

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHNS HOPKINS UNIVERSITY]

The Dependence of Crystallization Velocity on Molecular Structure¹

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Introduction

In discussing the formation of an ordered array of molecules, such as a crystal lattice, from a chaotic phase, such as a liquid or gas, one has to consider not only the mass and velocity of the components of the chaotic phase but their shape as well. Up to the present time there has been very little known about the influence of molecular structure or shape on crystallization. The experiments described in this paper were undertaken in the hope of obtaining some information along these lines. They deal with linear crystallization velocity, which is the rate at which an interface between the solid and liquid phases proceeds along a tube filled with the melted substance.

Because of the essentially planar structure of benzene and its simple derivatives³ and the increased ease of interpretation of results, several series of di- and trisubstituted benzenes were chosen for study. In addition, a few phenylated hydrocarbons and substituted naphthalenes were measured in order to ensure generality.

Experimental

I. Purification of Materials

In most cases the most convenient and efficient method of purification was recrystallization. Depending on the condition of the original samples, four to seven recrystallizations were made. The purified samples were then dried for a minimum period of a week in vacuum desiccators, evacuated with a Cenco pump.

A few compounds were distilled at reduced pressure through a still with a two and a half foot column, a middle cut being taken from the flat boiling fraction.

II. Apparatus and Method

Glass capillaries, obtained from the Corning Glass Company, served as crystallization tubes. The approximate dimensions of these were: length, 75 cm.; inside diameter, 1 to 2 mm.; wall thickness, 0.3 to 0.5 mm. The capillaries were cleaned by keeping in chromic acid for several days, then washing with water and ethyl alcohol. They were dried by heating evenly with a small gas flame while a current of nitrogen, previously dried by sulfuric acid (sp. gr. 1.84), was passed through them for fifteen minutes.

The small test-tubes for melting were cleaned with chromic acid, water and alcohol, plugged with cotton and dried in an oven at 110° for three hours.

The observation tube was made of Pyrex glass tubing, 2 cm. in diameter and 65 cm. long. By means of two side arms it was connected through small copper tubing, well insulated with asbestos, to a small rotary pump and the reservoirs for the bath

(1) From the Dissertation of Maurice E. Krahl submitted to the Board of University Studies of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1932.

(2) Eli Lilly and Co. Fellow in Chemistry.

(3) Wierl, *Ann. Physik*, **8**, 521 (1931).

liquid. The bath liquid was heated or cooled in the reservoirs to the temperature desired and pumped through the observation tube at a rate of approximately one liter per minute. The temperature was measured by means of a thermometer suspended in the observation tube. At intervals of ten centimeters along this observation tube fine lines were etched with hydrofluoric acid solution. To aid in accuracy of reading, the lines were made in pairs as two opposite segments of a circle around the tube. A total range of 50 cm. was available for the crystallization.

The heating tube, for melting the contents of the filled capillaries, was made from Pyrex glass tubing 1 cm. in diameter and 65 cm. long. This was wound evenly with a nichrome coil of suitable resistance.

A pentane thermometer, range -200 to 50° , was used for all temperatures below 0° . For the higher temperatures three mercury-filled thermometers were used interchangeably. These were checked against a Bureau of Standards thermometer.

Because of the wide range of temperature, it was necessary to have three different bath liquids at various times during the investigation. These were used as follows: below 0° 95% alcohol; 0 to 75° , water; above 75° , a colorless, transparent mineral oil sold commercially as "Oilax." The quantity of bath liquid and regulation was such that the maximum temperature fluctuation during the course of a single reading was 0.2° for water, 0.5° with alcohol and 0.5° with oil.

The timing was done with two Meylan stop watches. One was checked by the Meylan Watch Company before this investigation; the other was checked against the first.

The procedure in measurement may be described very simply. The material for crystallization was melted in a small test-tube and drawn into the capillary by suction. The ends of the capillary were then sealed off. If the material melted above room temperature, it was necessary to suspend the heating tube directly above the observation tube and to remelt the contents of the filled capillary, leaving a small amount of solid in the bottom for seeding. The capillary was then dropped into the observation tube, and, as the crystallization occurred from the seed at the bottom, a record was made of the time required for the solid-liquid interface to proceed between any two marks on the observation tube. Preliminary measurements showed that the direction of the growth up or down the tube did not affect the rate.

In measuring compounds with comparatively low rates, it was found by making duplicate successive determinations with two watches that a constant rate was reached by the time the growth interface was opposite the lowest mark on the observation tube. In more rapid crystallizations a constant rate was attained only after the growth had proceeded to a mark 10 or even 20 cm. from the bottom of the capillary. This point was determined for each individual substance and subsequent measurements made accordingly.

III. Data and Results

Preliminary Experiments.—A series of fifty-one observations with nine different capillary tubes, varying in outside diameter from one to two millimeters, showed that capillary size, number of remeltings, temperature of melting and time of aging did not affect the crystallization velocity of benzophenone by more than the experimental error of one per cent. It was essential that this be known to ensure reproducibility of later measurements.

Temperature Dependence of the Crystallization Velocity.—The actual form of the curve obtained when the crystallization velocity is plotted

against supercooling is shown in Fig. 1, which gives the experimental results for *m*-dihydroxybenzene. The particular curve given here is typical of the curves for the other substances whose maximum velocities are given in Tables I and II.

