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Calorimetric Study on Orientationally Disordered Crystals. Cyclohexene Oxide and Cyclohexanone[†]

Nobuo Nakamura, Hiroshi Suga,* and Syûzô Seki**
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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Low-temperature calorimetric quantities were determined for cyclohexene oxide and cyclohexanone in the temperature range between 13 and 300 K. Molar heat capacity at saturation pressure of the condensed phases, transition and melting temperatures, and enthalpies of transition and melting were measured by an on-line automated adiabatic calorimeter with intermittent heating mode. Purities of both calorimetric specimens were determined from their melting behavior. The following thermodynamic quantities, C_s°, S_s°, $[H_s^\circ(T)-H_s^\circ(0)]/T$, and $-[G_s^\circ(T)-H_s^\circ(0)]/T$ were tabulated at selected temperatures. The entropies of melting of both compounds were compared with those of cyclohexanol and cyclohexane. A factor affecting the entropy of melting was discussed from the viewpoint of non-globularity of the constituting molecules. The discussion was extended to the thermal stability of a number of orientationally disordered crystals so far studied.

Abrupt changes in the freedom of molecular motion within the crystalline solid are still among the most fascinating and least understood of physical properties. A class of crystals in which the orientational degrees of freedom of the constituent molecules are highly disordered was defined by Timmermans[1] as plastic crystals because of their high plasticity. In such a phase, the constituent molecules are located on a regular lattice with high crystallographic symmetry and reorient rapidly among several orientations. The other characteristic features of the phase are higher triple point and lower entropy of fusion in comparison with the crystal composed of less symmetric molecules. Actually it was the low entropy of fusion which led Timmermans to the recognition of plastic crystals as a unique intermediate state of matter. He set rather arbitrarily an upper limit of 5 cal K^{-1} mol^{-1} ($\simeq 21$ J K^{-1} mol^{-1}) to the entropy of fusion for the criterion of plastic crystals. He recognized that such crystals are typically made up of "globular" molecules. Here, the term "globular" means either spherical or pseudo-spherical by rotation around an axis. Thus, attention of various workers in this field has been paid mainly to the crystals composed of such symmetrical tetrahedral molecules as CX_4 type, octahedral molecules as MX_6 or C_2X_6 type, cyclic molecules as cyclohexane, and caged molecules as camphor.

When we had measured the thermodynamic properties of cyclohexanol,[2] we noticed that the entropy of fusion of less symmetric and less globular cyclohexanol was smaller than that of cyclohexane. At that time, we considered that the smaller entropy of fusion originated from association effect due to intermolecular hydrogen bonding in the liquid state of cyclohexanol. This effect was found really to exist in 2-methyl-2-propanol[3] and methanol. NMR observation[4] of the cyclohexanol, however, revealed highly disordered nature of orientational and positional degrees of freedom of the molecules in the crystal. Intra- and intermolecular dipolar broadening of protons are averaged out so extensively that chemical shifts of proton—OH, CH(α), CH(β), and CH(γ)—are able to observe even in the crystalline state. There might be a possibility that less globular shape of the molecule caused to reduce the entropy of melting. In order to consider factors of the constituent molecules that diminish the entropy of melting and hence enhance their characteristics as the plastic crystals, thermal properties of cyclohexene oxide and cyclohexanone were measured with an adiabatic calorimeter in the temperature range between 13 and 300 K. Both compounds are non-globular and lack their ability of hydrogen bonding formation. Previous DTA experiments[5,6] for both compounds revealed their ability to form plastic crystalline phases. Heat capacity data of cyclohexanone are available literally[7] only for a limited temperature range.

Experimental

Materials. Cyclohexene oxide (Tokyo Kasei Co. Ltd., G. R. grade) was fractionally distilled in a double-wall glass column operated at a high reflux ratio. Temperature of the still was monitored by a thermocouple. Fractions were compared by differential thermal analysis (DTA) to monitor the purity of that part. The best fraction of the distillate was further purified by vacuum distillation and finally distilled into calorimeter cell *in vacuo*. A part of the purified specimen was transferred into a DTA tube and was used for characterization of thermal behavior. Since the material is easily polymerizable at high temperature, the sample was kept below 5 °C. The purity of the calorimetric sample was determined to be $99.97_3\%$ from the analysis of equilibrium melting curve described later.

Cyclohexanone (Tokyo Kasei Co. Ltd., G. R. grade) was subjected to essentially the same purification process as that of cyclohexene oxide. The final purity was determined to be $99.91_9\%$.

