methyl groups compared with the hydrogen atoms that they displace.

Summary

1. The second order rate constants for the reaction of nitroethane with ammonia, methyl-, dimethyl- and trimethylamine in water at 0 and 5.2° are reported.

2. The values of the rate constants at 0° are calculated from equilibrium data for the reaction of ammonium ion, methyl-, dimethyl- and trimethylammonium ions with the anion of nitroethane.

3. The heats and entropies of activation for the above reactions are computed.

4. The interpretation of the data indicates that the activated complex is not as strongly solvated as the product ions but more solvated than the reactants.

5. The decreased base strength of trimethylamine appears to be due to the decreased solvation energy and hence increased reactivity of the trimethylammonium ion.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 24, 1947

CONTRIBUTION FROM THE ARMOUR RESEARCH FOUNDATION OF THE ILLINOIS INSTITUTE OF TECHNOLOGY]

Crystallization of *p,p'*-DDT from Binary Melts

BY VICTOR GILPIN,[1] WALTER MCCRONE, ANNETTE SMEDAL AND HELEN GRANT

Introduction

Little work has been reported in recent years on the linear crystallization velocity (C.V.) of supercooled melts of organic compounds. Undoubtedly, part of this lack of interest has been due to the belief that C.V. measurements have no physical significance, because the problem of conducting the heat of crystallization away from the solid-liquid interface has made true temperature measurements difficult.[2,3] This difficulty has arisen in two ways. In the first place, the majority of investigators have been interested in the maximum C.V.; as Michel[4] has shown, this quantity is of value as a criterion of purity, but, due to the rapid movement of the crystal front, the temperature recorded is that of the thermostat, not that of the interface. In the second place, most previous workers employed capillary tubes of several millimeters bore; the crystal front accordingly had only a small portion of its surface exposed to the thermostat.

It is believed that the method recently developed for microscopic quantitative analysis of *p,p'*-DDT[5] avoids both these difficulties, and permits the measurement of true equilibrium temperatures over a limited range. The method employs thin films of the melt (less than 0.1 mm.) which have a correspondingly larger fraction of the interface in contact with the thermostat. Measurements are made on the lower temperature branch of the C.V. *vs.* temperature curve, in which region the rates are relatively slow, and where, moreover, rate measurements are uncomplicated by the transition in the reverse direction. It should be possible to attempt theoretical interpretation of data obtained in this way. The aim of the present and future work is to provide such data.

No claim of originality is made for the method of measuring such rates under the microscope. Dreyer[6] appears to have been the first to measure the C.V. on microscope slides.

Experimental Results

Effect of Temperature.—The technique described previously for *o,p*-DDT/*p,p'*-DDT mixtures[5] was used to establish C.V. *vs.* temperature curves for various mixtures of *p,p'*-DDT with 1,3,5-triphenylbenzene (TPB) and with 5-methyl-2-isopropylphenol (thymol). Figure 1 shows the general form of such curves. To avoid crowding, some experimental curves were omitted. In agreement with much earlier work on binary melts[7] the scatter of experimental points becomes considerable for *p,p'*-DDT mixtures containing more than about twenty-five weight per cent. of a second component. Thymol results are indicated in the smoothed curves of Fig. 2, in the rate *vs.* composition form used previously,[5] because a rate *vs.* temperature plot leads to undue crowding here. A similar increase in C.V. on addition of certain types of impurities was first noted by Dreyer.[8]

In Fig. 4 of the previous publication,[5] the Arrhenius lines were drawn through the raw experimental data. Because of the scatter of experimental points, it is now believed that a better representation of the true trend of the Arrhenius lines is achieved by using smoothed data from the C.V. *vs.* temperature curves. In Fig. 3, the best line was drawn through the smoothed data for pure *p,p'*-DDT, and the other lines were drawn parallel (except for thymol). The same procedure was used in constructing the graph for TPB mixtures (Fig. 4). Only one point of the one per cent. thymol line has been included, and several thymol

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[1] Present address: School of Chemistry & Physics, Pennsylvania State College, State College, Pa.

(2a) Tammann, "Kristallisieren and Schmelzen," Leipzig, 1903; (2b) Frenkel, "Kinetic Theory of Liquids," Oxford University Press, London, 1947.

