been solidified from melts at different rates demonstrate that the degree of polycrystallinity as well as the perfection of the crystal lattice is dependent on the rate of cooling. Annealing completely quenched specimens (both oriented and unoriented) restores the crystalline lattice arrangement in an amount which increases with the annealing temperature. The macromolecular behavior has been related to that of ordinary monomeric systems.

2. Parallel with the X-ray results a continuous increase in Young's modulus with decreasing rate of cooling from the melt is observed, indicating an increased degree of crystallinity.

3. Both the X-ray and mechanical data are considered in terms of the segment theory of chain polymers.

4. The results obtained support the view that segments of the chain molecules may exist as crystalline, mesomorphic or as non-crystalline (amorphous) regions in the solid polymers.

SUMMIT, N. J. RECEIVED SEPTEMBER 19, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Effect of Solvation upon the Dissociation of Acetone Cyanohydrin

BY T. D. STEWART AND B. J. FONTANA

Following Lapworth's[1] study of the alkali catalysis of cyanohydrin formation, Ultée[2] determined the degrees of dissociation of a number of cyanohydrins, in the absence of solvent and with a trace of aqueous potassium hydroxide as catalyst. The pure substances, mostly aliphatic aldehyde and ketone derivatives, were dissociated to the extent of 10% or less. W. J. Jones[3] established the nature of the equilibrium as

$$\mathrm{R_2C(OH)CN} \overset{K_\mathrm{I}}{\rightleftarrows} \mathrm{R_2C{=}O + HCN} \qquad \text{(I)}$$

in both water and 98% ethanol through large variations in the initial concentrations of the reactants. Lapworth and Manske[4] made an extensive investigation of a number of cyanohydrins in 96% ethanol, using a trace of tripropylamine as catalyst. In seven compounds investigated by both Ultée and Lapworth, including one cyclic and one aromatic derivative, the same order for the degree of dissociation is observed (except for one minor reversal); hence it would appear that specific solvent effects are absent except as the pure cyanohydrins, being themselves alcohols, constitute a solvent medium comparable to ethanol. The possible effects of solvents as dipoles have been discussed by Moelwyn-Hughes and Sherman,[5] who conclude that dipolar interaction may involve from 200 to 15,000 calories. C. H. Li and T. D. Stewart[6] reported the dissociation of acetone cyanohydrin in a number of solvents, using in each case both secondary and tertiary amines. They assumed the equilibrium

$$\mathrm{R_2C(OH)CN + R_3N} \rightleftarrows \mathrm{R_2C{=}O + R_3NH^+ + CN^-} \qquad \text{(II)}$$

to account for the variation in titratable cyanide which accompanied variation in the character of the amine. Through this they obtained correct values for the relative basicities of the amines in water and the lower alcohols. On the basis of the present work their conclusions must be corrected. Although their data in water solution can be duplicated, in the alcohols it is found that amines exert a catalytic influence only and do not shift any equilibrium.[7]

The following experiments were performed to gain further information upon the nature of cyanohydrin dissociation.

Experimental Results

The Dissociation in Water.—In water alone acetone cyanohydrin dissociation reaches equilibrium in eighteen hours; with amine present attainment of equilibrium is instantaneous. Table I includes data of Li and Stewart and of Jones. K_I and K_II refer to equilibrium constants based

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[1] A. Lapworth, *Trans. Chem. Soc.*, **79**, 1268 (1901); **83**, 1001 (1903).

[2] A. J. Ultée, *Rec. trav. chim.*, **28**, 1, 248, 257 (1909).

[3] W. J. Jones, *J. Chem. Soc.*, **105**, 1560 (1914).

[4] A. Lapworth and R. H. F. Manske, *ibid.*, 2533 (1928); 1976 (1930).

[5] Moelwyn-Hughes and A. Sherman, *ibid.*, 101 (1936).

[6] C. H. Li and T. D. Stewart, THIS JOURNAL, **59**, 2596 (1937).

[7] In non-polar solvents the situation is more complicated. The source of Li and Stewart's difficulty was probably experimental, in not attaining true equilibrium in the absence of amine and in the case of secondary amines allowing too much time, thereby permitting some aminonitrile formation.

upon Equations I and II, respectively The latter has been corrected for the dissociation represented by Equation I (see Experimental Part).