Apparatus. Heat capacity measurements were made by the on-line automated calorimeter[8] built recently in our laboratory. The temperatures of the inner and the outer shields, and the tempering ring were controlled with separate temperature controllers. The electrical power supplied to the calorimeter heater was measured with a digital voltmeter operated by a program unit. Resistances of a working platinum thermometer were measured by a.c. double bridge and stored in a mini-computer. After reaching an equilibrium state, the equilibrium resistance value was converted into the

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** Present address: Department of Chemistry, School of Science, Kwansei Gakuin University, Nishinomiya 662.

IPTS-68 temperature scale and the heat capacity was calculated during the measurement. The sample cell equipped with horizontal perforated heat-distributing disks of platinum contained 29.901 g (0.30467 mol) of cyclohexene oxide and 26.081 g (0.26473 mol) of cyclohexanone, respectively.

Results

DTA. Thermal behavior of cyclohexene oxide at low temperatures was examined by use of DTA, the result being given in Fig. 1. Run 1 shows the cooling curve with a rate of $-1.5\ \mathrm{K\ min^{-1}}$. Run 2 and Run 3 are the subsequent heating curves, respectively. The heating curve Run 3 is in good agreement with that previously reported.[5] All the phase changes undercooled easily. A new intermediate phase was observed to appear always on cooling the liquid. From a comparison of respective peak areas, the intermediate phase as well as the high temperature phase are considered to be highly disordered state. Considering the manner by which the respective phase changes take place, the intermediate phase is expected to be a metastable phase.

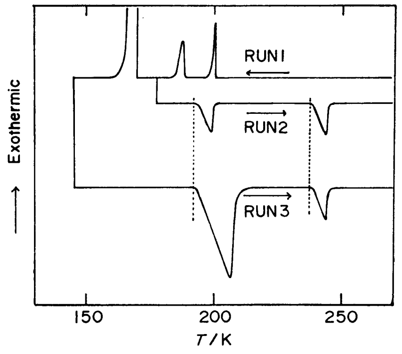

Fig. 1. DTA curves of cyclohexene oxide.

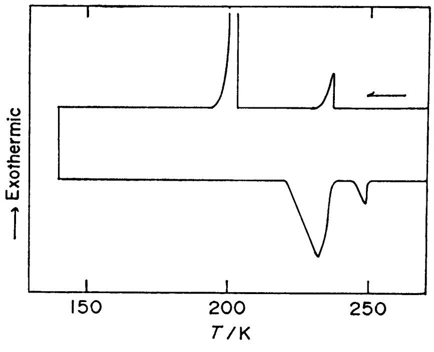

Fig. 2. DTA curves of cyclohexanone.

Figure 2 gives DTA curves of cyclohexanone for cooling and heating. Both of the solidification and solid-solid phase transition were found to undercool considerably. The peak due to the phase transition observed for heating is a little anomalous in shape and suggests a possibility that the transition proceeds in two or more steps. This possibility was examined carefully in later heat capacity measurement.

Heat Capacity. The experimental heat capacity determinations are presented in Table 1 for cyclohexene

