DMF, 50 ml of H_2O, and 50 ml of 1.12 M Cr^{2+} (0.0560 mole). Within an hour, gas evolution had ceased after producing 0.00170 mole with the following composition: 50% carbon dioxide, 50% carbon monoxide, and a trace of methane.

Chloroacetyl chloride (2.4 g, 0.021 mole) was added to a solution of 1.0 g (0.013 mole) of Na_2O_2 in 15 ml of H_2O at 0° and stirred for 0.5 hr. Solid chloroacetyl peroxide was filtered off, washed with ice water, and dissolved immediately in 100 ml of chilled DMF. This solution was placed in a dropping funnel and added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.12 M Cr^{2+} (0.0560 mole). A gas was rapidly evolved which contained only carbon dioxide and methane.

Acknowledgment. The authors are indebted to Dr. R. C. Neuman for authentic samples of ethylidene chloride, ethylidene iodide, and propylidene iodide, and to the National Science Foundation for support of this work.

Reactions in Frozen Solutions. VI.[1] The Reaction of Ethylene Chlorohydrin with Hydroxyl Ion in Ice

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Abstract: The reaction of ethylene chlorohydrin with sodium hydroxide in frozen aqueous solutions follows second-order kinetics, with rates up to 1000 times faster than in supercooled liquid solutions at the same temperatures. The effects of variation in concentration of reactants, of added solutes, and of temperature are consistent with a "concentration effect." The observed second-order rate constants are quantitatively correlated by the relationship $k_{obsd} = k_2C_b/C_s$, where k_2 is the normal second-order rate constant for reaction in liquid solution, C_b is the total concentration of the liquid "reaction regions" in a frozen solution, and C_s is the total concentration of all solutes in the initial unfrozen solution.

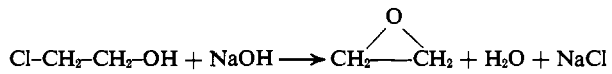
It has recently been shown that, for a number of different reactions in dilute solutions, rate accelerations occur when the solutions are frozen. In aqueous solutions, examples of rate increases in ice include anhydride, amide, and ester hydrolysis,[2,3] aminolysis of amides, esters and lactones,[4-6] as well as some oxidation and dehydration reactions.[7,8] For the case of acid- and base-catalyzed hydrolysis of acetic anhydride, Butler and Bruice[2] have presented evidence that the greater rate of reaction in ice is due to a concentration effect. The anhydride and the catalyst are brought together at high concentrations in regions of the frozen system which remain liquid. Since the reaction follows second-order kinetics, the rate is increased by the concentration change which accompanies the freezing out of water.

The "concentration effect" should be a general phenomenon. However, some experimental features of "frozen reactions" have seemed inconsistent with expectations for this effect. For most of the reported reactions in frozen aqueous solutions, other possibilities have been put forward. These suggestions include the possible involvement of ice itself in imposing some favorable substrate–catalyst orientation or by facilitating required proton transfers to or from substrate.[3-8]

Kinetic studies of two types of reaction in frozen organic solutions (the E2 base-catalyzed elimination reaction of *t*-butylperoxy formate in *p*-xylene[9a,b] and the SN2 reaction of methyl iodide and triethylamine in benzene[9c]) show that the observed results are completely consistent with the concentration effect. It has also been shown in general that the observation of changes in kinetic order, rate–temperature maxima, sensitivity to low concentrations of ordinarily inert solutes, and some other unusual features of reactions in frozen solutions are necessary consequences of the concentration effect.[9] Even when there is no change in mechanism and no *direct* involvement of the solid part of the frozen system, the concentration effect may give rise to observations greatly different from those for the same reaction under normal (*i.e.*, nonfrozen) conditions.[10]

As noted above, reactions in ice might involve interesting features not yet found in frozen organic solvents. An investigation of a simple, well-known bimolecular reaction in ice would best allow separation of factors due to concentration from those due to other effects. To further simplify the interpretation of results, the reactants (as well as products) should behave as more or less ideal solutes in the ice–aqueous solution phase equilibria.