TABLE I

ACETONE CYANOHYDRIN DISSOCIATION IN WATER AT 25°

Initial concentrations		Equil. concentrations			
Cyanohydrin	Triethylamine	Cyanohydrins	Cyanide	K_I	K_{II}
0.1000	0.1000	....	....		2.66[a]
.1096	.0680	0.0261	0.0835		2.65
.0610	.1553	.0008	.0602		3.01[b]
.1000	....	....	....	0.0649[a]	
.1000	....	....	....	.0796[c]	
.1227	....	.0602	.0625	.0649	
.1245	....	.0613	.0632	.0651	

[a] Li and Stewart. [b] This figure agrees well considering the experimental error in this case. [c] Jones.

In this solvent the activity of hydrocyanic acid is reduced to a greater degree by amine than is the activity of the cyanohydrin; the assumption of salt formation and complete ionization is reasonable.

The Dissociation in Alcohols and Acetone.—Whereas in water solution there is evidence of interaction between an amine and hydrocyanic acid, the data in Tables II and III show complete lack of interference with the equilibrium of Equation I by amine. With no amine present equilibrium is reached only after several days, while in its presence it is reached in a few minutes.

TABLE II

INDEPENDENCE OF ACETONE CYANOHYDRIN DISSOCIATION OF THE AMOUNT AND NATURE OF AMINE CATALYST IN PROPANOL (25°)

Initial concns.[a]		Equil. concn.
Cyanohydrin	Triethylamine	Cyanide
0.1036	0.3029	0.03959
.1077	.1573	.04042
.1035	.1003	.03993
.1006	.0704	.03948
.1049	.0164	.0406
.1017	none	.03945
	Tri-*n*-butylamine	
0.0938	0.02707	0.03741
.0951	.06147	.0376
	Diethylamine	
0.1009	0.1003	0.04021
.0996	.1030	.03972

[a] At initial concentrations higher than 0.1 *M*, in the absence of amine, erratic results were obtained. Successive samples taken from a presumed equilibrium mixture would apparently increase or decrease in dissociation; no such difficulty occurred in the presence of amine. Solutions containing secondary amine must be analyzed within an hour to avoid the slow aminonitrile formation; tertiary amine solutions may stand for a day without change.

TABLE III

THE DISSOCIATION OF ACETONE CYANOHYDRIN IN ALCOHOLS AND ACETONE AT 25°

Initial concns.		Equil. concn.	
Cyanohydrin	Triethylamine	Cyanide	K_I
	Methanol		
0.1222	0.05697	0.05797	0.0523
.1050	.09297	.05192	.0508
.05834	.036	.03523	.0537
	Ethanol		
.3724	.1974	.09393	.0318
.09933	.04153	.04265	.0321
.09855	.1519	.04198	.0312
.03160	.02548	.01957	.0318
.01512	.04974	.01086	.0277
	Butanol		
.1207	.05992	.04217	.0226
.1201	.2613	.04203	.0226
.06053	.04296	.02746	.0228
.02922	.03530	.01654	.0216
	2-Methylpropanol		
.1595	.036	.05180	.0249
.06307	.036	.02896	.0246
.03083	.036	.01749	.0229
	1,1-Dimethylethanol		
.1041	.07297	.04261	.0295
.06097	.04076	.03017	.0295
.02960	.02773	.01807	.0279
	Acetone		
			K_I/Acetone
.1118	.0739	.00094	.00845
.1076	.2217	.00094	.0088

The value of K_I decreases markedly at low initial concentrations of cyanohydrin; the effect is outside the experimental error and is believed due to small amounts of aldehyde in the alcohols.[8] In certain alcohols it served to obscure the true value of K_I, but close values taken at fairly high concentrations of cyanohydrin are as follows: propanol, 0.028; pentanol, 0.018; 2-propanol, 0.022; 2-butanol, 0.0247. The failure of amines to affect the degree of dissociation in alcohols is hardly to be expected in view of the dissociation constants of amines (*ca.* 1×10^{-5})[9] and hydrocyanic acid (1×10^{-13})[10] in methanol. If, however, the cyanohydrin and hydrocyanic acid differ little from the alcohol solvent in acidity, the amine would be distributed among them in proportion to the amounts of each present, leading to little interaction between the amine and solutes.

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(8) This aberration is presented in more detail in a note by the authors, THIS JOURNAL, **62**, 2878 (1940).

(9) L. D. Goodhue and R. M. Hixon, *ibid.*, **56**, 1329 (1934); **57**, 1688 (1935).

(10) L. S. Guss, private communication; I. M. Kolthoff and L. S. Guss, *ibid.*, **60**, 2516 (1938).

Within the group of alcohols studied, the equilibrium is shifted toward the cyanohydrin in the more basic or less acidic, *i. e.*, in those of increasing chain length. Most of this shift operates through interaction between acetone as a base and the solvent as an acid. On this basis, in tertiary butyl alcohol less dissociation should occur than in isopropyl alcohol; the reverse is true.