TABLE 1. MOLAR HEAT CAPACITY OF CYCLOHEXENE OXIDE

$\frac{T}{\mathrm{K}}$	$\frac{Cs}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{\Delta T}{\mathrm{K}}$	$\frac{T}{\mathrm{K}}$	$\frac{Cs}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{\Delta T}{\mathrm{K}}$
14.37	4.063	1.148	150.37	80.525	3.095
16.99	6.128	2.088	153.44	82.058	3.047
19.00	7.943	1.936	156.47	83.643	2.999
20.80	9.706	1.665	159.44	85.320	2.951
22.60	11.560	1.937	161.85	86.751	2.219
24.64	13.694	2.145	164 06	87.930	2.195
26.81	15.932	2.199	166 24	89.147	2.171
28.88	18.040	1.928	168.51	90.598	2.381
30.97	20.061	2.257	170.88	92.262	2.347
33.10	22.142	2.022	173.21	93.756	2.318
35.04	23.836	1.858	175.51	95.344	2 286
36.94	25.595	1.953	177.78	97.120	2 254
38.83	27.164	1.822	180.02	98.784	2.224
40.60	28.019	1.715	182.23	100.88	2.189
42.53	30.148	2.150	184.40	102.70	2.159
44.62	31.556	2.029	186.54	105.16	2.121
46.69	32.948	2.108	188.66	108.06	2.080
48.75	34.412	2.001	190 63	122.33	1.904
50.70	35.679	1.913	191.75	165.58	1.460
52.80	36.870	2.286			
55.04	38.236	2.192	195.56	128.52	2.372
57.20	39.752	2.106	197.93	124.36	2.366
58.72	40.523	2.343	201.28	124.81	2.246
61.02	41.669	2.256	203.52	125.05	2.240
63.24	42.785	2.181	205.76	125.38	2.231
65.39	43.815	2.115	207.98	125.60	2.609
67.47	44.912	2.054	209.48	125.97	2.219
69.50	45.804	2.001	211.78	126.26	2.212
71.48	46.783	1.951	213.99	126.63	2.205
73.41	47.564	1.909	216.19	127.18	2.196
75.30	48.473	1.866	218.39	127.36	2.191
77.14	49.235	1.830	220.57	127.83	2.182
78.95	50.173	1.792	222.75	128.19	2.175
80.73	50.853	1.762	224.92	128.61	2.167
82.59	51.706	1.964	227.09	129.06	2.159
84.54	52.517	1.929	229.24	129.55	2.150
86.45	53.272	1.896	231.39	130.09	2.141
80.12	50.563	2.839	233.52	130.67	2.131
82.92	51.817	2.761	235.64	132.02	2.113
85.65	52.939	2.694			
88.31	54.032	2.632			
90.92	55.115	2.574	239.03	146.90	1.169
93.46	56.110	2.522	240.35	147.28	1.457
95.96	57.134	2.473	242.04	147.81	1.935
98.41	58.056	2.429	244.54	148.52	2.126
100.82	59.061	2.386	246.66	149.09	2.117
103.19	60.003	2.347	248.77	149.69	2.108
105.51	60.971	2.312	250.87	150.39	2.099
107.81	61.811	2.276	252.97	150.97	2.090
110.07	62.858	2.241	255.12	151.56	2.211
112.29	63.666	2.212	257.32	152.31	2.200
114.49	64.588	2.182	259.52	152.93	2.190
116.99	65.606	2.823	262.06	153.72	2.894
119.79	66.814	2.775	264.94	154.63	2.875
122.54	67.842	2.733	267.81	155.55	2.858
125.26	69.083	2.691	270.66	156.46	2.839
127.93	70.146	2.653	273.30	157.37	2.768
130.56	71.410	2.615	276.06	158.15	2.754
133.16	72.500	2.584	280.51	159.66	4.913
135.72	73.701	2.543	283.24	160.64	2.512
138.25	74.754	2.511	285.76	161.27	2.520
140.75	75.805	2.480	288.46	162.45	2.873
143.21	77.075	2.446	290.77	163.08	3.105
145.64	78.283	2.414	293.87	163.97	3.089
148.04	79.402	2.384	296.96	164.98	3.069