The reaction of ethylene chlorohydrin with sodium hydroxide[11] is convenient for such an investigation of a reaction in ice. This reaction strictly follows second-order kinetics and rate constants are well established



$$\mathrm{Cl{-}CH_2{-}CH_2{-}OH + NaOH \longrightarrow \overset{O}{CH_2\!\!-\!\!-\!\!CH_2} + H_2O + NaCl}$$

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[1] *Cf.* part V: T. E. Kiovsky and R. E. Pincock, *J. Chem. Educ.*, **43**, 361 (1966). This research was sponsored by the U. S. Air Force Office of Scientific Research, Grant No. AFOSR 1102-66, and by the National Research Council of Canada.

[2] A. R. Butler and T. C. Bruice, *J. Am. Chem. Soc.*, **86**, 313 (1964).

[3] N. H. Grant, D. E. Clark, and H. E. Alburn, *ibid.*, **83**, 4476 (1961).

[4] N. H. Grant and H. E. Alburn, *Biochemistry*, **4**, 1913 (1965).

[5] T. C. Bruice and A. R. Butler, *J. Am. Chem. Soc.*, **86**, 4014 (1964).

[6] H. E. Alburn and N. H. Grant, *ibid.*, **87**, 4174 (1965).

[7] N. H. Grant and H. E. Alburn, *Science*, **150**, 1589 (1965).

[8] W. H. Prusoff, *Biochim. Biophys. Acta*, **68**, 302 (1963).

[9] (a) R. E. Pincock and T. E. Kiovsky, *J. Am. Chem. Soc.*, **87**, 2072 (1965); (b) *ibid.*, **87**, 4100 (1965); (c) *ibid.*, **88**, 51 (1966).

[10] R. E. Pincock and T. E. Kiovsky, *J. Chem. Educ.*, **43**, 358 (1966).

[11] *Cf.* A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 288.

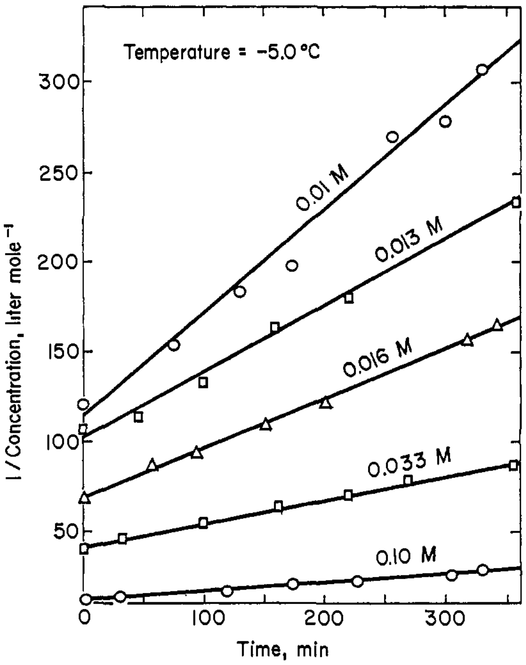

Figure 1. Second-order kinetic plots for reaction of equimolar ethylene chlorohydrin with sodium hydroxide in frozen aqueous solutions at −5.0°. Concentrations given are initial reactant concentrations in unfrozen solutions.

Table I. Observed Second-Order Rate Constants at Various Initial Concentrations for Reaction of Ethylene Chlorohydrin with Sodium Hydroxide in Frozen Aqueous Solutions at −5.0°

$[OH^-]_0 \times 10^2$, *M*	$[Cl(CH_2)_2OH]_0 \times 10^2$, *M*	$k_{obsd} \times 10^4$, l. mole^{-1} sec^{-1}	$k_{obsd}C_s \times 10^4$, sec^{-1}
10.0	10.0	8.35	2.50[a,b]
10.7	6.0	8.80	2.41
5.0	10.3	10.4	2.11
5.0	9.82	10.5	2.08
4.7	4.83	17.5	2.52
3.26	3.26	22.6	2.21
2.50	2.50	27.3	2.05
1.67	1.65	41.2	2.05
1.3	1.3	56.4	2.20
1.0	1.07	87.6	2.69
0.1	0.1	843.0	2.53[c]
0.1	0.1	953.0	2.86[c]

