TABLE II

VALUES OF ZERO-ORDER CONSTANT WITH RESPECT TO AMMONIA AT 600°

$p^0_{NH_3}$ atm.	Fract. convers. x	k_0 atm./sec. × 10^3
Tube A, empty, uncoated; t = 21 sec. (40 cc. per min. total flow)		
0.0625	0.995	(3.0)
.125	.714	4.3
.1875	.400	3.6
.250	.302	3.6
.3125	.183	2.8
.375	.103	1.8
.4375	.056	1.1
t = 3.3 sec.		
0.0625	0.373	6.9
.125	.125	4.3
Tube B, packed, uncoated, t = 21 sec.		
0.0625	0.97	(2.9)
.125	.811	4.9
.1875	.539	4.9
.250	.374	4.5
.3125	.186	2.8
.375	.116	2.1
.4375	.091	1.9

The question of isoluble intermediates was investigated with little success. Nitrite and nitrate ions could not be detected in the solution after absorption of ammonia. There was occasional evidence of nitrogen oxides (a very faint odor) but only in very low concentration. It was also found that under certain conditions starch–iodide test paper was colored slowly by the product gases, and that acidified permanganate was bleached, indicating a trace of peroxide. It is concluded that the products are very largely nitrogen and water.

TABLE III

EFFECT OF TEMPERATURE

Flow rate, 40 cc. per min. at 25° and 1 atm.; Tube A, empty, uncoated; 41 cc. volume

Temp., °C.	Fract. conv., x	t sec.	k_0 × 10^5
Initial comp., 6.25% NH_3			
400	0.015	27.3	3.4
450	.030	25.4	7.4
500	.103	23.7	27
550	.485	22.3	136
600	.995	21.0	296
Initial comp., 12.5% NH_3			
450	0.015	25.4	7.4
500	.025	23.7	13
525	.082	23.0	45
550	.204	22.3	114
600	.714	21.0	425

Further experiments by the static method are under way. Measurements of pressure change are planned, though this is not too satisfactory since the change in number of moles on complete reaction is only from 3.5 to 4. Such measurements will be supplemented by analysis.

Summary

The slow non-catalytic reaction between ammonia and oxygen has been studied by the flow method. It has been found that the fraction reacted increases rapidly as the ammonia concentration is decreased, indicating a zero (or negative) order. Thus ammonia appears to inhibit its own oxidation. Rates in empty and packed reaction tubes are about the same; but coating with potassium chloride causes a marked decrease in both cases.

PRINCETON, N. J. RECEIVED AUGUST 3, 1949

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

The Promoter Effect of Platinic Chloride on Raney Nickel. I. General Effects on Type W-6 Catalyst

BY DEWEY ROBERT LEVERING, FRED L. MORRITZ AND EUGENE LIEBER

In 1936, Lieber and Smith[1a] found that small amounts of platinic chloride, added to Raney nickel catalyst just prior to the start of the reduction, produced a marked enhancing effect on the activity of the catalyst for a variety of functional groups. It was clearly demonstrated that the promoting effect obtained was markedly beyond that which could be expected on the basis of the quantity of platinum metal used. Further studies[1b,1c] on the platinum chloride promotion dealt with the hydrogenation of nitro-compounds at one atmosphere pressure.

Since this early investigation there has been a marked enhancement in the activity of the Raney nickel catalyst itself due to improvements in the procedure for the preparation of the catalyst from the Raney alloy[2a] over that of the method[2b] used in the early investigation.[1a] Accordingly, it was considered important to investigate the promoter effect on the improved types of Raney nickel now available, particularly that designated

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[1] (a) E. Lieber and G. B. L. Smith, THIS JOURNAL, **58**, 1417 (1936); (b) J. R. Reasenberg, E. Lieber and G. B. L. Smith, *ibid.*, **61**, 384 (1939); (c) S. S. Scholnik, J. R. Reasenberg, E. Lieber and G. B. L. Smith, *ibid.*, **63**, 1192 (1941).

