well as certain stereospecific reactions of the diphenacyl halides with aniline and other basic reagents.

Experimental[16]

The following preparations of the diphenacyl halides are modifications of Widman's procedures.[5]

β-Diphenacyl Bromide.—A solution of 30 g. (0.15 mole) of phenacyl bromide (Eastman Kodak Co.) in 400 ml. of absolute ethanol was cooled in an ice-bath. To this solution was added, with mechanical stirring, a solution prepared by adding 3 g. (0.13 mole) of sodium to 150 ml. of absolute ethanol. After half of the base had been added, a fine white precipitate formed and the solution began to turn orange-red. The addition was complete in 45 minutes and the mixture was allowed to stand for 12 hours at room temperature. The solid was then filtered and recrystallized from ethanol, and then from benzene. The yield of white needles, m.p. 163–164.5°, was 20 g. (83%).

Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.58; H, 4.13. Found: C, 61.03, 60.10; H, 4.35, 4.32.

α-Diphenacyl Bromide.—A solution of sodium ethoxide, prepared from 0.60 g. (0.026 mole) of sodium and 50 ml. of absolute ethanol, was added to 10 g. (0.050 mole) of phenacyl bromide in 80 ml. of absolute ethanol. The reaction mixture was cooled in an ice-bath and stirred mechanically. The addition was completed in 5 minutes and the solid which formed was filtered immediately (within five minutes). Two recrystallizations from ether, carried out rapidly, yielded 2 g. (25%) of tiny crystals, m.p. 128–130°.

Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.58; H, 4.13. Found: C, 60.46; H, 4.26.

Dypnone Oxides.—Dypnone (10 g., 0.045 mole) prepared according to Calloway[17] was dissolved in 100 ml. of methanol. To this solution, 10 ml. (0.088 mole) of 30% hydrogen peroxide together with 12 ml. of 8% sodium hydroxide was added all at once. The reaction mixture was cooled at first and then shaken for 45 minutes on a mechanical shaker. The mixture was then cooled, diluted with water, and the white solid filtered. The crude material was dissolved in about 300 ml. of ethanol and allowed to crystallize slowly. White needles (1.5 g.) crystallized first, m.p. 159.5–162°. Dilution of the filtrate with water yielded 6.7 g. of plates, m.p. 93–94.5°. The over-all yield was 77%.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found (for low-melting isomer, m.p. 93–94.5°): C, 80.50; H, 6.13. (For high-melting isomer, m.p. 159.5–162°): C, 80.69; H, 5.93.

1,3-Diphenyl-4-bromobutene-2-one-1 (III).—A mixture of 10 g. (0.045 mole) of dypnone and 8.5 g. (0.047 mole) of N-bromosuccinimide (Arapahoe) was refluxed in 70 ml. of carbon tetrachloride for two hours. The solution was cooled rapidly and the succinimide filtered from the clear yellow solution. The yield of succinimide indicated nearly complete reaction. The solvent was removed under reduced pressure and the yellow oil was taken up in ethanol. Slow crystallization yielded 8.2 g. (59%) of yellow needles. After recrystallization from ethanol, the product melted 68.5–71°.

Anal. Calcd. for $C_{16}H_{13}OBr$: C, 63.81; H, 4.34; Br, 26.53. Found: C, 64.10; H, 4.66; Br, 26.80.

1,3-Diphenyl-2,3-epoxy-4-bromobutanone-1 (II).—Three grams (0.01 mole) of 1,3-diphenyl-4-bromobutene-2-one-1 was dissolved in 50 ml. of methanol, and 2.3 ml. (0.02 mole) of 30% hydrogen peroxide and 2.6 cc. of 8% sodium hydroxide was added all at once. The solution was cooled and stirred for 20 minutes. The voluminous white solid was then filtered. The crude material weighed 2.6 g. and melted 120–127°. Rapid recrystallization from ether yielded a product which did not depress the melting point of pure α-diphenacyl bromide. The ultraviolet and infrared spectra of the two products were identical in all respects.

The Action of Zinc and Sodium Iodide on α- and β-Diphenacyl Bromide.—A mixture of 5.0 g. (0.016 mole) of β-diphenacyl bromide, 8.0 g. (0.053 mole) of sodium iodide and 5.0 g. (0.076 mole) of zinc (washed with dilute hydrochloric acid, water and acetone) was refluxed in 200 ml. of dry methanol for 8 hours. The solution was then filtered and added to 300 ml. of cold water. The gelatinous precipitate which formed was filtered and both solid and filtrate were extracted with ether. Upon removal of the ether, 2.6 g. of oil was obtained from which 0.15 g. of white needles, m.p. 143–144.5°, was obtained by crystallization from ethanol. This product was identical (mixed melting point and infrared spectra) with authentic 1,2-dibenzoylethane.