[a] C_s = total solute concentration = $2[OH^-]_0 + [Cl(CH_2)_2OH]_0$. [b] The value of $k_{obsd}C_s$ should be constant in all runs (see text). [c] Reaction followed by changes in pH of thawed solutions (see Experimental Section).

right down to 0°.[12] A specific reaction of hydroxyl ion, rather than general base catalysis, has been established, and little or no salt effect is observed.[13] Buffered solutions are not necessary and complications arising from their use, as in other studies of reactions in ice, may be avoided. In addition, the reactants and products are all highly soluble in water and no net change in the number of solutes occurs during the reaction. Accordingly, no change of the total volume of liquid regions in a frozen solution is expected during a kinetic run. Under these conditions the complete separation of results arising from a concentration effect from those originating from any other possibility should be easily accomplished.

Results and Discussion

The reaction of ethylene chlorohydrin with sodium hydroxide in frozen aqueous solutions was studied by analysis for residual hydroxide ion in thawed samples of a run. Plots of reciprocal concentration (for equal reactant concentrations) or log ($[ClCH_2CH_2OH]/[OH^-]$) (for unequal reactant concentrations) against time gave the best straight lines, and second-order rate constants were obtained normally from the slopes of the lines. Although individual runs then showed second-order kinetics, the observed rate constants varied greatly from run to run. As shown in Table I, the largest values of k_{obsd} were found at the lowest initial reactant concentrations.

Figure 1 shows some runs, using equimolar but different initial concentrations of reactants at −5°, plotted as second-order reactions. The different slopes of the lines illustrate that the observed rate constants depend on the initial reactant concentrations of the unfrozen solutions. However, it may be noted from the figure that the time taken to decrease the concentration by one-half is essentially the same in all the runs (about 250 min). That the first half-life is independent of initial concentration is consistent with a "concentration effect" since, in the liquid regions of a frozen solution, the same concentration of reactants is produced by the contraction of volume brought about by crystallization of solvent. As the reaction in frozen solutions always begins at the same concentration, independent of the concentrations of the unfrozen solutions, the first half-life should be the same in every run.

A quantitative evaluation of this observed initial half-life for runs at equimolar concentration can be made using the usual relationship between half-life ($t_{1/2}$), rate constant (k_2), and concentration (C) for a second-order reaction, *i.e.*, $t_{1/2} = 1/k_2C$. The normal second-order rate constant at −5°, extrapolated from the data of McCabe and Warner,[12] is $k_2 = 1.0 \times 10^{-4}$ l. mole^{-1} sec^{-1}. The total concentration in the liquid reaction regions of a frozen aqueous solution at −5° is about 2.6 *M*,[14] and this concentration divided among the solutes, Na^+, OH^-, and $ClCH_2CH_2OH$, corresponds to 0.86 *M* initial reactant concentration. The expected half-life is then roughly $t_{1/2} = 1/(1.0 \times 10^{-4})(0.86)$ sec, or 195 min. This is reasonably close to the observed time of *ca.* 250 min.[15]

With an initial reactant concentration of 0.01 *M*, the observed rate under frozen conditions at −5° is about 100 times greater than the rate in an unfrozen solution at the same temperature. At a lower initial concentration the relative rate increase is still greater, but individual points of a run become more scattered (see Experimental Section). Careful pH measurements of thawed samples from a frozen run initially 10^{-3} *M* in

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[12] J. E. Stevens, C. L. McCabe, and J. C. Warner, *J. Am. Chem. Soc.*, 70, 2449 (1948); C. L. McCabe and J. C. Warner, *ibid.*, 70, 4031 (1948).

