	2.32
	46.6	55.0	.429	23.1	56.5	2.46
	50.5	53.2	.388	24.9	55.0	2.48
	61.5	47.8	.241	25.8	54.2	2.66
	64.7	46.3	.214	34.3	46.7	3.41
	72.6	42.4	.144	34.6	46.0	3.47
	84.7	37.5	.0702	41.0	40.8	4.15
	92.8	33.5	.0450	46.0	36.6	4.74
	100.0	30.7	.0225	61.2	24.1	7.08
				71.4	16.2	8.43
15	0.0	82.3	.169	0.0	82.2	0.166
	12.0	76.7	.123	6.2	76.7	.204
	54.9	55.0	.0343	29.7	55.0	.470
				34.3	51.1	.578
0	0.0	88.4	.0186	0.0	88.4	.0186
	22.8	76.7	.00864	12.3	76.7	.0297
	64.6	65.0	.00198	34.3	55.0	.0772

Reaction Product in Mixed Solvents.—Previous investigators[9] have stated that ethylene oxide is the product of the reaction of ethylene chlorohydrin with hydroxyl ion in aqueous solution. This has been confirmed by our investigations. We considered it necessary, however, to establish the nature of the reaction product in our water-non-aqueous solvent mixtures and in anhydrous ethanol and anhydrous methanol. The possible products would seem to be ethylene glycol, ethylene oxide or (in alcoholic solutions) an hydroxy ether of the Cellosolve type. Any attempt to separate ethylene oxide from the glycol and the hydroxy ether by distillation is complicated by the hydrolysis of the oxide to glycol which is quite rapid at temperatures as high as 80°. Our evidence was obtained by

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(11a) Akerlof, THIS JOURNAL, 54, 4125 (1932); Akerlof and Short, *ibid.*, 58, 1242 (1936).

TABLE III

SUMMARY OF RESULTS IN ISOPROPANOL–WATER AND *t*-BUTANOL–WATER MIXTURES AT 30°

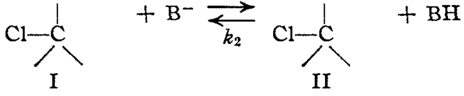
In isopropanol–water			In *t*-butanol–water		
Wt. % isopropanol	Dielectric constant	*k* (min.⁻¹)	Wt. % butanol	Dielectric constant	*k* (min.⁻¹)
0.0	76.7	1.13	0.0	76.7	1.13
5.0	73.2	1.55	10.4	67.9	2.05
8.6	70.6	1.81	18.8	60.6	2.66
11.4	67.9	2.11	39.8	42.7	3.08
20.4	62.2	2.66	63.2	24.7	3.47
24.7	59.2	2.81			
29.7	56.7	3.02			
37.4	50.2	3.23			
48.0	42.8	3.60			
59.2	34.9	4.10			
70.3	27.6	4.68			

adaptation of Lubatti's method[12] for determining ethylene oxide in gas mixtures: To samples which had reacted to completion, standard solutions of hydrochloric acid and calcium chloride were added in such amounts that a slight excess of acid and 30 g. of chloride ion per 100 ml. were present. Under these conditions ethylene oxide is converted back to ethylene chlorohydrin and an equivalent of acid is consumed. The rate of this reversal in acid solution has been studied.[8] Similar experiments with known solutions of glycol and hydroxy ether showed that no acid was consumed by these substances. That glycol does not react with acid under these conditions is supported by other investigators.[13] Although the method did not yield results of the desired precision and reproducibility, and has since been greatly improved, the acid consumed in various experiments was between 90 and 105% of the amount calculated assuming ethylene oxide was the only product of reaction. It seems safe to say, therefore, that ethylene oxide was the principal product in all of the solvent mixtures used in this investigation as well as in water, in anhydrous methanol and in anhydrous ethanol.

