ethylamine and platinic chloride, and triethyl-aminechloroplatinate on the more active forms of Raney nickel in the hydrogenation of several functional groups have been studied.

A rapid method is described for estimating the amount of nickel in wet Raney nickel catalyst.

A Kinetic Study of the Neutral Hydrolysis of Ethylene Fluoro-, Bromo- and Iodohydrin[1]

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Introduction

During the course of an investigation of the alkaline hydrolysis of the ethylene halohydrins, it was necessary to establish that the reaction of the halohydrins with water was slow compared to the one being studied. Because a kinetic study of the neutral hydrolysis of the ethylene halohydrins showed promise of enabling one to obtain information about the polar effect in substitution reactions, experiments were carried out to determine velocity constants as a function of temperature and solvent composition and also to establish the nature of the products. Rate constants for ethylene chlorohydrin had been reported previously.[3]

Experimental

The ethylene fluorohydrin, bromohydrin and iodohydrin were obtained from the same stock solutions described in a previous paper.[4] Anhydrous ethanol was obtained by refluxing U. S. P. ethanol, obtained from U. S. Industrial Chemicals, Inc., with lime. The middle fraction from a distillation under anhydrous conditions was used in the kinetics experiments. Anhydrous copper sulfate did not turn blue when placed in it.

The thermostat used for the kinetics experiments held the temperature to within 0.01° as determined by Beckmann thermometers, which were calibrated with a N. B. S. platinum resistance thermometer. The reaction vessels were made by extending the tops of 200-ml. Pyrex iodine flasks. This enabled the flasks to be immersed in the thermostat liquid so that the ground-glass stoppers were below the liquid level. This served to cut down distillation and subsequent condensation in the flasks.

The velocity constants were obtained by withdrawing 20-ml. samples from the reaction flasks, analyzing for halide by the Volhard method,[5] and calculating the concentration of halohydrin by assuming that the amount of halide formed was equal to the amount of halohydrin which had disappeared. Velocity constants were taken from the slope of the best straight line obtained by plotting the logarithm of halohydrin concentration against time. Duplicate runs checked within ±1%.

The analyses for ethylene glycol and acetaldehyde in dilute aqueous solution were accomplished by a modifica-tion of the method given by Shupe.[6] Analyses of this type were carried out on samples taken from a neutral hydrolysis experiment carried to approximately 70% conversion under conditions where the vapor pressure of oxygen over the solution was less than 4 mm. Essentially the same analyses were carried out on samples taken from experiments in which ethanol-water was the solvent.

The amount of halohydrin reacted was determined by titrating the acid formed from the neutral hydrolysis, using methyl red as the indicator. The first step in the acetaldehyde analysis was to add 5% sodium bisulfite to the sample to form the addition complex with the acetaldehyde. The solution was allowed to stand for half an hour. The excess bisulfite was then destroyed by 0.5 N iodine solution. This having been done, a more careful adjustment to the starch end-point was made by addition of a small amount of bisulfite, followed by addition of 0.02 N iodine solution. Four per cent. borax-five per cent. sodium carbonate solution was then added to the sample to destroy the complex. The liberated bisulfite was then titrated with the standardized iodine solution to the starch end-point. The amount of acetaldehyde was calculated from the amount of standardized iodine required to react with the bisulfite liberated from the complex.

The analysis for ethylene glycol was made as follows: The solution was neutralized to the methyl red end-point with standardized carbon dioxide-free base. The acetaldehyde was then removed by boiling. Addition of 0.03 M potassium periodate oxidized the glycol to formaldehyde. The formaldehyde was then analyzed as described above for acetaldehyde except that the end-point was taken as the appearance of iodine color and standardized iodine, an amount not quite necessary to react with the liberated bisulfite, was added before addition of the borax-sodium carbonate solution. From the amount of standardized iodine necessary to destroy the bisulfite obtained by the decomposition of the formaldehyde-bisulfite complex, the amount of formaldehyde was determined. The amount of glycol in the original sample was determined from the fact that two moles of formaldehyde are formed from the oxidation of one mole of ethylene glycol.