Table 2. Molar heat capacity of cyclohexanone

T K	Cs J K^{-1} mol^{-1}	ΔT K	T K	Cs J K^{-1} mol^{-1}	ΔT K
13.78	4.158	1.645	153.34	86.092	2.360
15.47	5.927	1.753	155.68	87.029	2.338
17.44	7.989	2.172	158.01	88.008	2.318
19.20	10.070	1.356	160.32	88.967	2.297
21.00	12.241	2.236	162.60	89.931	2.276
23.32	15.154	2.404	164.87	90.853	2.257
25.76	18.176	2.490	167.12	91.774	2.238
28.14	21.032	2.268	169.35	92.760	2.218
30.37	23.595	1.999	171.90	93.991	2.890
32.50	25.890	2.250	174.88	95.139	2.634
34.84	28.302	2.435	177.50	96.584	2.603
37.17	30.681	2.220	180.09	97.479	2.583
39.40	32.720	2.250	182.66	98.766	2.555
41.78	34.835	2.504	185.20	99.959	2.531
44.48	36.999	2.901	187.73	101.19	2.507
47.15	39.012	2.447	190.22	102.52	2.481
49.54	40.732	2.317	193.90	104.49	4.890
52.07	42.621	2.739	197.55	106.54	2.409
54.66	44.265	2.452	199.95	108.02	2.384
57.06	45.771	2.347	202.32	109.42	2.360
59.37	46.937	2.263	204.67	111.12	2.335
61.57	48.348	2.179	206.99	112.89	2.308
63.82	49.458	2.316	211.65	117.61	2.433
66.10	50.704	2.244	214.00	121.85	2.275
68.31	51.829	2.181	216.23	128.91	2.186
70.73	52.928	2.656	218.32	147.22	1.987
73.39	54.192	2.656			
76.01	56.559	2.584	222.72	147.44	2.400
78.56	56.612	2.516	225.15	142.27	2.460
81.05	57.703	2.458	227.61	141.45	2.467
83.48	58.727	2.406	230.07	142.57	2.451
85.86	59.728	2.357	232.52	143.47	2.537
88.19	60.748	2.311	234.95	144.01	2.328
90.48	61.666	2.270	237.36	146.50	2.395
92.70	62.539	2.233			
94.92	63.333	2.199			
97.10	64.225	2.164	244.75	160.18	0.684
99.25	65.120	2.132	245.67	158.49	1.259
101.37	65.881	2.104	247.46	158.92	2.208
103.46	66.739	2.075	249.66	159.95	2.197
105.55	67.145	2.114	251.96	160.52	2.401
107.86	68.394	2.453	254.36	161.59	2.405
108.05	68.473	2.446	255.39	161.69	2.318
110.48	69.395	2.420	257.70	162.51	2.308
112.88	70.426	2.381	260.02	163.14	2.391
115.25	71.266	2.353	262.40	163.99	2.380
117.59	72.225	2.323	264.95	164.77	2.710
120.28	73.264	3.066	267.65	165.95	2.693
123.16	74.321	2.698	270.34	166.70	2.682
125.84	75.428	2.661	273.01	167.51	2.669
128.49	76.383	2.628	275.67	168.55	2.654
131.10	77.445	2.595	278.32	169.55	2.640
132.88	78.081	2.579	280.95	170.24	2.629
135.44	79.209	2.546	283.58	171.35	2.614
137.97	80.169	2.519	286.18	172.17	2.602
140.48	81.095	2.492	288.78	173.35	2.586
142.95	82.182	2.465	291.31	174.27	2.577
146.61	83.368	2.429	293.87	174.96	2.541
148.58	84.267	2.405	296.40	175.96	2.527
150.97	85.313	2.381	298.92	176.72	2.517
			301.43	177.92	2.501

oxide and in Table 2 for cyclohexanone, along with the approximate temperature increments. In most cases, the temperature increments were small enough to eliminate the need of curvature correction. Correction of the vaporization was found to be negligible in both cases. The imprecision of the experimental heat capacity was usually less than 0.1%, except in the transition and melting regions. The loss of precision in these ranges was caused by slow thermal and compositional equilibration. Accuracy uncertainty in heat capacity is about 1% below 20 K and 0.2% above 50 K. The heat capacity data are reproduced graphically in Figs. 3 and 4, respectively.

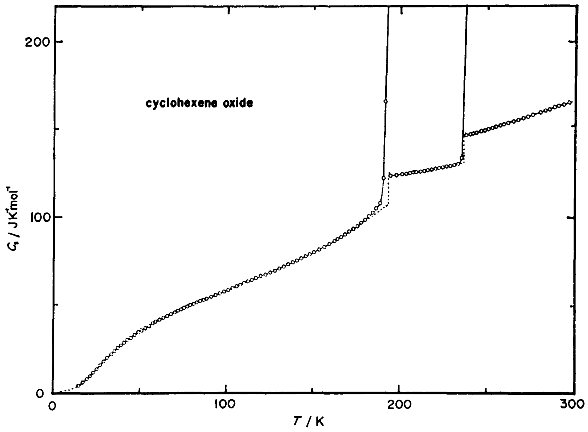

Fig. 3. Molar heat capacity of cyclohexene oxide.

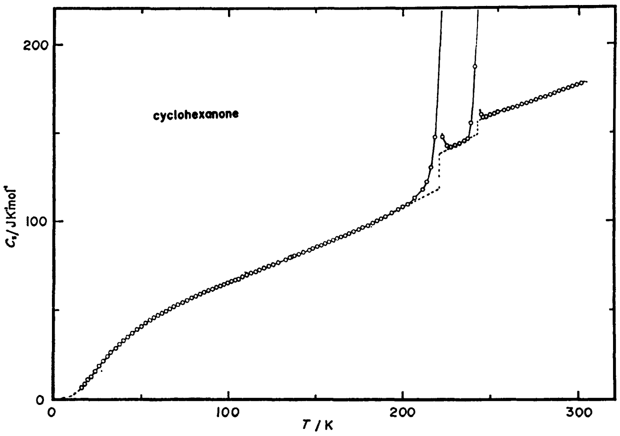

Fig. 4. Molar heat capacity of cyclohexanone.