In pure acetone as solvent the dissociation is slow and the amine does not alter the equilibrium. This indicates that the solutes as acids are distributed between the solvent and catalyst as bases, and that in base strength the latter are comparable to each other in this medium.

The Dissociation in Non-Polar Solvents.—For the sake of brevity only part of the data obtained are given in Table IV. It is seen that triethylamine, instead of increasing the dissociation, actually decreases it. Values in the absence of catalyst could not be obtained because of the extreme slowness of the reaction, but since the dissociation is not altered seriously when the amine is less than 0.01 *M* the values at that concentration of catalyst are considered representative of the pure solvent. Insolubility of the cyanohydrin in hexane prevents determination in that solvent.

TABLE IV

THE DISSOCIATION OF ACETONE CYANOHYDRIN IN NON-POLAR SOLVENTS AT 25°

Initial concns. Cyanohydrin	Initial concns. Triethylamine	Equil. concn. Cyanide	K_I
	Carbon Tetrachloride		
0.1037	0.1562	0.0359	0.0190
.1105	.0690	.0438	.0283
.1102	.0107	.0506	.0430
.0567	.0050	.0329	.0457
	Benzene		
.1097	.1428	.0568	.0612
.1099	.1112	.0592	.0692
.1032	.0383	.0644	.1069
.1144	.0107	.0729	.1281
.0577	.0050	.0432	.1282
	Dioxane		
.0960	.0979	.0215	.0062
.1266	.0528	.0352	.0135
.1248	.0078	.0413	.0205
.2180	.0143	.0569	.0201
	Chloroform		
.1015	.1005	.0712	.168
.1137	.0517	.0809	.200
.1091	.0107	.0839	.279
.0529	.0050	.0457	.290

The results in carbon tetrachloride and benzene are somewhat less reliable than in other solvents because of the volatility of hydrocyanic acid. The solutions stood one day to reach equilibrium; greater time produced a discoloration of the carbon tetrachloride solution and while a slow reaction of the amine with the chlorinated solvents was evident in three days in the absence of cyanohydrin, in its presence there was no apparent reaction.

The effect of amine in repressing dissociation in these solvents is most simply explained through the assumption of a cyanohydrin–amine complex, which more than compensates for any hydrocyanic acid–amine complex.

Dioxane appears to be a weaker base than is triethylamine, since the latter displaces it from its cyanohydrin complex (see below). If the activity coefficient of the amine in acetone is comparable to that in dioxane, this places acetone as a stronger base than dioxane.[11] There remains the question of identity in type of complex in all cases. While the strong bases are catalysts for the dissociation and form complexes, the weaker bases such as dioxane are not catalysts even though their cyanohydrin complexes are very stable.

Chloroform as pure solvent increases the dissociation as compared to carbon tetrachloride. This is due to the interaction of acetone and chloroform. Similarly benzene exhibits a marked acidic property.[12]

Heat of Dissociation.—K_I has been evaluated at different temperatures in some cases, and the values of ΔH are given in Table V.

TABLE V

THE HEAT OF DISSOCIATION OF ACETONE CYANOHYDRIN IN VARIOUS SOLVENTS

Solvent	K_I 35°	K_I 25°	K_I 0°	ΔH (cal./mole)
Water	0.110	0.0649		9,590
Ethanol	.0565	.0319		10,430
		.0319	0.00647	10,360
Benzene	.204	.128		8,445
Chloroform		.285	.0696	9,120

Relative Rates of Dissociation.—Significant differences occur in the rates of dissociation in different solvents with a given catalyst as shown in Figs. 1 and 2. The order of effectiveness is butanol > chloroform, carbon tetrachloride >

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(11) W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939); **8**, 170, 516 (1940), from spectrographic analysis finds ethers to be stronger bases than ketones.

(12) Compare G. F. Zellhoefer, M. J. Copley and C. S. Marvel, THIS JOURNAL, **60**, 1337 (1938); **61**, 3550 (1939), for evidence of hydrogen bond formation.

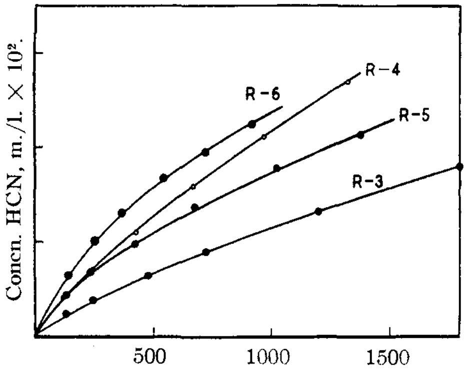

Fig. 1.—Rates of dissociation of 0.100 *M* acetone cyanohydrin in benzene (R_3), chloroform (R_4), carbon tetrachloride (R_5) and butanol (R_6): catalyst 0.0106 *M* triethylamine; temp., 25°.