(3) Luyet, *Biodynamica*, No. 48, 28 (1939).

(4) Michel, *Bull. soc. chim. Belg.*, 48, 105 (1939).

(5) McCrone, Smedal and Gilpin, *Ind. Eng. Chem., Anal. Ed.*, 18, 578 (1946).

(6) Dreyer, quoted in (1).

(7) Bogojawlensky, *Z. physik. Chem.*, 27, 585 (1898).

(8) Dreyer, *ibid.*, 48, 467 (1940).

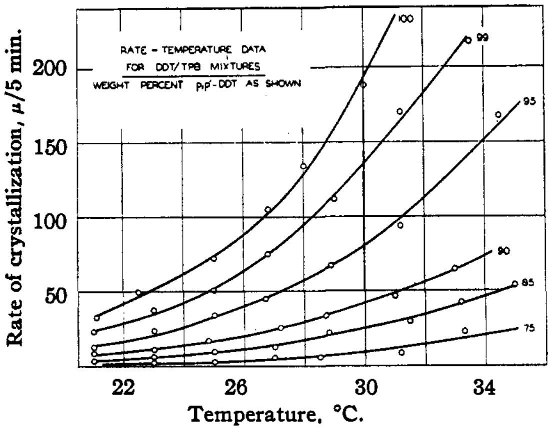


Fig. 1.—The effect of temperature on C.V. of p,p'-DDT/TPB mixtures.

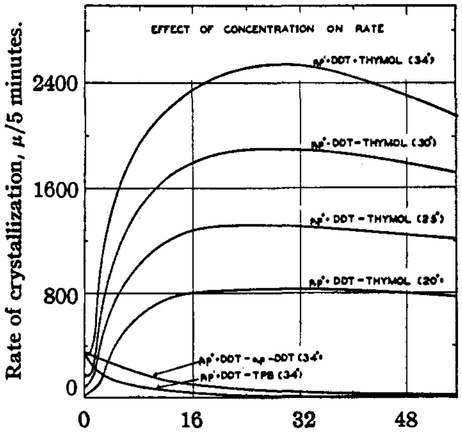


Fig. 2.—The effect of concentration on C.V. of p,p'-DDT/thymol mixtures.

lines have been omitted, to avoid crowding the graph. Because of very poor reproducibility of results for thymol mixtures, of compositions between 99 and 92% DDT, no data were recorded in this range.

Figures 3 and 4 show the Arrhenius-type relation.

$$\text{C.V.} = Be^{-E_c/RT}$$

holding remarkably well at lower temperatures. At these lower temperatures, the apparent activation energy of crystallization (E_c) for p,p'-DDT is 33.4 kcal., and this does not change when this compound is growing from mixtures containing TPB, o,p-DDT, or very small amounts of thymol. In other words, these compounds do not make it easier or harder for p,p'-DDT to crystallize. They do decrease the rate, however by lowering the value of B. The importance of B, which may include an entropy term, suggests that structural symmetry of the second component may play some part in the rate determining process in these mixtures. Larger concentrations of thymol, however, do lower the apparent activation energy to 12.1 kcal., and do appear to make it easier for p,p'-DDT to crystallize in thymol mixtures.

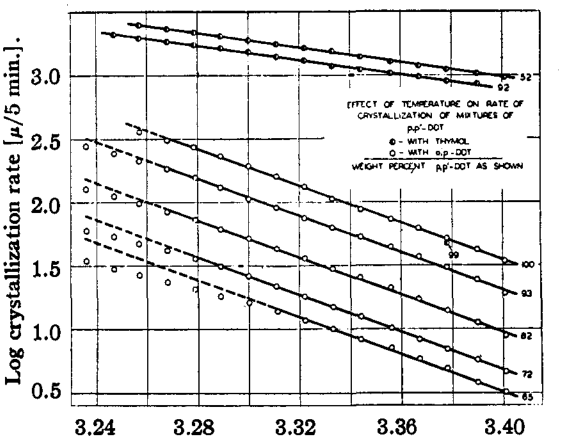


Fig. 3.—Arrhenius-type relations for mixtures of p,p'-DDT with o,p-DDT and thymol.