Phase Transition. Cyclohexene oxide showed a sharp transition at 193.10 K. The thermal equilibrium was extremely difficult to attain during the transition. Hence, a temperature about 100 min after an energy input was regarded conveniently as an equilibrium temperature and was used for the calculation of apparent heat capacity. Figure 5 gives a plot of enthalpy increment against temperature during the course of phase transition of cyclohexene oxide. The transition proceeded in a single step and the temperature of transition was determined as the one at which the heat capacity reached its maximum value. The enthalpy of transition was determined from the total enthalpy

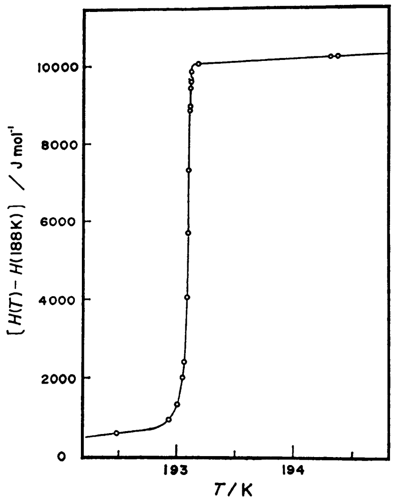

Fig. 5. Enthalpy change of cyclohexene oxide around the transition temperature.

change between equilibrium temperatures below and above the transition temperature. The isothermal increment was calculated by subtracting from the total enthalpy those part associated with the "normal" heat capacity given by dotted lines in Figs. 3 and 4, respectively. The results of replicate determinations of the enthalpies of transition for both compounds are summarized in Table 3.

Table 3. Molar enthalpies of transition

T_i/K	T_f/K	ΔH_t/J mol^{-1}
Cyclohexene oxide (T_t=193.10 K)		
180.2622	196.6566	9536.2
180.0479	197.3844	9534.0
ΔH_t=9535.1±1.1 J mol^{-1}		
ΔS_t=49.39±0.01 J K^{-1} mol^{-1}		
Cyclohexanone (Tt=220.83 K)		
211.8566	224.7534	8659.5
211.7343	224.6700	8659.7
ΔH_t=8659.6±0.1 J mol^{-1}		
ΔS_t=39.22±0.01 J K^{-1} mol^{-1}		

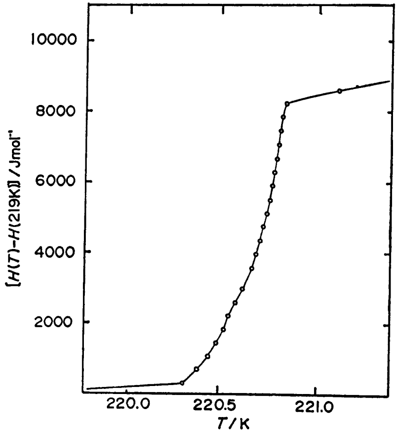

Fig. 6. Enthalpy change of cyclohexanone around the transition temperature.

Enthalpy increment during the course of the phase transition of cyclohexanone is plotted in Fig. 6 as a function of temperature. Here, the phase transition takes place over a temperature range and does not proceed uniformly. In order to make clear this situation, apparent heat capacities were calculated over the transition range and they are given in Fig. 7. Evidently, the transition proceeds in two steps. This observation accords well with suggestion by Crowe and Smyth⁹⁾ from their dielectric study and with phase diagram study of cyclohexanone–CCl_4 system by Miltenburg.⁷⁾ Würflinger and Kreutzenbeck have found a third modification of cyclohexanone by DTA under high pressures. They reported that the triple point among the three crystalline phases coincided with atmospheric pressure within the limits of experimental error. They could not reveal a superposed second solid-solid transition at atmospheric pressure by their DTA experiment, possibly because of their high heating rate.

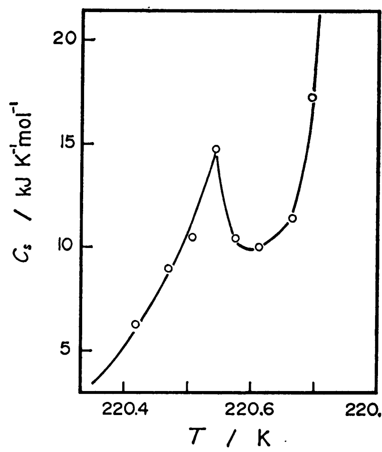

Fig. 7. Apparent heat capacity of cyclohexanone around the transition temperature.

Cataliotti and Paliani¹⁰⁾ reported the existence of an additional phase transition in cyclohexanone at 168 K. However, this or any other phase transition was not observed by the present calorimetric work.