[2] (a) H. Adkins and H. R. Billica, *ibid.*, **70**, 695 (1948); (b) H. Adkins and L. W. Covert, *ibid.*, **54**, 4116 (1932).

as "W-6."[2a] These studies have resulted in a number of significant observations, a preliminary report of which has been presented.[3] The present paper summarizes the results obtained on the general effects of platinic chloride in the W-6 catalyzed hydrogenation of various functional groups with particular regard to the combined action of triethylamine and platinic chloride on the velocity of reduction. A preliminary report is also presented on the comparative promoting effect of triethylaminechloroplatinate, $(Et_3N)_2H_2PtCl_6$, preformed as a salt, since in the use of triethylamine and platinic chloride there is present a large excess of the base over the concentration of the promoter. In view of the necessity of having precise amounts of nickel present in order to obtain comparative rate data, a rapid method for weighing wet Raney nickel containing an absolute weight of nickel is described.

Experimental

Comparative hydrogenations were carried out at room temperature under a pressure of 45 p. s. i. of hydrogen in a 250-ml. glass bottle shaken at about 190 oscillations per minute. The reaction mixture (containing 0.05 mole of hydrogen acceptor, except where noted) was made up to a volume of 100 ml. with dry ethyl alcohol and contained 3 g. of wet W-6 Raney nickel.[2a] The wet catalyst was weighed by spooning some drained Raney nickel mud into a tared beaker containing dry ethyl alcohol. This was duplicated as exactly as possible for all runs, check determinations being made frequently. Those reactions in which the same starting materials were used and which have been plotted on the same graphs were run on the same day. No preparation of W-6 Raney nickel was used which was more than ten days old. The products of the hydrogenations were worked up, their identity established and the yields determined.

The data obtained are summarized in Table I in which the promoter concentration comprised 0.220 millimole of platinic chloride. The times of hydrogenation recorded are for the complete reduction to the given product. Rate curves for the reduction of isovaleraldehyde, nitroethane, phenylacetonitrile and *p*-nitrotoluene are presented in Figs. 1-4.

Effect of Variation in Promoter Concentration.—The effect of variation of platinic chloride concentration was determined for the hydrogenation of benzaldehyde (0.05 mole) in the presence of 2 ml. of triethylamine and 3 g. of wet W-6 catalyst, the general procedure for conducting the hydrogenation being the same as described above. The data obtained are summarized in Fig. 5 and reference 3.

Triethylaminochloroplatinate.—This was prepared by adding triethylamine, in stoichiometric quantity, to an alcoholic solution of chloroplatinic acid. The yellow-orange precipitate was filtered on a Buchner funnel, washed successively with alcohol and ether and then dried in a vacuum desiccator. The yield is quantitative.

Anal. Calcd. for $(Et_3N)_2H_2PtCl_6$: Pt, 31.9. Found: Pt, 31.2.

Comparative Promoting Effect of Triethylaminechloroplatinate.—This was tested for the hydrogenation of nitrobenzene and benzaldehyde. The data obtained are summarized in Table II.

Procedure for Rapid Weighing of Wet Raney Nickel.—The relationship between the volume of wet W-6 and the actual amount of nickel present was determined by measuring the wet catalyst in a graduated centrifuge tube, centrifuging at 3750 r. p. m. for five minutes, determining the centrifuged volume, and finally determining the amount of nickel by gravimetric analysis.