[13] L. O. Winstrom and J. C. Warner, *ibid.*, 61, 1205 (1939).

[14] From the cryoscopic constant of water (K_F = 1.9), at −5° the concentration of the liquid regions in a frozen aqueous solution would be $C = \Delta T/K_F = 5/1.9 \simeq 2.6$ *M*.

[15] To allow for temperature equilibration, the first sample of a run was taken 10–30 min after freezing the samples; thus the observed initial half-life should be greater than the value calculated above, as is the case.

each reactant showed that the reaction proceeded with the expected half-life of about 200–230 min at −5°. This is almost 1000 times faster than the rate of reaction in a supercooled liquid solution at this temperature.

A series of runs at different temperatures but with the same concentration of ethylene chlorohydrin and sodium hydroxide showed that the frozen reaction had a maximum rate at *ca.* −5° (see Table II). Addition of sodium chloride, sodium nitrate, or ethanol had the same rate-depressing effect per mole of solute on the reaction in frozen solutions (Table III). Both of these observations are general characteristics of the concentration effect.[9,10]

Table II. Effect of Temperature on the Reaction of 0.05 *M* Ethylene Chlorohydrin with 0.05 *M* Sodium Hydroxide in Frozen Aqueous Solutions

Temp, °C	k_{obsd} × 10^4, l. mole^{-1} sec^{-1}	$k_{\text{obsd}}C_s$ × 10^4, sec^{-1}
−0.7	6.34	0.96
−1.3	10.5	1.57
−3.0	15.2	2.27
−4.0	16.5	2.48
−4.5	15.7	2.36
−5.0	17.5	2.52
−7.5	13.9	2.06
−10.0	11.5	1.76
−14.9	6.18	0.925
−2.9	9.40	1.96[a]

[a] This run was at 0.05 *M* NaOH and 0.108 *M* ethylene chlorohydrin.

Table III. Effect of Added Solutes on the Reaction of 0.05 *M* Ethylene Chlorohydrin with 0.05 *M* Sodium Hydroxide in Frozen Aqueous Solutions at −4.0°

Solute concn × 10^2, *M*	k_{obsd} × 10^4, l. mole^{-1} sec^{-1}	$k_{\text{obsd}}C_s$ × 10^4, sec^{-1}
None	16.5	2.48[a]
3.56 NaCl	10.9	2.50
6.50 NaCl	9.91	3.27
10.7 NaCl	8.18	3.39
2.74 $NaNO_3$	12.8	3.00
6.09 $NaNO_3$	10.4	3.38
12.65 $NaNO_3$	8.33	3.35
4.36 C_2H_5OH	14.2	2.72
8.83 C_2H_5OH	11.4	2.70

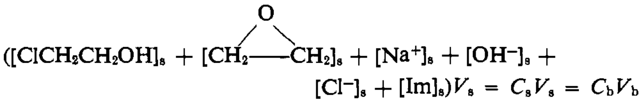
[a] C_s = total solute concentration (including added solutes).

If effects other than the concentration effect are also operative in this reaction, then deviations from the following quantitative treatment of the $ClCH_2CH_2OH$–NaOH reaction in ice should appear.

The application to this reaction of the general equation for the concentration effect gives the following relationship.[9,10]

$$\frac{d[OH^-]_s}{dt} = -k_2[OH^-]_h[ClCH_2CH_2OH]_h\frac{V_h}{V_s} \qquad (1)$$