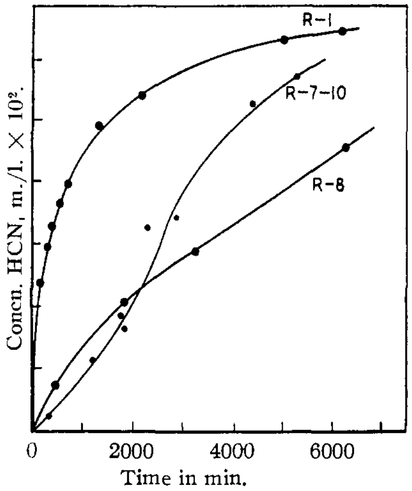

Fig. 2.—Rate of dissociation of acetone cyanohydrin in propanol (R_1), cyanohydrin 0.0830 *M*, no catalyst; dioxane (R_{7-10} at 25°, R_8 at 35°) cyanohydrin 0.0830 *M*, catalyst triethylamine 0.0106 *M*.

benzene ≫ dioxane. The pure solvents could not be compared because of the virtual nonexistence of the reaction in pure non-polar solvents and because of the danger of small amounts of catalyst present in the polar solvents. In water and the lower alcohols the catalyzed reaction is too fast to measure. Attempts now under way to obtain the rate law in benzene for the dissociation show that the reaction is very complex. In dioxane the slowness of the reaction, the inhibition period (at 25°), and the low value of K_I (Table V) with a marked repression of the dissociation by amine, all point to a dioxane–cyanohydrin complex of great stability. Since in benzene (unpublished work by H. Heckel of this Laboratory) the dissociation appears to involve a cyanohydrin–amine complex and a second cyanohydrin molecule, it is thought that in dioxane the inhibition period is due to slow formation of cyanohydrin–amine complex up to a steady state concentration, slow because of the necessity of replacing the dioxane molecule. At 35° the steady state is rapidly reached.

An ionizing solvent such as water may well permit an approach to the Lapworth mechanism of dissociation.

Experimental Part

Preparation of Materials.—Acetone cyanohydrin was prepared by the conventional methods[2,6] and distilled *in vacuo* after adding a few drops of concentrated sulfuric acid from an all-glass apparatus which had been thoroughly treated with acid, washed, and dried. A pure sample does not discolor nor develop odor of hydrocyanic acid on standing: b. p. 47–48° (2 mm.), 73–74° (10 mm.), 77–78° (14 mm.). A sample analyzing 99.6% pure gave $n^{25}D$ 1.3894.

Amines.—The commercial Eastman Kodak Co. product was stored over potassium hydroxide pellets for several weeks and fractionated from fresh potassium hydroxide through a one-meter Podbielniak type column; boiling range less than 0.2°.

Acetone.—Three liters were refluxed over 50 g. of solid potassium permanganate for several hours, distilled off and redistilled from anhydrous potassium carbonate; about 75 cc. of pure acetic anhydride was added (for drying) and the mixture fractionated through a three-meter (*ca.* 18-plate) column; b. p. (760) 56.17°; $n^{25}D$ 1.35633.

Alcohols. Method A.—Commercial c. p. absolute alcohol was refluxed over lime for several days, distilled off through a one-meter column and fractionated through a three-meter column from fresh lime.

Method B.—Hexane or benzene (50 cc.) was added to 2 liters of commercial alcohol and the azeotrope removed by distillation; this was followed by distillation through the three-meter column.

Method C.—Commercial c. p. propanol was 0.2 *M* in allyl alcohol. It was treated with bromine to a yellow color, hydrolyzed in 6 *N* sodium hydroxide (two moles per mole of bromine) and distilled from the alkali. Treatment B was then applied.

Method D.—Commercial *t*-butyl alcohol was added to water and the azeotrope removed through the three-meter column. Method B was then used for drying the distillate.

Alcohol	Purification	B. p. (760), °C.	$n^{25}D$
Methanol	A	64.55	1.32710
Ethanol	A	78.42	1.35966
Propanol	B	97.49	1.38404
	C	97.53	1.38377
		97.59	
2-Propanol	B (hexane)	82.28	1.37527
Butanol	A	117.69	1.39735
2-Butanol	A	99.58	1.39519
2-Methylpropanol	B (hexane)	107.94	1.39379
1,1-Dimethylethanol	D M. p.	25.5	
Pentanol	B (benzene)	137.73	1.40896
		137.91	

Samples of propanol were also distilled from lime as in A; 2-propanol was also distilled from metallic calcium; lime was avoided in the treatment of 1,1-dimethylethanol and pentanol.