Enthalpy of Melting and Sample Purity. The enthalpy of melting was determined as the isothermal

Table 4. Summary of melting experiments for cyclohexene oxide

f	$1/f$	$T_m(f)$/K
0.307	3.255	237.8037
0.397	2.516	237.8324
0.560	1.786	237.8620
0.722	1.384	237.8864
0.884	1.131	237.9126
T°_m=238.14 K		
x=0.027 mol %		

T_i/K	T_f/K	ΔH_m/J mol^{-1}
234.3244	239.0720	1064.6
234.3658	239.3133	1064.3
ΔH_m=1064.5±0.2 J mol^{-1}		
ΔS_m=4.470±0.010 J K^{-1} mol^{-1}		

TABLE 5. SUMMARY OF MELTING EXPERIMENTS FOR CYCLOHEXANONE

f	$1/f$	$T_m(f)$/K
0.2901	3.447	243.195
0.3658	2.734	243.434
0.4470	2.237	243.636
0.5342	1.872	243.802
0.6234	1.604	243.942
0.7174	1.394	244.063
0.8147	1.229	244.163
0.9124	1.096	244.253

T°_m=245.21 K
x=0.081 mol %

T_i/K	T_f/K	ΔH_m/J mol^{-1}
235.9724	247.9974	1327.91
235.8726	247.9145	1327.45

$\Delta H_m=1327.6\pm0.3$ J mol^{-1}
$\Delta S_m=5.414\pm0.010$ J K^{-1} mol^{-1}

segment of the enthalpy required to heat from an initial equilibrium temperature of the crystal to a final temperature of the liquid. Here, a normal heat capacity was assumed, being represented as the dotted lines in Figs. 3 and 4.

For the determination of the melting point and the purity of the sample, a fractional melting experiment was carried out. The equilibrium temperatures $T(f)$ were observed at several fractions f of the sample melted. The melting temperature plotted against the reciprocal fraction did not give a straight line, indicating a possibility of solid-soluble impurity scheme. Following the theoretical treatment by Mastrangelo-Dornte,[11] we have estimated the total amount of impurities x and the triple point of pure compound T°_m. These melting data are summarized in Tables 4 and 5.

Thermodynamic Functions. The experimental heat capacities were smoothed by a spline fit and then numerically integrated to obtain the final tabular values of the standard thermodynamic functions. They are listed in Tables 6 and 7 at selected round temperatures. Below the lowest temperature attained, the heat capacity data were extrapolated by means of the Debye law. The parameters of the Debye functions were assigned as $\theta=140$ and 132 K for six degrees of freedom for cyclohexene oxide and cyclohexanone, respectively.

Discussion

Characterization of the plastically crystalline state is a topic of current solid-state chemical and physical interest.[12] The appearance of the plastic crystal state has been attributed to the onset of molecular reorientational motion in the solid and can be expected for globular molecules, *i.e.*, molecules of high symmetry and nearly spherical shape. The distinct difference between the phase behavior of pentane and of neopentane is cited in many textbook[13] as showing the importance of globularity of the constituent molecules in the formation of plastic crystals. A suggestion[14] that plastic crystals might better be called "crystals with globular molecules" reflects this widespread recognition.

The values of ΔS_m for cyclohexene oxide and cyclohexanone are comparable in magnitude to that of cyclohexanol,[2] 5.68 J K^{-1} mol^{-1} and less than that of cyclohexane,[15] 9.56 J K^{-1} mol.$^{-1}$ The relevant thermodynamic data are summarized in Table 8. This fact means that the calorimetric feature as the plastic crystalline behavior is enhanced by reduction of globularity of the constituent molecules. As pointed out already, the subject of plastic crystals began from the recognition by Timmermans that the crystal has considerably small entropy of melting and that the

TABLE 6. MOLAR THERMODYNAMIC FUNCTIONS OF CYCLOHEXENE OXIDE

$\frac{T}{\text{K}}$	$\frac{C^\circ_s}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{S^\circ_s}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{[H^\circ_s(T)-H^\circ_s(0)]/T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{-[G^\circ_s(T)-H^\circ_s(0)]/T}{\text{J K}^{-1}\text{ mol}^{-1}}$
20	8.921	3.450	1.656	1.794
30	19.12	8.994	5.882	3.112
40	28.10	15.82	10.32	5.498
50	35.12	22.87	14.61	8.268
60	41.11	29.82	18.54	11.28
70	46.01	36.54	22.12	14.42
80	50.53	42.98	25.39	17.59
90	54.70	49.18	28.42	20.75
100	58.71	55.15	31.25	23.90
120	66.86	66.57	36.50	30.07
140	75.56	77.51	41.45	34.06
160	85.63	88.24	46.32	41.92
180	98.83	99.04	51.38	47.66
200	124.62	159.25	104.18	55.07
220	127.67	171.26	106.17	65.09
240	147.20	187.16	112.71	74.45
260	153.08	199.17	115.58	83.59
280	159.52	210.75	118.49	92.26
300	166.12	221.98	121.44	100.53