This equation relates the rate of loss of hydroxide ion (as measured in thawed solutions) to concentrations and volumes of the liquid "reaction regions" in the frozen solutions.[16] The concentrations $[OH^-]_h$ and $[ClCH_2CH_2OH]_h$ and the total volume of the reaction regions, V_h, were not directly measured. In order to substitute for these variables, the assumptions made are that the reagent concentrations in the liquid part of a frozen solution are related to the reagent concentration in the thawed solution by $[OH^-]_hV_h = [OH^-]_sV_s$ and by $[ClCH_2CH_2OH]_hV_h = [ClCH_2CH_2OH]_sV_s$. In addition, since all the solutes involved are highly soluble



$$([ClCH_2CH_2OH]_s + [\overset{\large O}{CH_2\!-\!-\!CH_2}]_s + [Na^+]_s + [OH^-]_s + [Cl^-]_s + [Im]_s)V_s = C_sV_s = C_bV_b$$

where $[Im]_s$ is the concentration of any impurity or other added solute, C_h is the total concentration of the liquid reaction regions of a frozen solution, and C_s is the total concentration of solutes in the thawed solution.

Substitution of these relations into eq 1 gives the following rate expression.

$$\frac{d[OH^-]_s}{dt} = -\frac{k_2C_h}{C_s}[OH^-]_s[ClCH_2CH_2OH]_s \qquad (2)$$

As C_s has a constant value throughout the reaction (1 mole of soluble reactant is replaced by 1 mole of soluble product), and both k_2 and C_h are functions only of temperature, then this reaction in frozen solutions is predicted by eq 2 to be second order under all conditions. This is consistent with the experimental observations mentioned above.

From eq 2, it is also seen that the observed second-order rate constants for runs with frozen solutions are related to normal second-order rate constants (unfrozen solutions) as follows.[17]

$$k_{\text{obsd}} = k_2C_h/C_s \qquad (3)$$

For comparison of observed rate constants to values predicted by eq 3, C_h may be obtained from the liquid–solid phase relationships of the ethylene chlorohydrin–water system, and k_2 by extrapolation from higher temperatures of the rate data available from normal liquid phase kinetic studies. C_s is known from the total initial solute concentration for each run (*i.e.*, $C_s = [ClCH_2CH_2OH]_0 + [Na^+]_0 + [OH^-]_0 + [Im]_0$).

At constant temperature the predicted relationship of k_{obsd} to C_s is shown by the line in Figure 2. The close fit of experimental points to the theoretical curve indicates that this reaction in frozen solutions is well accounted for by the concentration effect. This is also shown in Table I by the nearly constant values of the product of observed rate constant times the total solute concentration, *i.e.*, $k_{\text{obsd}}C_s$. This constancy arises from the relationship $k_{\text{obsd}}C_s = k_2C_h$ and the fact that both k_2 and C_h are dependent only on temperature.

The temperature variation of this reaction in frozen solutions is shown in Figure 3, where experimental values of $k_{\text{obsd}}C_s$ at various temperatures are compared

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(16) The subscript h refers to the reaction regions of a frozen system, s refers to the thawed system, and 0 refers to initial nonfrozen solution concentrations.

(17) Since $C_sV_s = C_bV_b$, then k_{obsd} is also equal to k_2V_s/V_b. The observed rate constant differs from the rate constant k_2 by the ratio of volume of solution to volume of reaction regions in a frozen solution. Since a given number of moles of reactant is replaced during a run by the same number of moles of products, the volume V_h does not vary during a run. However, in separate runs a greater initial concentration of solutes, C_s, gives a greater volume, V_b, and a decrease in k_{obsd} occurs (see Table I).