Three and one-half grams of α-diphenacyl bromide, and proportionate amounts of the other reagents, gave, under identical conditions, 0.35 g. of 1,2-dibenzoylethane.

NEW HAVEN, CONNECTICUT

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(16) Analyses are by Micro-Tech Laboratories, 8000 Lincoln Avenue, Skokie, Ill. The infrared spectra were determined with a Perkin-Elmer double beam infrared spectrophotometer, Model 21. Ultraviolet absorption measurements were made with a Beckman Model DU Spectrophotometer.

(17) N. Calloway and L. Green, THIS JOURNAL, **59**, 809 (1937).

[COMMUNICATION NO. 1492 FROM THE KODAK RESEARCH LABORATORIES]

The Decyanoethylation of Polyvinyl β-Cyanoethyl Ether

BY J. F. WRIGHT AND L. M. MINSK

RECEIVED MAY 13, 1952

When polyvinyl β-cyanoethyl ether is hydrolyzed with sodium hydroxide in a water–methyl cellosolve system, a decyanoethylation to polyvinyl alcohol results rather than hydrolysis of the nitrile group to yield a polymeric acid. This decyanoethylation has been studied through isolation and analysis of the polymer. First-order reaction kinetics are followed. The rate constant is directly proportional to the concentration of catalyst and independent of the concentration of polymer. The Arrhenius activation energy, ΔH, was found to be 30,600 cal. per combined monomer mole.

Introduction

The cyanoethylation of alcohols is reported to be an equilibrium reaction,[1] and the product, in the presence of alkali, is capable of regenerating the original alcohol and a polymer of acrylonitrile as:

$$ROH + CH_2{=}CHCN \rightleftharpoons ROCH_2CH_2CN$$

However, few examples of this behavior are found, the usual course of the reaction being a conversion of the nitrile group to a carboxyl. In this paper, the results of a kinetic study of the cleavage of polyvinyl β-cyanoethyl ether to regenerate polyvinyl alcohol are reported. The non-polymeric fragment was not investigated. The course of the reaction was followed by isolating the polymer, after intervals of reaction time, and analyzing it for carboxyl and nitrogen.

Ethylene glycol monomethyl ether was used as the reaction medium since it is both a solvent for the polymer and water-miscible. Sodium hydroxide, in water solution, was added as the catalyst. The upper concentration of catalyst that

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(1) H. A. Bruson, in "Organic Reactions," R. Adams, editor, and others, Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 90.

TABLE I

REPRESENTATIVE HYDROLYSIS EXPERIMENTS

Time in hours	Precipitant	Solvent for redoping	% Carboxyl[a]	% N $(a - x)$	Mole % Cyanoethylated PVA	Log $(a - x)$[b]	k[c]
Normality of NaOH, 0.111; normality of completely cyanoethylated polymer, 0.859; temp., 60.0 ± 0.4°							
0	Distilled water	Acetone	3.4	14.0	93.6	1.971	
$^{1}/_{3}$	Distilled water	Acetone	3.3	12.4	73.5	1.866	
$^{3}/_{4}$	Absolute alcohol	Acetone	3.4	9.6	47.4	1.676	1.04[d]
$1\,^{13}/_{60}$	Absolute alcohol	Acetone	6.6	8.3	38.4	1.584	0.730
$1\,^{43}/_{60}$	Absolute alcohol	Distilled water	6.6	6.1	24.9	1.396	.778
$2\,^{5}/_{12}$	3A alcohol	Distilled water	2.6	4.5	17.0	1.230	.700
$2\,^{19}/_{20}$	3A alcohol	Distilled water	2.3	3.4	12.3	1.090	.682
							0.722 ± 0.03
Normality of NaOH, 0.140; normality of completely cyanoethylated polymer, 0.859; temp., 60.0 ± 0.4°							
0	Distilled water	Acetone	5.6	13.1	81.6	1.912	
$^{1}/_{8}$	Distilled water	Acetone	6.0	10.6	55.6	1.745	1.16
$^{5}/_{6}$	Absolute alcohol	Distilled water	5.9	6.9	29.4	1.468	1.28
$1\,^{7}/_{12}$	3A alcohol	Distilled water	0.9	3.9	14.4	1.158	1.08
$2\,^{7}/_{12}$	3A alcohol	Distilled water	1.6	2.6	9.0	0.954	0.82[e]
$3\,^{1}/_{60}$	3A alcohol	Distilled water	1.6	1.9	6.5	0.813	0.85[e]
							1.17 ± 0.07