Table 7. Molar thermodynamic functions of cyclohexanone

$\frac{T}{\mathrm{K}}$	$\frac{C_s^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{S_s^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{[H_s^\circ(T)-H_s^\circ(0)]/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{-[G_s^\circ(T)-H_s^\circ(0)]/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$
20	10.90	4.139	3.074	1.065
30	23.12	10.91	7.759	3.151
40	33.20	19.02	12.93	6.091
50	41.16	27.31	17.80	9.506
60	47.45	35.39	22.24	13.15
70	52.61	43.47	26.22	17.26
80	57.16	51.19	29.80	21.38
90	61.42	58.51	33.08	25.43
100	65.35	65.49	36.12	29.38
120	73.08	78.58	41.63	36.35
140	80.94	90.77	46.69	44.09
160	88.86	102.35	51.47	50.88
180	97.43	113.46	56.09	57.38
200	108.00	124.30	60.73	63.57
210	115.61	129.69	63.14	66.55
230	142.46	180.50	106.40	74.10
250	159.85	198.38	115.17	83.21
260	163.16	204.72	116.96	87.76
280	170.07	217.06	120.50	96.56
300	177.20	229.03	124.04	104.99

Table 8. Thermodynamic data associated with phase changes of cyclohexane and some of its derivatives

Substance	$\frac{T_t}{\mathrm{K}}$	$\frac{\Delta S_t}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{T_m}{\mathrm{K}}$	$\frac{\Delta S_m}{\mathrm{J\,K^{-1}\,mol^{-1}}}$
Cyclohexane	186.09	36.20	279.84	9.56
Cyclohexanol	265.5	33.25	299.05	5.68
Cyclohexene oxide	193.10	49.39	238.14	4.47
Cyclohexanone	220.83	39.22	245.21	5.41

crystal is of high crystallographic symmetry.

The f.c.c. lattice is the one most frequently encountered for the plastic crystalline phase in which the constituent molecules have intense orientational disorder. Actually, cyclohexane, cyclohexanone and cyclohexanol are known to crystallize in f.c.c. lattice.[16] That of cyclohexene oxide has not yet been determined. However, X-ray powder diffraction experiment[5] gave a characteristic photograph of the plastic crystals; relatively intense background and a few diffuse Bragg scattering associated with large Debye-Waller factor. While the parent molecule, cyclohexane, has D_{3d} symmetry, the three oxy-derivatives can not be expected to have any symmetry element other than mirror. Microwave experiment[17] of cyclohexene oxide shows that the molecule has no symmetry.

In order to fulfil a high crystallographic site symmetry at the lattice point, molecules must reorient among several orientations. The time-averaged distribution of a molecule tends towards spherical symmetry, hence the closest packed structure is realized. A less symmetric molecule has to compensate by taking a greater number of molecular orientations than a symmetric molecule. Short-range repulsive interactions between neighboring molecules cause the reorientational motion of an asymmetric molecule to couple more closely with lattice vibrational motion, because the asymmetric molecule must reorient itself by displacing its center of mass from the lattice point. Observation of anomalously large Debye-Waller factors for these crystals reflects this coupling effect. The stronger the coupling, the smaller will be the entropy of melting, since partial positional disordering occurs concomitantly with orientational disordering at the phase transition. The stronger the coupling, the narrower will be the temperature range of plastic crystalline phase, since vibrational motion is highly excited at the phase transition. According to the simple picture by Lindemann,[18] melting might be expected when the mean amplitude of lattice vibration becomes some fraction of the lattice distance.