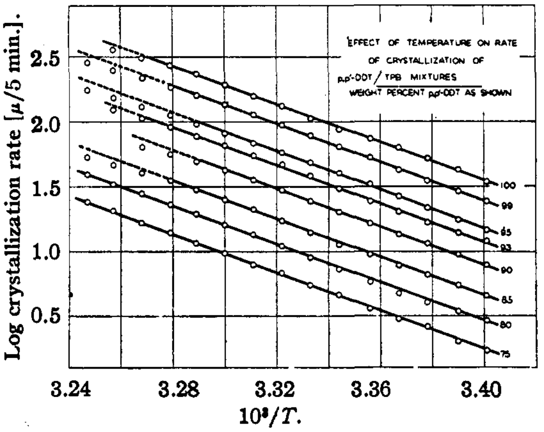


Fig. 4.—Arrhenius-type relations for p,p'-DDT/TPB mixtures.

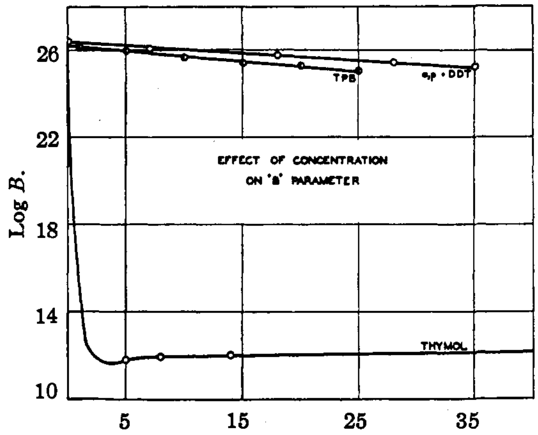
A survey of earlier work reveals only three compounds for which enough of the lower temperature branch of the C.V. *vs.* temperature curve has been reported to make possible a calculation of E_c. Dreyer's figures[6] for benzil-o-carboxyllic acid yield a value of 32.9 kcal. From the data of Michel[4] on cholesterol methyl carbonate, E_c is calculated to be 13.2 kcal. The glycerol data of Volmer and Marder[9] give a value of 10.2 kcal. for E_c. A theoretical interpretation of these activation energies must await further experimental work.

The B parameter bears a linear relation to the concentration of o,p-DDT and TPB, as shown in Fig. 5. If mole fraction is plotted, instead of weight fraction, the lines for o,p-DDT and TPB do not coincide. This disagrees with von Pickardt[10] but agrees with Dreyer.[8]

It is possible to derive equations relating the

(9) Volmer and Marder, *Z. physik. Chem.*, **A154**, 97 (1931).

(10) Von Pickardt, *ibid.*, **48**, 17 (1902).



Concentration of second component, weight per cent.

Fig. 5.—Relation of the concentration to Arrhenius "B" parameter.

variables for crystallization of mixtures containing *o,p*-DDT or TPB. These equations are more accurate in predicting rates, over a wider variety of conditions, than the equation developed previously.[5] For *p,p'*-DDT, or for mixtures in which E_c does not change

$$\text{C.V.} = Be^{-33{,}400/RT}$$
$$\text{or } \log \text{C.V.} = \log B - 7.30 \times 10^3/T$$

From Fig. 5

$$\log B = 26.36 - 3.06 \times 10^{-2}C \text{ (for } o,p\text{-DDT mixtures)}$$
$$\log B = 26.27 - 5.05 \times 10^{-2}C \text{ (for TPB mixtures)}$$

where C.V. is in microns per five minutes, and C is the weight per cent. impurity.