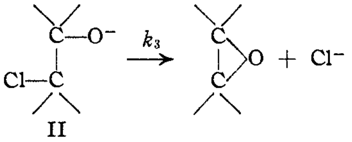
Discussion

The fact that ethylene oxide is the product obtained in all of the experiments performed in this investigation indicates that the second order reaction between ethylene chlorohydrin and hydroxyl ion, alkoxyl ion or mixtures of the two reactants cannot proceed by the usual displacement type of mechanism. Furthermore, the data obtained in methanol–water and in ethanol–water mixtures is unusual and cannot be explained on a basis of the expected influence of the dielectric constant of the solvent upon the reaction rate.

Mechanism.—It seems possible to give a qualitative explanation of all the facts which have been observed by assuming the mechanism suggested by Winstein and Lucas,[14,15] namely



(1)



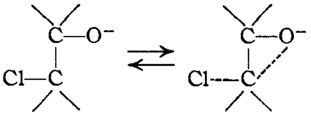
(2)

If Step 1 is an equilibrium step for which the equilibrium constant is K and Step 2, in which the anion goes through the activated state to form ethylene oxide with a rate constant k_3, is slow, then

$$\frac{-\mathrm{d}[\mathrm{B}^-]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{Cl}^-]}{\mathrm{d}t} = \frac{k_3K}{[\mathrm{BH}]}[\mathrm{CH_2Cl{-}CH_2OH}][\mathrm{B}^-]\frac{\gamma^0_{\mathrm{I}}\gamma^-_{\mathrm{B}^-}}{\gamma^0_{\mathrm{BH}}\gamma^-_{\mathrm{II}}} \qquad (3)$$

where k (observed) $= k_3K/[\mathrm{BH}]$, when B^- is the base conjugate to a pure solvent BH. It is obvious that according to this mechanism the rate of reaction should be proportional to the concentration of the chlorohydrin and to the concentration of the anion base (OH^-, CH_3O^- or $C_2H_4O^-$). Furthermore the mechanism accounts for the negligible kinetic salt effect. (As a first approximation,[15a] ionic strength would have little influence on the value of the activity coefficient quotient in Eq. 3).

Influence of Dielectric Constant of Solvent.—One would expect the dielectric constant of the medium to have little effect on the equilibrium (Step 1) because the electrostatic contribution to the free energy of reaction would be small. On the other hand, the conversion of the anion into the activated complex



is quite like the formation of the activated complex in the bimolecular displacement of halide from alkyl halides by hydroxyl ion; there is a distribution of charge and one would expect an increase in rate as the dielectric constant of the medium is decreased.[16] The expected effect is observed in 1,4-dioxane–water mixtures, but it seems obvious that some factor other than dielectric constant has an important influence in the alcohol–water mixtures, especially in methanol–water and ethanol–water.

Influence of Acid–Base Level of Solvent.—If one postulates that ethanol is a stronger acid than water and that methanol is a still stronger acid than ethanol, then hydroxyl ion will be leveled somewhat in these mixed solvents by the reaction $OH^- + ROH \rightleftarrows RO^- + H_2O$. The extent of the reaction, and hence the reduction in the base level of the medium will depend upon the

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[12] Lubatti, *J. Soc. Chem. Ind.*, **51**, 361T (1932).

[13] Norris, Watt and Thomas, THIS JOURNAL, **38**, 1079 (1916).

[14] Winstein and Lucas, *ibid.*, **61**, 1576 (1939).

[15] This mechanism for the reaction of chlorohydrins with strong bases has received further confirmation in the recent work of Kadesch, *ibid.*, **68**, 46 (1946).

[15a] La Mer, *Chem. Rev.*, **10**, 179 (1932); *J. Franklin Inst.*, **225**, 709 (1938).

[16] Hughes, *Trans. Faraday Soc.*, **37**, 609 (1941); Hughes and Ingold, *ibid.*, **37**, 666 (1941); Harned and Samaras, THIS JOURNAL, **54**, 15 (1932); Scatchard, *Chem. Rev.*, **10**, 236 (1932).