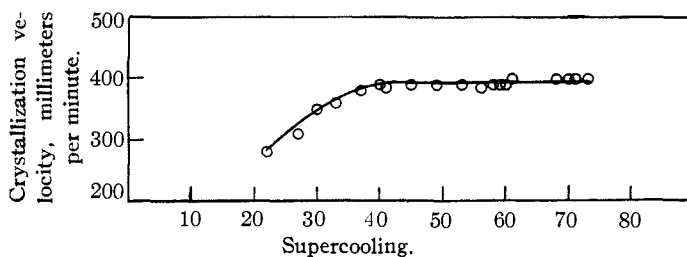


Fig. 1.

Linear Crystallization Velocities of Some Substituted Benzenes and Phenyl Substituted Hydrocarbons.—The experimentally determined velocities for a few simple di- and trisubstituted benzenes, and for some phenyl substituted methanes, ethanes and ethylenes are given in Table I.

TABLE I

Compound	M. p., °C.	ΔT	Maximum velocity, meters per minute
<i>o</i> -Dichlorobenzene	-17.6	19-36	2.2
<i>m</i> -Dichlorobenzene	-24.8	21-28	0.70
<i>p</i> -Dichlorobenzene	52.9	20-35	25
<i>p</i> -Dibromobenzene	87.3	27-54	7.5
1,2,4-Trichlorobenzene	17.0	25	0.025
1,3,5-Trichlorobenzene	63.4	25-33	7
1,3,5-Tribromobenzene	119.6	29-52	2.4
<i>o</i> -Dihydroxybenzene	104.0	29-59	1.7
<i>m</i> -Dihydroxybenzene	116.0	37-74	0.40
<i>p</i> -Dihydroxybenzene	169.0	35-47	6.3
<i>o</i> -Diaminobenzene	103.8	41-56	7
<i>p</i> -Diaminobenzene	140.0	37-47	10
<i>m</i> -Dinitrobenzene	89.7	49-59	6
<i>p</i> -Dinitrobenzene	172.1	41-50	15
<i>o</i> -Bromobenzoic acid	148.0	32	0.80
<i>m</i> -Bromobenzoic acid	153.0	14	0.255
<i>m</i> -Bromoaniline	18.5	22-63	0.048
<i>p</i> -Bromoaniline	66.4	43	1.6
Diphenyl	69.0	16	7.5
Diphenylmethane	25.2	23-27	0.53
Triphenylmethane	93.1	25-30	0.027
1,2-Diphenylethylene	123.9	25-37	2
1,1-Diphenylethylene	8.2	21-25	0.016
1,2-Diphenylethane	50.8	30-36	0.70
1,1-Diphenylethane	-25.9	27-40	Less than 0.001
1,1,1-Triphenylethane	94.3	39	0.08
1,1,2-Triphenylethane	48.0	28	Less than 0.001

The number of significant figures in the values of the velocities is that justified by the accuracy of the measurement. ΔT is the range of supercooling, expressed in degrees below the melting point, in which the maximum velocity was maintained. The width of this region varies because at great supercooling the rate of spontaneous nuclei formation became too great to permit linear velocity measurements. In cases where this prevented a constant maximum being reached, only one temperature is given.

Linear Crystallization Velocities of Some Substituted Naphthalenes.—The number of substituted naphthalenes which can be measured is limited by two factors, the high melting points and the difficulty of purification of such compounds. Results with a few of the most usable compounds are given in Table II.

TABLE II

Compound	M. p., °C.	ΔT	Maximum velocity, meters per minute
α -Naphthol	96.0	44	0.275
β -Naphthol	122.0	53	6
α -Chloronaphthalene	-26.1	27-38	0.029
α -Iodonaphthalene	4.2	11-16	.001
β -Iodonaphthalene	54.0	7	.30

The values for β -chloronaphthalene, which have not been included, and for β -iodonaphthalene are of doubtful value because of the extremely short range of supercooling which was permitted by the rapid spontaneous nuclei formation.

Discussion and Conclusions

The crystallization velocities given in Tables I and II are additions to and corrections of those previously reported.⁴

Since the dependence of the crystallization velocity on temperature has been discussed by Tammann,⁵ no further mention of it need be made here.

From Tables I and II the generality of the effect of molecular structure on crystallization rates is apparent. Of the isomeric disubstituted benzenes, the order of decreasing velocity in each series is para, ortho, meta. For the trisubstituted chlorobenzenes the symmetrical 1,3,5 isomer has a much greater velocity than the 1,2,4. Similarly, the 1,2 disubstituted ethylenes and ethanes crystallize much faster than the less symmetrical 1,1 isomers. From the evidence thus far available, it appears that the β -mono substituted naphthalenes crystallize faster than the isomeric α -compounds.

It appears from these experimental results that there exists a relationship between crystallization velocity and molecular symmetry. Before this relationship can be made a definite one, all of the properties of the liquid and crystal states which influence crystallization velocity must be considered.

(4) Krahl, *THIS JOURNAL*, **54**, 1256 (1932).

(5) Tammann, "Aggregatzustände," Leipzig, 1922, pp. 247-272.

By taking account of the probable form of the molecules, as well as the properties referred to above, an explanation has been found for the variations in velocity which are shown experimentally. In order that this explanation may be shown to be valid for all crystallization processes, whether from liquid or vapor, it is necessary to have further experimental evidence concerning the structure of the molecules of the substances whose crystallization velocities have been measured. To this end, x-ray investigations of interatomic distances are now being carried out in this Laboratory for a number of compounds in the gaseous state. As soon as this final point has been definitely established, the explanation referred to above for the effect of molecular symmetry on crystallization rates will be published.

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Summary

1. The linear velocities of crystallization have been measured for thirty-four compounds of related molecular structure. The results bear out the hypothesis that, of a series of isomers, the most symmetrical compound crystallizes fastest.

2. It has been shown that the temperature and time of melting, the number of remeltings and the time of aging of the melt do not affect the crystallization rate.

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