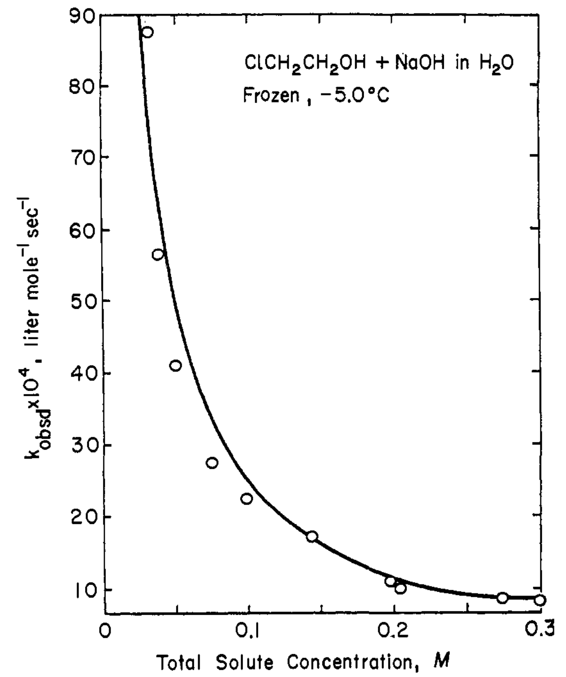

Figure 2. Relation of observed second-order rate constants for reaction of ethylene chlorohydrin with sodium hydroxide in frozen aqueous solutions at $-5.0°$ to total initial solute concentration (C_s). The curve is calculated from $k_{obsd} = k_2C_h/C_s = (1.07 \times 10^{-4})(2.3)/C_s$.

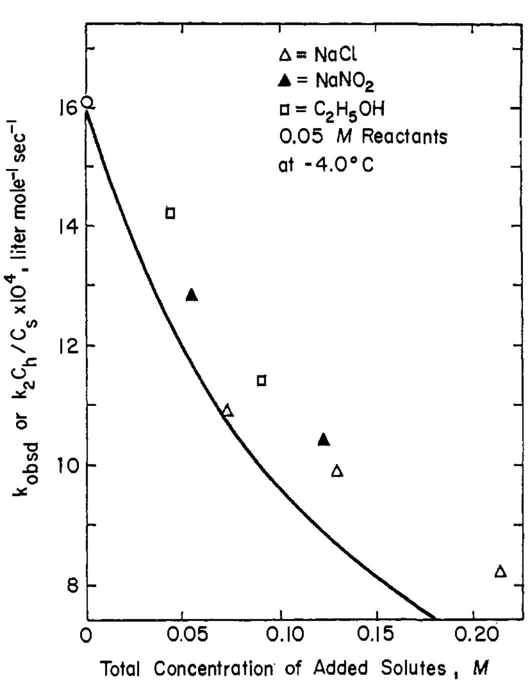

Figure 4. Effect at $-4.0°$ of added solutes on the reaction of 0.05 *M* ethylene chlorohydrin with 0.05 *M* sodium hydroxide in frozen aqueous solutions. The curve is calculated from $k_{obsd} = k_2C_h/C_s = (1.26 \times 10^{-4})(1.9)/(0.15 + \mathrm{Im}_0)$ where Im_0 is the total concentration of added solutes.

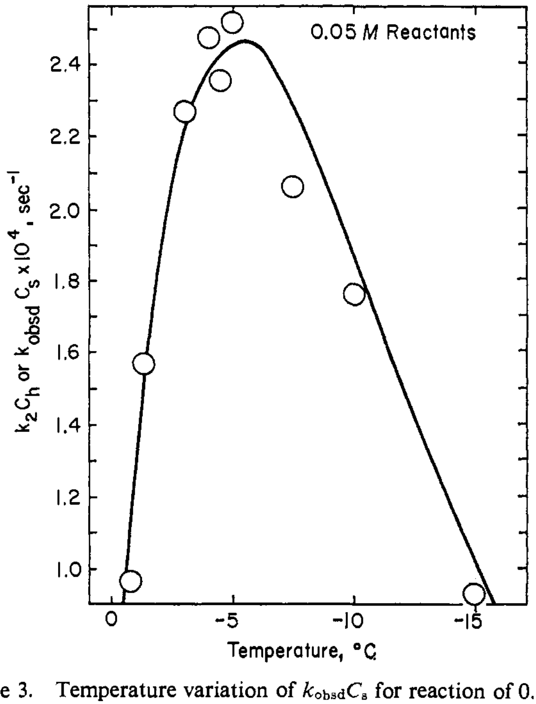

Figure 3. Temperature variation of $k_{obsd}C_s$ for reaction of 0.05 *M* ethylene chlorohydrin with 0.05 *M* sodium hydroxide in frozen aqueous solutions. The curve gives calculated values of k_2C_h; circles are experimental values of $k_{obsd}C_s$.

to calculated values of k_2C_h. The maximum in the curve, caused by the competitive effects of increases in C_h and decreases in k_2 as the temperature is lowered, and the close relationship of $k_{obsd}C_s$ to k_2C_h are apparent from the diagram.