Experimental Results

Bimolecular velocity constants for the hydrolysis of ethylene chloro-, bromo- and iodo-hydrins in pure water as solvent were obtained by dividing the observed first order constants by the concentration of water. These constants are given as a function of temperature in Fig. 1. The observed first order constants and the corresponding bimolecular constants are given in Table I. This table also gives values of the activation energies and the logarithms of the frequency terms which are related to the velocity constants by the equation

$$\log k \text{ (liters moles}^{-1} \text{ sec.}^{-1}) = \log A - \Delta E/2.303 \, RT$$

(1) Abstracted from part of a thesis submitted by C. L. McCabe to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science.

(2) Monsanto Chemical Company Fellow, 1947-1948.

(3) Radulescu and Muresanu, Bull. soc. sci. Cluj, Roumanie, 7, 128 (1932).

(4) McCabe and Warner, THIS JOURNAL, 70, 4031 (1948).

(5) Pierce and Haenisch, "Quantitative Analysis," John Wiley and Sons, Inc., New York, N. Y., 1937, p. 219.

(6) Shupe, J. Assoc. Official Agr. Chem., 26, 249 (1943).

An approximate value of the velocity constant for the hydrolysis of ethylene fluorohydrin also is given in Table I.

TABLE I

THE NEUTRAL HYDROLYSIS OF THE ETHYLENE HALO-HYDRINS

Halohydrin	Temp., °C.	k (exptl.) first order, sec.$^{-1}$	k (bimol.), liters moles^{-1} sec.$^{-1}$	log A	ΔE, kcal. mole^{-1}
Ethylene fluorohydrin	70.0	3.0×10^{-9}	5.5×10^{-11}		
Ethylene chlorohydrin	56	6.1×10^{-8}	1.12×10^{-9}		
	65	1.36×10^{-7}	2.5×10^{-9}		
	79	7.0×10^{-7}	1.27×10^{-8}	8.4	26.2
	99	5.0×10^{-6}	9.35×10^{-8}		
Ethylene bromo-hydrin	40	7.9×10^{-8}	1.43×10^{-9}		
	60	1.05×10^{-6}	1.92×10^{-8}	10.0	27.0
	70	3.45×10^{-6}	6.35×10^{-8}		
Ethylene iodohydrin	60	3.75×10^{-7}	6.90×10^{-9}		
	70	1.36×10^{-6}	2.50×10^{-8}	10.8	28.9
	80	4.30×10^{-6}	7.97×10^{-8}		

During the course of some of the experiments on the neutral hydrolysis of ethylene iodohydrin in water, the reaction mixture became colored by the formation of iodine. The presence of iodine did not disturb the hydrolysis because the plots of log concentration vs. time did not deviate from linearity. When oxygen was excluded from the reaction mixture, the solution did not become colored; hence it seemed evident that the free iodine was produced by the air oxidation by hydriodic acid.

In Table II, the results of the analysis of the reaction mixture for ethylene glycol and acetaldehyde are given. It is evident that in the neutral hydrolyses of each of the halohydrins the major product is ethylene glycol. A small amount of acetaldehyde is formed in each case.

TABLE II

PRODUCT ANALYSES FOR THE NEUTRAL HYDROLYSIS OF THE ETHYLENE HALOHYDRINS IN WATER AT 70°

Halohydrin	Acetaldehyde, %	Glycol, %	% Acetaldehyde / % Glycol
Ethylene chlorohydrin	1.3	98.5	0.013
Ethylene bromohydrin	1.4	98.1	.014
	1.9	98.6	.019
	1.5	..	...
	2.5	97.3	.026
Ethylene iodohydrin	3.9	92.8	.042
	3.2	95.2	.033