TABLE I

GENERAL EFFECTS OF PLATINIC CHLORIDE ON W-6 HYDROGENATION OF VARIOUS FUNCTIONAL GROUPS

Hydrogen acceptor	Grams	Catalyst	Time, min.	Product
Acetone	5.8	W-6	180	Isopropyl alcohol
		W-6[a]	98	
		W-6[b]	49	
		W-6[c]	No reaction	
Benzophenone	9.1	W-6	60	Benzohydrol, 100% yield, m. p. 68°
		W-6[a]	21	
		W-6[b]	31	
		W-6[c]	No reaction	
Benzaldehyde	5.3	W-6	170	Benzyl alcohol, 65% rec., b. p. 201-202°; 3,5-dinitrobenzoate, m. p. 112-113°
		W-6[a]	60	
		W-6[b]	6	
		W-6[c]	17	
Anisaldehyde	6.7	W-6[a]	130	*p*-Methoxybenzyl alc., 86% rec., m. p. 25°
		W-6[b]	29	
o-Methoxybenzaldehyde	6.7	W-6[a]	70	*o*-Methoxybenzyl alc., 89% rec., b. p. 245-250°
		W-6[b]	38	
Heptaldehyde	5.2	W-6	321	Heptyl alc., b. p. 173-175°, 71% rec.
		W-6[a]	152	
		W-6[b]	46	
Isovaleraldehyde	8.6	W-6[a]	231	Isoamyl alc., b. p. 125-131°, 91% rec.
		W-6[b]	28	
p-Dimethylaminobenzaldehyde	7.4	W-6[a]	83	*p*-Dimethylaminobenzyl alc., b. p. 123° (1.0 mm.). 81%
		W-6[b]	22	
Cyclohexene	8.2	W-6	15	Cyclohexane, b. p. 80° 50% rec.
		W-6[b]	13	
Diisobutylene	11.2	W-6	71	Isoöctane, b. p. 98-99°
		W-6[b]	65	
		W-6[c]	45	
Cinnamic acid	7.4	W-6	51	β-Phenylpropionic acid, m. p. 47-48°, 95%
		W-6[a]	60	
		W-6[b]	54	
		W-6[c]	46	
Cinnamaldehyde	6.2	W-6	126	γ-Phenylpropyl alc., b. p. 234-237°, 88%
		W-6[a]	34	
		W-6[b]	40	
Phenylacetonitrile	5.9	W-6	105	Benzylamine
		W-6[a]	Incomplete	Dibenzylamine
		W-6[b]	58	
		W-6[c]	50	
p-Nitrotoluene	6.9	W-6	37	*p*-Toluidine, m. p. 43°, 92%
		W-6[a]	59	
		W-6[b]	15	
		W-6[c]	15	
Nitroethane	3.7	W-6	Incomplete	Ethylamine 94.7% by titration; phenylthiourea, m. p. 104-105°
		W-6[a]	Incomplete	
		W-6[b]	23	
		W-6[c]	27	

The catalysts were: W-6 Raney Ni alone; [a] W-6 + 2 ml. Et_3N; [b] W-6 + 2 ml. Et_3N + 0.220 mmole.$PtCl_4$; [c] W-6 + 0.220 mmole.$PtCl_4$.

The data indicated an apparent density, with regard to actual nickel content, of 1.00 for the centrifuged wet W-6 catalyst.

Effect of Variation in Nickel Content of W-6 on the Hydrogenation of Acetone.—A series of hydrogenations were made keeping the amount of hydrogen acceptor (0.10 mole of acetone) and the amount of promoter (2.0 ml. Et_3N) constant and varying the amount of W-6 catalyst. The data obtained are summarized in Fig. 6.

Discussion

In the early investigations of Lieber and Smith[1a] it was observed that 0.220 millimole of

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(3) D. R. Levering and E. Lieber, THIS JOURNAL, 71, 1515 (1949).

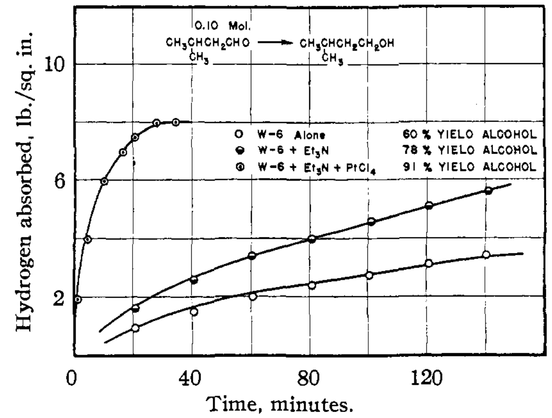

Fig. 1.—Comparative rates of hydrogenation of isovaleraldehyde with unpromoted and promoted W-6 catalyst.

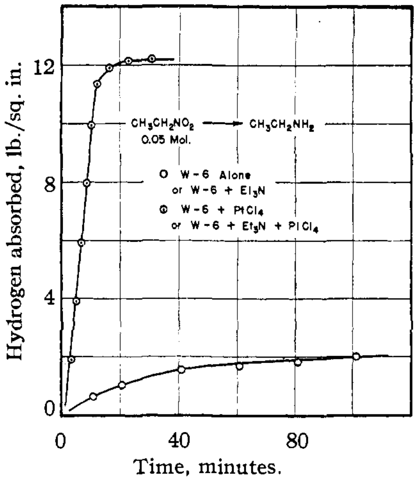

Fig. 2.—Comparative rates of hydrogenation of nitroethane.