Finally, the effect at $-4.0°$ of the solutes NaCl, $NaNO_3$, and ethanol on the observed rate constant is illustrated in Figure 4. This gives the relationship predicted from eq 3 in the form $k_{obsd} = k_2C_h/C_s = (1.26 \times 10^{-4})(1.9)/(0.15 + \mathrm{Im}_0)$. The observed rate constants are slightly greater than predicted; however, with a total of 1.9 *M* salt and reactant concentration in the liquid regions of the frozen solutions, the actual reaction conditions differ from those used in obtaining the second-order rate constants, k_2, at higher temperatures. Such small variation of the predicted from observed values might be due to inexact values of k_2 or C_h as well as salt or solvent effects at the high solute concentrations of the reaction conditions.

Summary. The characteristics of the ethylene chlorohydrin–sodium hydroxide reaction in frozen aqueous solutions are fully accounted for by the concentration effect alone. When treated according to eq 1, which correlates concentration changes during a run and the volume changes between various runs, the observed rate constants can be quantitatively related to known values of the liquid phase rate constant and to known properties of the ice–solution phase equilibria. For this reaction in ice, there is no evidence of effects other than those arising from concentration changes.

In general, the kinetic treatment applied to the above reaction illustrates a method which can be used to predict rates in frozen aqueous solutions according to the "concentration effect." Similar procedures should be used in other examples of reactions in frozen solutions in order to quantitatively separate out results due to concentration. The possible existence of other effects can then be determined. In the reaction of ethylene chlorohydrin with sodium hydroxide, application of the kinetic treatment is particularly straightforward; all the products and reactants are soluble in the studied range of temperature and there is no change in the total number of moles of solute during a run.

This reaction also shows the greatest rate acceleration (relative to identical supercooled solutions at the same temperature) that has so far been observed for a frozen state reaction. At the lowest concentration studied (0.001 M reactants), while the frozen system at $-5.0°$ is 99.9% solid, the reaction is accelerated by a factor of 1000. Although there is a tendency to loosely describe all frozen systems as solid, it is apparent that as far as the ethylene chlorohydrin is concerned, the important part of the system studied here is the normal (but concentrated) liquid which makes up only *ca.* 0.1% of the total volume.

Experimental Section

Materials. Ethylene chlorohydrin (2-chloroethanol, Eastman Organic Chemicals) was distilled through a 75-cm Vigreux column. After discarding a large forerun, a center fraction with bp 128.5–130° was collected. Deionized water was boiled to remove carbon dioxide and stored in a flask protected with an Ascarite tube. For runs at the lowest concentrations (0.001 M), the water used was distilled from acidic permanganate and then from barium hydroxide.

Sodium hydroxide solutions were made up from British Drug Houses concentrated volumetric solutions or by dissolving U.S.P. grade pellets. These solutions were standarized against potassium acid phthalate. Reagent grade sodium chloride and sodium nitrate were dried at 110° for 2 hr before using. Absolute ethanol was refluxed with and distilled from anhydrous calcium oxide.

Kinetic Studies. Ethylene chlorohydrin solutions were made up fresh each day by weighing out the material and diluting with water. The required amount of this solution was mixed with the appropriate volume of sodium hydroxide solution and then diluted with water to give the concentration desired for a run. After thorough mixing, the solution was divided into several vials. Freezing of these individual samples of a run was usually accomplished simply by placing the samples in a Dry Ice–acetone bath. Sometimes the samples were supercooled to the temperature of a run and then dipped quickly into a Dry Ice–acetone bath to initiate crystallization.