TABLE III

SOLVOLYSIS OF HALOHYDRINS IN ETHANOL-WATER MIXTURES AT 70°

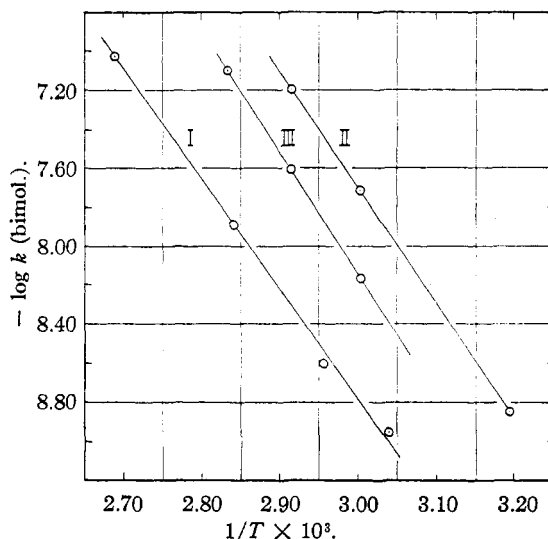| Halohydrin	Wt. % ethanol	$\dfrac{D-1}{2D+1}$	k sec.$^{-1}$ first order
Ethylene bromohydrin	0.0	0.4883	3.45×10^{-6}
	20.0	.4861	2.54×10^{-6}
	59.1	.4783	1.02×10^{-6}
	80.0	.4703	4.62×10^{-7}
Ethylene iodohydrin	0.0	.4883	1.36×10^{-6}
	20.0	.4861	1.04×10^{-6}
	60.0	.4780	4.83×10^{-7}

Fig. 1.—Rate constants as function of temperature in hydrolysis of halohydrins: I, ethylene chlorohydrin; II, ethylene homohydrin; III, ethylene iodohydrin.

First order velocity constants at 70° for the solvolysis of ethylene bromo- and iodohydrins in ethanol–water mixtures as a function of the dielectric constant, D, are given in Table III.

Discussion of Results

One of the conclusions which can be drawn from the data of Table II and from the observation that the concentrations of hydrogen ion and halide ion are almost equal at the end of an hydrolysis experiment is that the major reaction is

$$\begin{array}{c} CH_2OH \\ | \\ CH_2X \end{array} + H_2O = \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} + H^+ + X^-$$
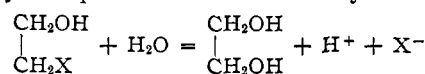
In ethanol–water mixtures, the amount of ethylene glycol formed is not equivalent to the amount of halide ion resulting from the solvolysis. Hence, it has been assumed that there is simultaneous hydrolysis and alcoholysis; the product of the latter in the present reaction being Cellosolve. This course has been established in similar reactions.[7] The individual velocity constants could be obtained from the experimental first order constants and the ratio of glycol to Cellosolve in the product through the relationship

$$k \text{ (exptl.)} = k_a[EtOH] + k_w[H_2O]$$

In both water and ethanol–water mixtures, the reactions of ethylene halohydrins followed first order kinetics to high percentage conversions. For this reason, it was not necessary to correct for back reactions. Furthermore, this showed that the reactions were not acid catalyzed.

In an effort to determine whether these solvolytic reactions proceed by a unimolecular (SN$_1$) or a bimolecular (SN$_2$) mechanism. we have reviewed the criteria[8] evolved for determining

(7) Hughes, Ingold and Bird, J. Chem. Soc., 225 (1943).

(8) Hughes, Trans. Faraday Soc., 37, 603 (1941).

the mechanism in reactions of this type. Several of these criteria cannot be applied to our study. For example, we cannot compare the rate for displacement of halogen by water with the rate of displacement by the strong base OH$^-$, since with OH$^-$ as reactant, the product is ethylene oxide.[4] The effect of solvent change on reaction rate seems most useful as a criterion of the mechanism in our reactions. In numerous instances, Hughes, Ingold and co-workers have pointed out that the velocity constant for solvolysis changes much faster with solvent composition in the case of a SN$_1$ than in a SN$_2$ reaction. However, they have not made any quantitative comparisons. This has been done in Fig. 2 by plotting log k(exptl.) vs. $(D - 1)/(2D + 1)$ for the solvolysis of ethylene bromo- and iodohydrin in ethanol–water mixtures and for several similar solvolytic reactions taken from the literature. Of those taken from the literature, reactions I, II and VI have been judged unimolecular, SN$_1$, by other criteria and reactions IV, V, VII and IX have been judged bimolecular, SN$_2$. Thus, these reactions seem clearly to fall into two groups relative to the influence of dielectric constant of solvent upon rate, and support is found for our postulate that the solvolysis of the halohydrins, reactions III and VIII, occurs by a bimolecular mechanism.
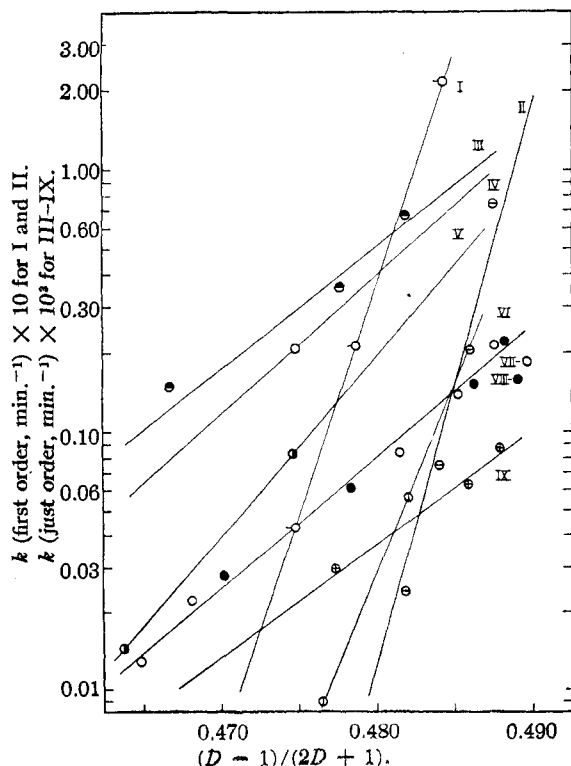