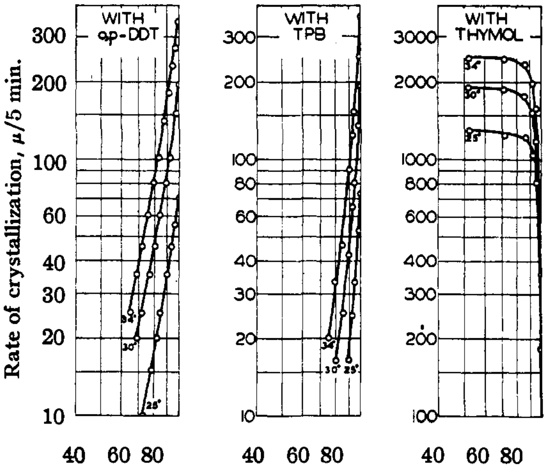
Table I compares rates predicted by these equations with the observed values. The deviation of calculated from observed values becomes considerable at the highest experimental temperatures, where the Arrhenius equation ceases to hold accurately.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED VALUES OF C.V.

	o,p-DDT mixtures			TPB mixtures		
T, °C.	C, wt.%	C. V., obs.	C. V., calcd.	C, wt.%	C. V., obs.	C. V., calcd.
21	2	29	30	1	24.5	25.0
21	10	15	16	5	14.5	15.0
21	26	5	5	10	7.8	8.5
25	4	55	55	1	53	53
25	10	37	36	10	17	18
25	28	10	10	20	5.8	6.5
29	1	145	145	1	113	132
29	11	70	71	10	36	39
29	30	19	19	25	7.9	6.9
33	2	277	295	1	215	230
33	24	55	58	7	106	115
33	33	28	31	25	16.6	14.2

Effect of Concentration.—The nature of the crystallization of *p,p'*-DDT is such that the crystal front advances, apparently, into a melt of nearly constant composition. Consequently, the isothermal rates measured for a given concentration are constant, unless the second component exceeds about 25%, when irregularities begin to appear. The same phenomenon occurs for many organic compounds if the capillary method is used. Were this not so, it would be impossible to measure the C.V. at different concentrations, for the C.V. of the major component of the mixture would change as the impurity concentration increased ahead of the crystal front.



Concentration–weight per cent. of *p,p'*-DDT.

Fig. 6.—Effect of second component on C.V. of *p,p'*-DDT.

The apparent "order" of the crystallization process in mixtures may thus be calculated, using the van't Hoff method (Fig. 6). From the slopes of the isothermal curves it is found that the order falls with decreasing *p,p'*-DDT concentration. For *o,p*-DDT mixtures, the order falls from about seven to nearly five; for TPB mixtures the corresponding decrease is approximately from twelve to seven. Rawitzer[11] applied essentially the same method to the data of Tammann[12] for benzil/azobenzene and dinitrophenol/acetanilide mixtures. The lines plotted by Rawitzer, however, were straight, and values of the apparent order varied between six and nine, according to the isotherm and mixture chosen. It is hard to understand why the present work and Rawitzer should disagree on the constancy of the order for a given isotherm, unless it be that the nature of the process differs for different compounds and mixtures.

By curve fitting methods it is possible to straighten the curving isotherms. For example, the *o,p*-DDT mixture yields the relation

$$\text{C.V.} = K(C + 100)^{13.7} = K' \ (c + 1)^{13.7} \ (c = \text{weight fraction } p,p'\text{-DDT})$$

Adequate discussion of these kinetics must await further experimental studies.

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(11) Rawitzer, *Z. anorg. allgem. Chem.*, 175, 321 (1928).

(12) Tammann and Botschwar, *ibid.*, 157, 27 (1926).

Acknowledgments.—The authors wish to thank A. Van Hook and C. A. Winkler for reading the manuscript.

Summary

The linear rate of crystallization of p,p-DDT from some supercooled binary melts has been determined, as a function of temperature and melt concentration. The second component of the melt may increase or decrease the rate. The apparent activation energy for the crystallization of pure p,p'-DDT is 33.4 kcal.

CHICAGO, ILL. RECEIVED JULY 7, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, AND THE DEPARTMENT OF MEDICINE, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY, THE PRESBYTERIAN HOSPITAL]

Fractionation and Physical-Chemical Studies of a Commercial Preparation of the Specific Polysaccharide of Type I Pneumococcus[1]

BY ROBERT A. ALBERTY AND MICHAEL HEIDELBERGER

The specific polysaccharide of Type I pneumococcus (SI)[2] is similar to the proteins in its electrochemical and solubility characteristics because it is also an amphoteric colloidal electrolyte. For this reason an attempt was made to apply the alcohol fractionation techniques which have been developed in the purification and separation of plasma proteins[3,4] to the purification of this polysaccharide. As with proteins, electrophoresis has proved a useful method for analyzing crude products[5] and those obtained by fractionation and in determining the isoelectric points of the components.