[a] Calculated as weight per cent. $CH_2{=}CH{-}OCH_2{-}CH_2{-}COOH$. [b] $(a - x)$ represented by mole per cent. cyanoethylated polyvinyl alcohol. [c] k calculated, using the second value for $(a - x)$ and all those following. [d] Neglect. [e] Neglect, as reaction near completion where results depart from first-order kinetics.

could be added was limited by the tendency of the alkali to precipitate the reaction products before completion of the reaction. Temperatures from 25 to 60° were investigated and maintained through the use of water-baths, thermostatically controlled to ±0.4°.

An acid-catalyzed hydrolysis, under conditions otherwise identical to those given, did not yield the expected polyvinyl β-carboxyethyl ether. On using an excess of hydrobromic acid, the original product was recovered unchanged after 47 hours at 60°.

Experimental

Preparation of β-Cyanoethyl Polyvinyl Alcohol.—Completely cyanoethylated polyvinyl alcohol was prepared by the method of Houtz,[2] in which 560 g. of polyvinyl alcohol (Elvanol 90-25) was treated in 4,666 ml. of acrylonitrile. The primary solutions from several reactions were mixed, made just acid to congo red with hydrobromic acid and precipitated in distilled water. The product was further purified by redissolving in acetone and precipitating in water, and was dried at room temperature in a vacuum desiccator under constant water-pump vacuum.

Anal. Calcd. for $(CH_2{=}CH{-}OCH_2CH_2CN)_n$: C, 61.8; H, 7.2; N, 14.4. Found: C, 61.0, 60.7; H, 7.2; N, 14.6, 14.6, 14.3; $\eta = 0.69 = 2.303 \log \eta_r/0.250$, where η_r is relative viscosity.

Alkaline Hydrolysis.—The polyvinyl β-cyanoethyl ether solution was prepared by dissolving 200 g. of the polymer in 2000 ml. of ethylene glycol monomethyl ether (Eastman Technical Grade) with shaking.

The solution was then put in a constant-temperature bath where it was stirred mechanically during the entire course of the reaction. Two hundred ml. of aqueous sodium hydroxide (1.5–2.0 N) was added after being brought to bath temperature. The addition was carried out slowly over a period of from 3 to 5 minutes to avoid localized precipitation. As soon as the alkali had been mixed in well, two samples of the solution were withdrawn, one of 20 ml. to be titrated with 0.1 N HCl, another of approximately 500 ml. to be precipitated. Several 400–500-ml. samples of solution were precipitated during the course of the reaction. When the final sample of solution was withdrawn, another 20-ml. sample was titrated with 0.1 N HCl. The average of the two titrations was used as the alkali concentration in the reaction mixture. As the reaction proceeds, the polymer becomes water-susceptible and finally completely water-soluble. The first samples withdrawn were precipitated in water and, when the hydrolysis had reduced the nitrogen content to about 9 to 10%, the polymers were precipitated in alcohol.

Before being precipitated, the samples of solution were made just acid to congo red with hydrobromic acid. The samples of polymer were further purified by being dissolved and reprecipitated in the appropriate solvent and precipitant, as given in Table I. These samples were dried to constant weight at room temperature under constant water-pump vacuum.

All samples were analyzed for nitrogen by the micro-Dumas method[3] and for carboxyl by direct titration in a pyridine:water:ethylene glycol monomethyl ether solution, the ratios being varied as necessitated by the solubility of the polymer. The nitrogen was calculated to combined vinyl β-cyanoethyl ether and the carboxyl to the corresponding acid. The difference between the total of these and 100% was considered to be combined vinyl alcohol. This assumption was substantiated by the reanalysis of the product, after the reacetylation of a partially decyanoethylated sample. In this case, the sum of the vinyl acetate, the vinyl β-cyanoethyl ether and corresponding acid totaled 100% within the limit of experimental error, and the molar ratios remained constant.

This reacetylation was carried out on a sample containing 9.3% nitrogen corresponding to 64.4% polyvinyl β-cyanoethyl ether, 1.8% of the corresponding acid, and 33.8% polyvinyl alcohol as obtained by difference. This represents 53.7 mole per cent. polyvinyl alcohol. The polymer was dissolved in pyridine and heated on a steam-bath with excess acetic anhydride for 24 hours. The sample was then precipitated in water, redissolved in acetone, and then reprecipitated in water. The product was dried to constant weight and analyzed for acetyl, nitrogen and carboxyl.