Fig. 2.—Solvolysis of alkyl halides in ethanol–water mixtures at 70°: I, t-butyl bromide; II, t-butyl chloride; III, ethylene iodohydrin; IV, methyl bromide; V, ethyl bromide; VI, neopentyl bromide; VII, ethyl iodide; VIII, ethylene bromohydrin; IX, n-butyl bromide.

Hinshelwood, Laidler and Timm[9] advanced a theory which qualitatively predicts the effect of polar substituents on the activation energy in substitution reactions. This theory predicts that when there is no well-defined negative center in the attacking reagent, the influence of substituents in the reacting molecule on the activation energy will be determined by their effect on the energy of the bond which is to rupture. Our results with ethylene iodohydrin, when compared (Table IV) with those previously obtained for methyl and ethyl iodides support the theory.

TABLE IV

THE INFLUENCE OF POLAR SUBSTITUENTS ON THE RATE OF NEUTRAL HYDROLYSIS OF ALKYL IODIDES

Alkyl halide	Solvent	k_{uo} (days^{-1})	ΔE (kcal.)
CH$_2$OHCH$_2$I	H$_2$O	0.00060	28.9
CH$_3$I[10]	H$_2$O	.000130	25.8
CH$_3$CH$_2$I[11]	H$_2$O	.0268	21.2

If substitution for hydrogen on the carbon holding the halogen influenced the activation energy through changing the charge on the carbon atom, the effect of replacing hydrogen by the electron attracting–CH$_2$OH would be to decrease the activation energy, while the effect of replacing hydrogen by –CH$_3$ would be to increase the activation energy. From Table IV, it can be seen that the opposite is true.

Summary

1. Velocity constants, activation energies and frequency factors have been determined for the reaction between water and ethylene bromohydrin and iodohydrin. An upper limit on the rate constant for the reaction between ethylene fluorohydrin and water has been determined.

2. Analyses of the reaction products in the neutral hydrolysis of ethylene chlorohydrin, bromohydrin and iodohydrin have been made. Ethylene glycol is the principal reaction product in each case.

3. The variation of the velocity constant in the neutral solvolysis of ethylene bromohydrin and iodohydrin with solvent composition in water–ethanol mixtures has been determined at 70°. By comparison of these results with data on other similar reactions, it is concluded that the neutral solvolysis of the halohydrins proceeds by a bimolecular mechanism.

4. A comparison of the hydrolysis of ethylene iodohydrin with the hydrolysis of methyl and ethyl iodides, leads to the conclusion, that substitution for hydrogen on the carbon holding the halogen influences the activation energy through the effect on the energy of the bond which is to rupture.

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(9) Hinshelwood, Laidler and Timm, J. Chem. Soc., 848 (1936).
(10) Moelwyn-Hughes, Proc. Roy. Soc. (London), A164, 295 (1938).
(11) Moelwyn-Hughes, J. Chem. Soc., 1157 (1938).