acid strength of ROH and the ratio [ROH]/[H_2O] in the solvent mixture. The extent to which the carbanion is formed in the equilibrium step of the process (Step 1) undoubtedly depends upon the base level of the system, and a decrease in basicity would, therefore, cause a decrease in rate. It is tentatively suggested that in methanol–water mixtures, the influence of methanol in decreasing the basicity over the entire range of composition is sufficient to more than compensate for the expected increase in rate due to decreasing dielectric constant. It seems logical to assume that ethanol is a weaker acid than methanol and hence has less influence on the basicity. We may assume, at low ethanol concentrations, that the dielectric constant effect is predominant, but that at the higher concentrations the decreased basicity brings about a decrease in rate, thereby accounting for the observed maximum in the rate constants as a function of ethanol composition. The fact that rate constants in the alcohol–water mixtures extrapolate smoothly to the rate constants for reaction with alkoxyl ion in the anhydrous alcohols supports this explanation. Accurate information on acid-base levels in ethanol–water and methanol–water mixtures is sorely needed and is being sought in this laboratory.

Summary

1. The rate of reaction of ethylene chlorohydrin with hydroxyl ion (or with alkoxyl ion) has been measured in 1,4-dioxane–water, methanol–water, ethanol–water, isopropanol–water and *t*-butanol–water mixtures at 30° up to high concentrations of the non-aqueous solvent. Measurements in anhydrous ethanol and methanol are included. For the first three solvent mixtures, rate measurements were also made at 0 and 15°.

2. In methanol–water mixtures, the reaction rate decreased continuously with increase in methanol concentration. With the addition of ethanol to water, the rate at first increased, reached a maximum value at about 38% ethanol (30°), and then decreased at higher ethanol concentrations. In the other solvent mixtures, the rate increased with a decrease in dielectric constant over the entire range of solvent composition.

3. It has been established that ethylene oxide is the principal reaction product in all of the solvents used, including anhydrous ethanol and anhydrous methanol.

4. The Winstein–Lucas mechanism which postulates an initial equilibrium step in which a proton is removed from the chlorohydrin to form an anion, followed by an intramolecular displacement of chloride by the negatively charged oxygen, is consistent with (a) the bimolecular character of the reaction, (b) the absence of an appreciable kinetic salt effect, (c) the formation of ethylene oxide as the principal product, and (d) the increase in rate with decrease in dielectric constant is the principal factor influencing the rate. This mechanism is also capable of giving a qualitative explanation of the unusual results obtained in methanol–water and ethanol–water mixtures by taking into account the possible influence of the acid–base level in these solvents upon the initial equilibrium step.

PITTSBURGH 13, PENNSYLVANIA

RECEIVED FEBRUARY 5, 1948

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INC.]

Measurements on the Absorption of Microwaves. III. Losses of Camphor Dissolved in Cyclohexane

BY D. H. WHIFFEN[1]

The general outline of the type of absorption of electromagnetic radiation of about a centimeter wave length by mobile liquids and solutions has already been established.[2,3] Before investigating some of the details or exceptional systems, it was thought profitable to measure one system carefully; such a system may also be useful for comparing various methods of measurement.

Solutions of camphor in cyclohexane seem to have several advantages for this purpose. Firstly, the use of solutions makes a large range of loss tangents available according to the concentration employed. Secondly, cyclohexane is easily purified so as to give an almost negligible loss; this is in contrast to benzene which is difficult to keep dry. Thirdly, camphor was chosen because of its large dipole moment, its rigidity, its high solubility, the ease of purification by sublimation, and because preliminary experiments had indicated that its solutions in cyclohexane obeyed the Debye loss curve[4] with a relaxation time of 7×10^{-12} sec., which corresponds to a maximum loss at 1.3 cm. wave length.

Experimental

Cavities.—The loss tangents were obtained from the Q of a cavity resonator completely filled with the test liquid. The details of the resonator used at 3.3 cm. are shown in Fig. 1. This is a cylindrical cavity which can be resonant in the $H_{1,1,2}$ mode[5] when filled with a liquid

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[1] Present address: St. John's College. Oxford, England.

[2] Whiffen and Thompson, *Trans. Faraday Soc.*, **42A**, 114 and 122 (1946).

[3] Jackson and Powles, *ibid.*, **42A**, 101 (1946).

[4] Debye, "Polar Molecules," Chemical Catalog Co., Reinhold Publ. Corp., New York, N. Y., Chap. V.

[5] Lamont, "Waveguides," Methuen, New York, N. Y.