Nitrogen, 6.8%—equivalent to 47.1% vinyl β-cyanoethyl ether.

Vinyl β-carboxyethyl ether, 0.4%.

Acetyl, 25.4%—equivalent to 50.8% vinyl acetate, representing 54.7 mole per cent. polyvinyl acetate in the mole-

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[2] Ray C. Houtz (assigned to E. I. du Pont de Nemours and Co., Inc.), U. S. Patent 2,341,553 (1941) (Example 1).

[3] We are indebted to the Microanalytical Section of these laboratories for these analyses. Representative samples were also analyzed by the Kjeldahl procedure and found to agree.

cule after acetylation, as compared to the calculated value of 53.7 mole per cent.

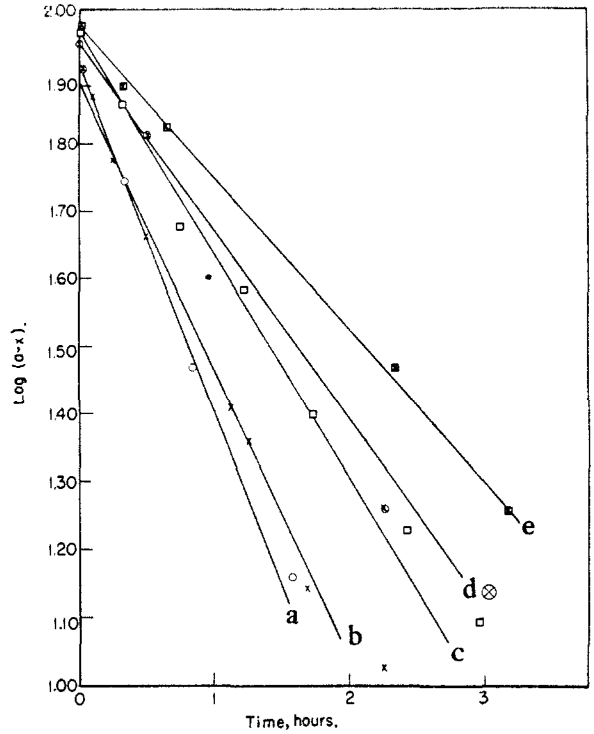

Fig. 1.—Effect of catalyst concentration and polymer concentration on the rate constant at 60°: (a), ○ N_{NaOH} = 0.140, N_{polymer} = 0.859; (b), × N_{NaOH} = 0.111, N_{polymer} = 0.859; (c), □ N_{NaOH} = 0.092, N_{polymer} = 0.859; (d), ⊗ N_{NaOH} = 0.087, N_{polymer} = 0.606; (e), ☒ N_{NaOH} = 0.059, N_{polymer} = 0.468.

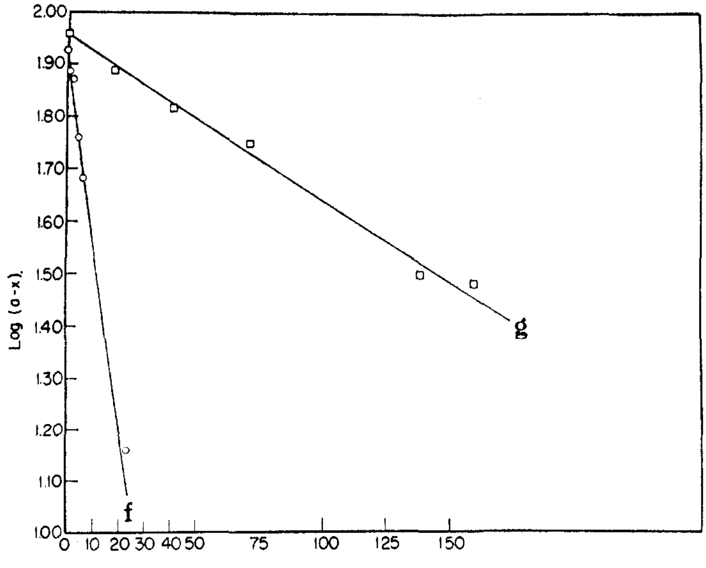

Fig. 2.—Effect of temperature on the rate constant: curve f at 40°; curve g at 25°.