TABLE II

COMPARATIVE EFFECT OF BASIC CHLOROPLATINATES AS PROMOTERS FOR W-6 HYDROGENATIONS

Hydrogen acceptor	Catalyst	Time, min.
Nitrobenzene 0.05 mole	W-6 alone	36
	W-6 + Et_3N	107
	W-6 + 0.22 mmole $PtCl_4$	20
	W-6 + Et_3N + 0.22 mmole $PtCl_4$	15
	W-6 + 0.22 mmole $(Et_3N)_2H_2PtCl_6$	9[a]
Benzaldehyde 0.05 mole	W-6 alone	44
	W-6 + Et_3N	30
	W-6 + 0.22 mmole $(Et_3N)_2H_2PtCl_6$	22
	W-6 + Et_3N + 0.22 mmole $PtCl_4$	2

[a] Aniline recovered in 95% yield, b. p. 182°; acetanilide, m. p. 111.5°.

platinic chloride was the minimum quantity which would manifest promoting action on the old type Raney nickel.[2b] By the use of the more active form of Raney nickel, and especially in the presence of triethylamine, the promoter effect is observable at extremely low concentrations of platinum, the lowest concentration reported in this paper being 0.002 millimole which

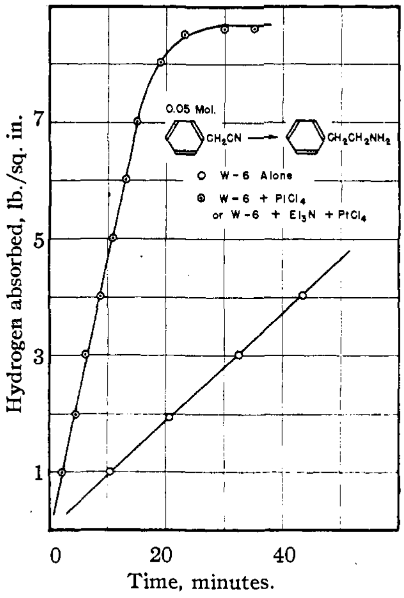

Fig. 3.—Comparative rates of hydrogenation of phenylacetonitrile.

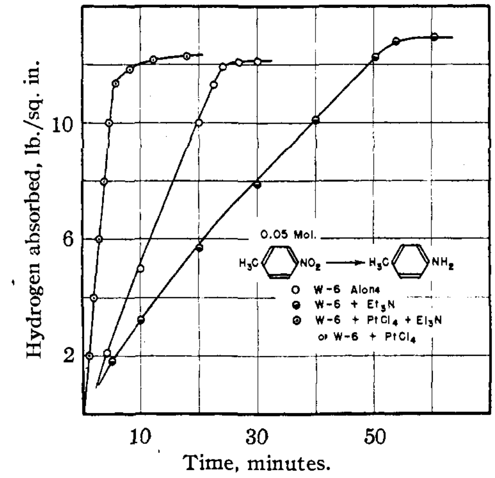

Fig. 4.—Comparative rates of hydrogenation of *p*-nitrotoluene.

corresponds to 0.4 milligram of platinum. The combination of triethylamine and platinic chloride enables the hydrogenation of ketones to proceed smoothly and rapidly, whereas, in the absence of triethylamine, platinic chloride is a poison for the Raney nickel hydrogenation (Table I). Very marked promoting actions were obtained for the hydrogenation of the nitro-, aldehyde (both aliphatic and aromatic) and nitrile groups. Purely olefinic double bonds respond weakly to the promoting action.

The importance of rapid hydrogenations, as a factor in the determination of yield of product, is illustrated by the reduction of isovaleraldehyde to isoamyl alcohol. It will be noted from Table I and Fig. 1 that the more rapid the hydrogenation

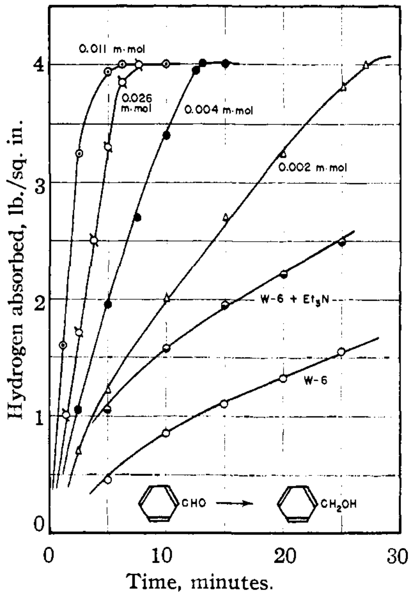

Fig. 5.—Effect of variation of platinic chloride concentration on the comparative rates of hydrogenation of benzaldehyde.

the higher the yield of alcohol. This is undoubtedly due to the fact that two competing reactions are taking place: (1) condensation reactions of the aliphatic aldehyde in the presence of Raney nickel and (2) the reduction of the aldehyde group.