At various times, individual samples were removed from the constant temperature bath and quickly thawed by shaking under hot tap water. Analysis of the samples was carried out by titration with standard hydrochloric acid solution (usually 0.05 M) with phenolphthalein as indicator. Microburets of 5- and 2-ml capacity were used, the 2-ml buret being equipped with a micrometer plunger. For runs at low concentrations of base pH measurements on individual thawed samples were made using a Radiometer Model 4 pH meter which was standardized against pH 10 buffer. No correction was made for the deviation of the activity coefficient from unity. For example, a run with 0.001 M reactants gave the following pH readings at the given times: 10.967 at 0 min, 10.848 at 46 min, 10.718 at 99 min, 10.681 at 150 min, 10.698 at 188 min, 10.632 at 239 min, 10.493 at 409 min, and 10.385 at 607 min.

Kinetic data were treated according to normal second-order kinetic equations. Rate constants were calculated from the slopes of the lines in plots of reciprocal concentration against time or plots of log $[ClCH_2CH_2OH]/[OH^-]$ against time. Runs at the lowest concentration showed some scatter (see Figure 1). This seemed due to experimental difficulties in measuring low concentrations of base rather than to real variations in the amount reacted. As indicated by changes in pH, this reaction in frozen solutions proceeds even with initial concentrations less than 10^{-3} M, but individual thawed samples gave very erratic pH readings at these low concentrations of base.

The value of C_b was obtained by measuring the freezing point of aqueous solutions containing various concentrations of ethylene chlorohydrin. The concentration–temperature relationship down to $-10°$ was the same as reported for ethanol in water.[18] In terms of decrease in freezing point per mole of solute, sodium chloride and sodium hydroxide differ little from either ethanol or ethylene chlorohydrin in the temperature range of interest (down to *ca.* $-10°$).[19]

The values of k_2 at 1° intervals were calculated (IBM 7040 computer) from the equation[12] k_2 (l. mole^{-1} sec^{-1}) = $10^{16.8}/60e^{-23,300/RT}$. Runs using supercooled liquid samples showed that our method of analysis gave rate constants in agreement with McCabe and Warner[12] (at $-1.4°$ found, 2.06×10^{-4} l. mole^{-1} sec^{-1}; at $-1.0°$, calculated 2.04×10^{-4} l. mole^{-1} sec^{-1}).

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(18) "Handbook of Chemistry and Physics," 46th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1965, p D-135.

(19) Reference 18, pp D-158, D-159.

Reactions of Alkyldifluoramines with Acids[1]

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Contribution No. 266 from the Chemical and Structural Products Division,
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Abstract: The reaction of *t*-butyldifluoramine with boron trifluoride gave the stable salt, N-fluoro-N-methylisopropylidenimonium fluoroborate. This rearrangement also occurred in the reaction of *t*-butyldifluoramine with sulfuric acid, and the above cation was identified by nmr spectra of the resulting solution. Ethyldifluoramine reacted with sulfuric acid to give acetonitrile, which was hydrated under the experimental conditions to give acetamide. 1-Difluoraminobutane and 2-difluoraminobutane reacted with sulfuric acid, and nmr spectra indicated that the products were the N-fluorimonium ions resulting from migration of the propyl and ethyl groups, respectively.

The reaction of triphenylmethyldifluoramine with concentrated sulfuric acid has been reported by Graham and Parker[2] to give difluoramine and triphenylmethyl cation.

$$(C_6H_5)_3CNF_2 \xrightarrow{H_2SO_4} (C_6H_5)_3C^{\oplus} + HNF_2$$

Thus, the difluoramino entity functions as a leaving group under the driving force of the formation of the highly stable trityl cation. It was of interest to determine whether this type of cleavage would occur in the reaction of acids with other difluoramino derivatives, not capable of producing such a highly stabilized carbonium ion.

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(1) Supported by the Office of Naval Research and the Advanced Research Projects Agency. Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, and the Third International Fluorine Symposium, Munich, Sept 1965.

(2) W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1963).