The complete data for two typical reactions are shown in Table I. In Figs. 1 and 2 are shown graphically the results of the experiments wherein catalyst and polymer concentrations and temperature were varied, when these results are applied to the first-order equation

$$k = 2.303/t \log (Co/C)$$

where

k = rate constant

Co = initial amount of β-cyanoethyl ether expressed in mole per cent.

C = amount after lapse of time, t (both based on the nitrogen analysis)

The experimental conditions for the data graphed in Figs. 1 and 2 are shown in Table II.

Table II

Experimental Conditions for Data Plotted on Figs. 1 and 2

Curve	Temp., °C.	Normality Polymer	Normality NaOH	k	$k_p = K/N_{\text{NaOH}}$
a	60	0.859	0.140	1.18	0.843
b	60	.859	.111	0.917	.826
c	60	.859	.092	.722	.784
d	60	.606	.087	.653	.752
e	60	.468	.059	.466	.791
f	40	.859	.120	7.90×10^{-2}	
g	25	.859		6.55×10^{-3}	

When the hydrolysis products were isolated, those containing more than approximately 40 mole per cent. polyvinyl β-cyanoethyl ether were water-insoluble. Those containing less than approximately 25 mole per cent. polyvinyl β-cyanoethyl ether were entirely soluble in water from 0° to the boiling point. The copolymers having between 25 and 40 mole per cent. β-cyanoethyl ether exhibited an inverse temperature solubility. The temperature at which the polymer came out of solution at a concentration of 0.25 g./10 ml. of solution was called the "critical solution temperature" (C.S.T.). In one case, a sample containing 6.1% nitrogen and having a C.S.T. of 67–68° exhibited a C.S.T. drift with time in solution such that, within 72 hours, the polymer was completely soluble at all temperatures. Reprecipitation and subsequent drying showed no change in analysis, although the C.S.T. phenomenon was no longer exhibited. Figure 3 shows the C.S.T. to be inversely proportional to the mole per cent. cyanoethylated over a narrow range.

Results and Discussion

It is generally agreed that treatment of β-cyanoethyl ethers with mineral acids produces a hydrolysis of the nitrile to carboxyl.[4,5] Alkaline treatment, however, may produce similar hydrolysis of the nitrile[5] or may cause a cleavage at the ether oxygen.[1,6]

The data of Table I show that, when polyvinyl β-cyanoethyl ether is subjected to alkaline treatment, a decyanoethylation results which may occur either through a direct removal of acrylonitrile or by a hydrolysis of the nitrile group to carboxyl, followed by removal of acrylic acid, or through both occurring simultaneously. The data indicate the direct decyanoethylation to be the principal reaction though the presence of a small amount of carboxyl in the reaction product may be an indication that initial hydrolysis of the nitrile, followed by the removal of acrylic acid, occurs but to a much lesser extent. This decyanoethylation follows first-order kinetics.

Although the kinetic study of the reaction is limited by the inherent difficulties in isolating,

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[4] J. H MacGregor and C. Pugh, *J. Chem. Soc.*, 535 (1945).

[5] R. V. Christian, Jr., and R. M. Hixon, This Journal, **70**, 1333 (1948).

[6] Wm. P. Utermohlen, Jr., *ibid.*, **67**, 1505 (1945).

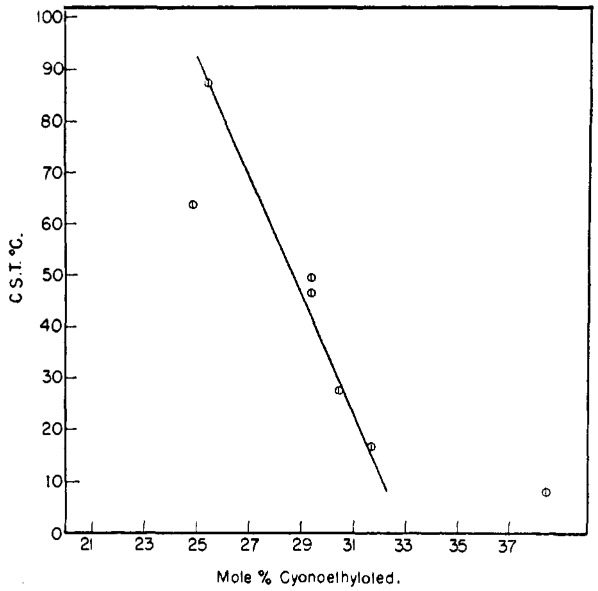

Fig. 3.—Dependence of solution temperature on mole per cent. cyanoethylated.

handling and purifying polymers, it is interesting that the laws of classical kinetics are so closely adhered to, as illustrated in Table I and Figs. 1 and 2, within the temperature and concentration range studied.