The most marked promoting action was obtained for the hydrogenation of nitroethane (Fig. 2). Surprisingly, W-6 catalyst alone was ineffective for the reduction of nitroethane under the conditions used. However, by the introduction of platinic chloride promoter, in 0.220-millimole concentration, either alone or in combination with triethylamine, the reduction was initiated by a short induction period (several minutes) in which very little hydrogen was absorbed; this was followed by a considerable temperature rise of the reaction mixture with rapid absorption of hydrogen. The final reduction product, ethylamine, was obtained in excellent yield. The nitroaliphatics are being studied separately as a group and will be subsequently reported upon. Triethylamine has a marked poisoning action on the reduction of the nitro group when used alone with W-6 catalyst (Fig. 5).

Following the procedure of Adkins and Billica[2a] we have been unable to exactly duplicate the activities reported by them. However, as Adkins[4] has pointed out, the precise duplication of rates of hydrogenation is hardly to be expected since the rate is determined by the quality of the solvent, the starting material, the hydrogen, catalyst, the apparatus and temperature of the room. Further the precise rates of hydrogenation are unimportant, since we are concerned with *comparative* effects produced by promoters.

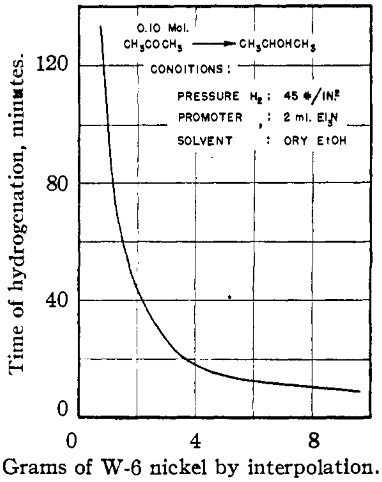

Fig. 6.—Variation in time of hydrogenation of acetone with actual nickel content of wet W-6 Raney catalyst.

It was recognized early in this investigation that the speed of hydrogenation varied with the amount of W-6 catalyst used. Accordingly, great care was taken in duplicating the weighings used for the rate studies in as exact a manner as possible. The method outlined in the experimental section offers a rapid method for exactly determining the amount of actual nickel present in a Raney nickel type reduction. The importance of this for rate studies is illustrated in Fig. 6. The range of 1 to 3 g. of catalyst comprises the most rapidly changing section of the curve, where small deviation in the amount of nickel can lead to large differences in the time of hydrogenation.

In those reductions employing the combination of triethylamine and platinic chloride, it is important to observe the sequence of adding platinic chloride *last* to the reaction mixture; otherwise a considerable poisoning action can take place, especially noted in the hydrogenation of carbonyl compounds. In those cases employing the combination of triethylamine and platinic chloride we have observed the formation of a precipitate of the basic chloroplatinate, undoubtedly $(Et_3N)_2H_2PtCl_6$. This invited the supposition that *preformed* basic chloroplatinates would serve as promoters for Raney nickel hydrogenations. This has been verified in a preliminary fashion for the hydrogenation of nitrobenzene and benzaldehyde, summarized in Table II. The data are too sparse as yet to draw any general conclusions; however, it appears that the basic chloroplatinates are more effective promoters for the reduction of nitro compounds, while the presence of an excess of triethylamine over platinic chloride is most effective for an aromatic aldehyde. The investigation of the promoter action of salts of chloroplatinic acid is being continued. Other noble type metals will also be studied.

Summary

The activating effects of platinic chloride, tri-

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(4) H. Adkins, private communication.

ethylamine and platinic chloride, and triethylaminechloroplatinate 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.

CHICAGO, ILLINOIS RECEIVED JULY 18, 1949

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

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

BY HELEN D. COWAN, C. L. MCCABE[2] AND J. C. WARNER

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 modification 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 iodohydrins 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

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

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[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).