Experimental

The electrophoresis experiments were carried out in the usual Tiselius apparatus equipped with a cylindrical lens schlieren optical system. The mobilities were calculated by using the conductivity of the buffer in Donnan equilibrium with the electrophoresis sample determined at the temperature of the thermostat, 1°. Because of the high viscosity of the polysaccharide solutions the concentrations of the electrophoresis samples were made 0.5% or less.[6] Throughout the paper, mobilities on the descending side are given, as well as analyses obtained by averaging the results from the ascending and descending patterns.

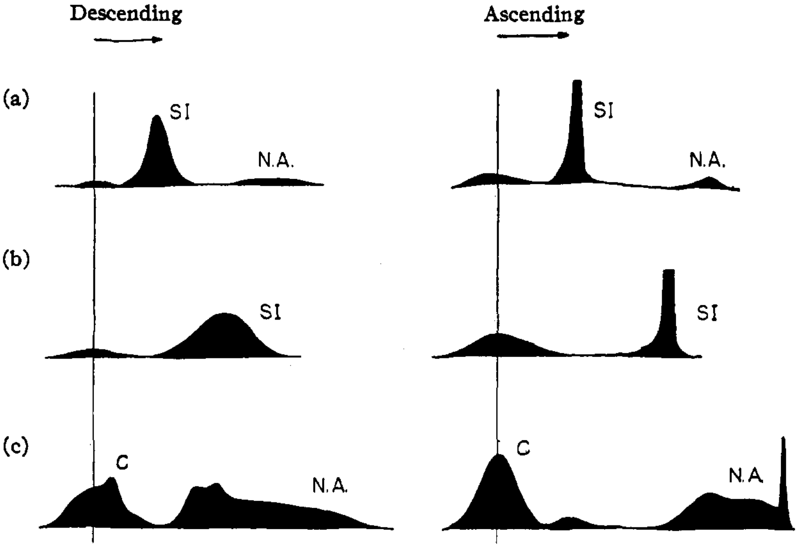

Fig. 1.—Electrophoresis diagrams: (a) commercial preparation, pH 3.90, $\Gamma/2 = 0.10$, after 144 minutes at 3.60 volts/cm.; (b) fraction A, pH 6.90, $\Gamma/2 = 0.10$, after 79 minutes at 3.28 volts/cm.; (c) fraction C, pH 6.90, $\Gamma/2 = 0.10$, after 80 minutes at 3.26 volts/cm.

The SI polysaccharide used as starting material was prepared by E. R. Squibb and Sons and supplied by the Commission on Pneumonia of the U. S. Army Epidemiological Board. The electrophoresis pattern for this preparation at pH 3.9, 0.10 ionic strength acetate buffer, is shown in Fig. 1a. The fast component which makes up 19% of the area of the moving peaks in the pattern contains nucleic acid, and the largest peak represents the SI polysaccharide. These components were identified after electrophoresis by withdrawal of small samples from various levels in the electrophoresis cell by means of a syringe with a long needle. The sample taken just below the fastest ascending peak showed the typical ultraviolet absorption of nucleic acid, with a

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[1] Presented before the Symposium on Sugars and Amino Sugars in Biochemistry, American Chemical Society Meeting, Atlantic City, April, 1947.

[2] (a) Avery and Heidelberger, *J. Exptl. Med.*, **42**, 367 (1925); (b) Heidelberger, Goebel and Avery, *ibid.*, **42**, 727 (1925); (c) Heidelberger, Kendall and Scherp, *ibid.*, **64**, 559 (1936).

[3] Cohn, Strong, Hughes, Mulford, Ashworth, Melin and Taylor, THIS JOURNAL, **68**, 459 (1946).

[4] Deutsch, Gosting, Alberty and Williams, *J. Biol. Chem.*, **164**, 109 (1946).

[5] As indicated in preliminary tests carried out several years ago with Dr. Dan H. Moore at Columbia University.

[6] The relative viscosity of a 0.1% solution of SI in 0.9% sodium chloride is 1.69; ref. 2c.