The intercept on the ordinate in Figs. 1 and 2 is due to some reaction taking place, during the mixing, before the initial sample was withdrawn. The time of this withdrawal was designated as zero time.

The data showing the effects of sodium hydroxide concentration on the reaction are plotted in Fig. 4. The relationship is linear within the limits of experimental error but intercepts the abscissa. The quantity of sodium hydroxide represented by the intercept is equal within the limits of experimental error to the vinyl β-carboxyethyl ether present.

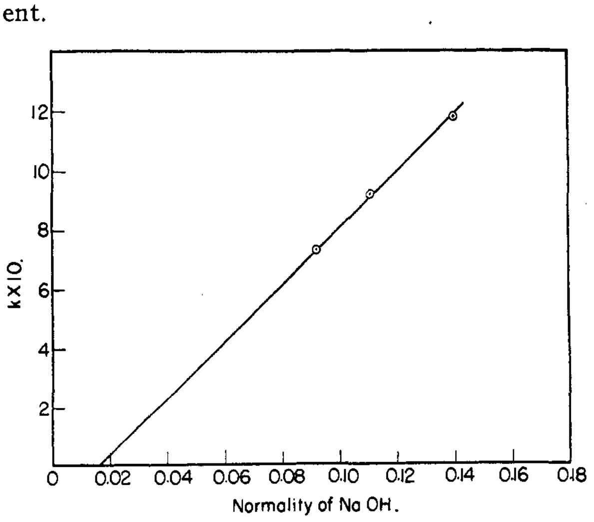

Fig. 4.—Dependence of k, the rate constant, on catalyst concentration expressed as normality of sodium hydroxide.

Both alkali and polymer concentration were varied by increasing the quantity of solvent in experiments designated d and e in Table II. It is evident from Table II, since the value of the rate constant divided by the alkali concentration approaches a constant, that the rate constant is independent of the polymer concentration.

In Table III are shown the data to illustrate the effect of temperature on rate of reaction.

TABLE III

EFFECT OF TEMPERATURE ON RATE OF REACTION

t	k
333	9.17×10^{-1}
323	3.74×10^{-1}
313	7.90×10^{-2}
298	6.55×10^{-3}

The Arrhenius temperature relationship is followed, as illustrated in Fig. 5. From the slope of the line in Fig. 5 and the Arrhenius equation, the Arrhenius activation energy, ΔH, is found to be 30,600 cal. per mole.

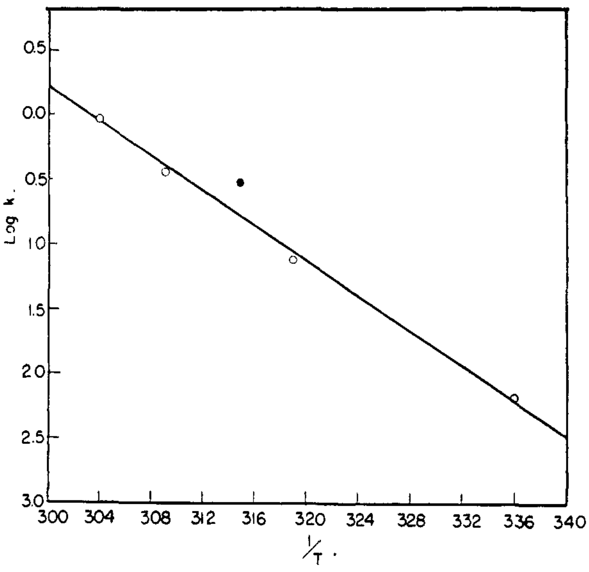

Fig. 5.—Dependence of k, the rate constant, on temperature of hydrolysis.

Since this work has been carried out, MacGregor[7] has confirmed the results by reporting that fission at the ether linkage producing the original alcohol does occur. He also states that hydrolysis of the cyanoethyl groups to carbamylethyl only occurs to a negligible extent. Figures showing the course of the reaction rates are also shown in which a reversal in the reaction is illustrated, although attributed to the formation of carboxyethyl groups. It may very well be that the reverse reaction occurs owing to a shift in the equilibrium because of the consumption of the excess acrylonitrile through hydrolysis.

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[7] J. H. MacGregor, *J. Soc. Dyers Colourists*, **67**, 66 (1951).