In order to test this intuitive idea, the relation between the entropy of melting and the temperature range of the plastic crystalline phase is examined for some plastic crystals composed of molecules with various symmetries. A list of some plastic crystals is given in Table 9, along with data for ΔS_m in units of $\mathrm{J\,K^{-1}\,mol^{-1}}$. For the range of entropies of melting suggested by Timmermans for plastic crystals ($<21\ \mathrm{J\,K^{-1}\,mol^{-1}}$) we consider three groups: category A ($\Delta S_m/\mathrm{J\,K^{-1}\,mol^{-1}}>14$); category B ($14>\Delta S_m/\mathrm{J\,K^{-1}\,mol^{-1}}>7$); category C ($7>\Delta S_m/\mathrm{J\,K^{-1}\,mol^{-1}}$). We note that category A contains octahedral molecules or almost spherical molecules while many diatomic or tetrahedral molecules and some cyclic or caged molecules are to be found in category B. Category C contains the least globular molecules. Inert gas molecules like argon and krypton have entropies of melting between categories A and B ($\approx 14\ \mathrm{J\,K^{-1}\,mol^{-1}}$). They show rather high plasticity and the vapor snake phenomenon[19] near their mp. Although these crystals exhibit no phase transition, they can be legitimately considered as plastic crystals. The fact that ΔS_m values for non-globular molecules are less than those for spherical molecules (Ar, Kr) suggests strongly the importance of the orientation-position coupling effect. This coupling will also affect the temperature range in which stable plastic crystals can exist. The plastic crystals belonging to category A have a wide temperature range of existence. This is

Table 9. Entropies of fusion of some plastic crystals

A $\frac{\Delta S_\mathrm{m}}{\mathrm{J\,K^{-1}\,mol^{-1}}} > 14$	C_2Cl_6(18.0)	$C_2(CH_3)_6$(18.8)
	SF_6(22.6)	MoF_6(15.3)
	$C(CH_3)Cl_3$(18.8)	$C(CH_3)_3OH$(22.4)
	bicyclo[2,2,2]octane (18.7)	
	adamantane (23.7)	*d*-borneol (17.2)
B $14 > \frac{\Delta S_\mathrm{m}}{\mathrm{J\,K^{-1}\,mol^{-1}}} > 7$	N_2(9.51)	O_2(8.15)
	CH_4(10.4)	SiH_4(7.5)
	GeH_4(7.78)	CF_4(7.82)
	CCl_4(10.0)	CBr_4(10.9)
	$C(CH_3)_4$(12.7)	$C(CH_3)_3Cl$(8.11)
	$C(CH_3)_3$ SH(9.04)	$C(CH_3)_2Cl_2$(9.78)
	PtF_6(13.4)	
	C_6H_{12}(9.29)	C_7H_{14}(9.09)
	d-camphor(11.7)	
	1-azabicyclo[2.2.2] octane(13.4)	
C $7 > \frac{\Delta S_\mathrm{m}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$(CH_3)_3CCOOH$(6.5)	$(CH_3)_3CC_2H_5$(3.3)
	C_5H_{10}(3.35)	$C_6H_{11}OH$(5.68)
	$C_6H_{10}O$ cyclohexanone(5.41)	
	$C_6H_{10}O$ cyclohexene oxide (4.48)	

exemplified typically by 220 K for hexamethylethane, and 335 K for adamantane. On the other hand, the compounds belonging to category C are characterized by quite narrow plastic crystal ranges: 45 K for cyclohexene oxide; 34 K for cyclohexanol; 25 K for cyclohexanone.

The present conclusion that non-globularity of the constituent molecules operates to diminish the value of ΔS_m and to narrow the plastic crystal range has some limitations. If the non-globularity of molecule exceeds some critical value, the hindering potential opposing randomization of orientation of the molecule increases too much for the orientationally disordered state to be realized before the melting point is reached. In this sense, cyclohexanone may be considered as an extreme case of a cyclohexane derivative that can exist as a plastic crystal. Pople and Karasz[20)] were the first to take account of the fact in a rather qualitative way. In view of the complex nature of the intermolecular forces in this particular crystal, it is still not possible to define a critical parameter in a quantitative way.

Although the physical significance of the smallness of ΔS_m of plastic crystals has still to be clarified satisfactorily, this calorimetric feature should be correlated with the mechanical feature of the crystals. Dunning[16)] suggested that the high plasticity may be analogous to the high-temperature creep of metals, which has been ascribed to the diffusional motion of vacancies through the crystalline lattice. It is this motion that also accounts for the easiness of self-diffusion observed in a number of plastic crystals and may have some correlation with the unusual freezing behavior called "vapor snake phenomenon."[19)] Organic crystals in which the self-diffusion has been observed by NMR study were all characterized by their low values of ΔS_m. A kinetic parameter governing the self-diffusion in the highly disordered crystal was correlated well with the melting parameter[21)] of the crystal. Valuable advances will be made by such correlation between more than one property of the plastic crystals.

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