Carbon tetrachloride and chloroform were stored over calcium chloride for several months, distilled after decantation, refluxed over "Drierite" and fractionated from fresh drierite through the three-meter column: CCl_4, b. p. 76.67°, $n^{25}D$ 1.45754; $CHCl_3$, b. p. (754.6) 60.91°, $n^{25}D$ 1.44345.

Benzene.—Commercial thiophene-free benzene was dried over sodium and fractionated from fresh sodium through the three-meter column: b. p. (760) 80.15°, $n^{25}D$ 1.49658.

Dioxane was stored over potassium hydroxide pellets for several weeks, distilled and dried over potassium carbonate, then decanted and distilled from sodium through the three-meter column: b. p. (760) 101.19°, $n^{25}D$ 1.4022.

Procedure was essentially the same as by Li and Stewart.[6] Solutions were prepared by adding weighed amounts of cyanohydrin and amine to the solvent in calibrated flasks, and diluting to volume after temperature equilibrium was reached. Aliquots were added to excess 0.02 *N* silver nitrate in 0.25 *N* nitric acid with vigorous mixing; silver cyanide was filtered off, washing with 0.25 *N* nitric acid, and the excess silver titrated with thiocyanate, using ferric alum indicator. Practice was required to obtain the correct end-point in some cases due to coagulation of the silver thiocyanate. In some cases the total cyanide content was determined as a check on the composition and procedure. Equilibrium in some cases was approached from solutions composed of weighed or analyzed amounts of acetone, hydrocyanic acid and amine, with good agreement. In rate determinations the amine was first added, then an approximate amount of cyanohydrin, and the latter at zero time obtained by analysis. End-points were accurate to 0.04 cc. and except for very low or very high degrees of dissociation the analyzed concentrations were reproducible to 0.2%. Values of K_I in some solvents could be reproduced to 1%, in others a 3% uncertainty exists.

If a and b are, respectively, the initial amine and cyanohydrin concentrations (moles/liter) and c the equilibrium concentration of titratable cyanide, then in the absence of amine (Equation I)

$$K_I = (c)^2/(b - c)$$

In water solution, in the presence of amine, Equation II is assumed, correcting for Eq. I.

$$K_{II} = \frac{c(c - K_I(b/c - 1))^2}{(a - c + K_I(b/c - 1))(b - c)}$$

Summary

The dissociation of acetone cyanohydrin into acetone and hydrocyanic acid is catalyzed by amines in all solvents; the catalyzed reaction is immeasurably rapid in water and the lower alcohols, measurable in butanol and non-polar solvents and extremely slow in dioxane. The degree of dissociation is increased by amines in water, is totally unaffected in nine different alcohols and in acetone by amine, and is decreased in carbon tetrachloride, benzene, chloroform and dioxane. These results are contrary to the findings of Li and Stewart. The pure solvents, or with a trace only of catalyst, affect the rates and equilibria of dissociation in a manner correlatable with their capacities to form hydrogen bond complexes and to act as proton sources. The simple Lapworth dissociation mechanism may be true only in water solutions. The heats of dissociation in four types of solvent vary from 8400 to 10,400 cal./mole. The results indicate that in alcohols hydrocyanic acid and amines do not react to a measurable extent.

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[CONTRIBUTION FROM THE RESEARCH DIVISION OF THE NEW JERSEY ZINC COMPANY (OF PA.)]

Studies of the Ternary Systems $ZnSO_4$–H_2SO_4–H_2O from −5 to 70° and ZnO–SO_3–H_2O at 25°

BY L. C. COPELAND[1] AND O. A. SHORT[1]

Introduction

The phase diagram for the ternary system zinc sulfate–sulfuric acid–water has been the subject of investigation of several authors. Most of the articles, however, have been limited to one or two temperatures and in general show poor agreement. The present paper is an effort to complete the data from −5 to 70° and to show the range of existence of the various hydrates of zinc sulfate. No data were obtained, however, above 60% sulfuric acid except in the case of a few measurements at 25°. Some data obtained for the basic range of the system zinc oxide–sulfur trioxide–water at 25° indicate the formula of basic zinc sulfate at this temperature.

Ternary System $ZnSO_4$–H_2SO_4–H_2O

Experimental Method.—Baker c. p. analyzed chemicals were used throughout the study with no additional puri-

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