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Apparent Violation of the Third Law without a Detectable Glass Transition in Simple Molecular Solids: Calorimetric Entropy of *p*-Bromochlorobenzene[#]

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The heat capacities of crystalline and liquid *p*-bromochlorobenzene were measured by adiabatic calorimetry between 6 and 350 K. The crystal melts at 337.99 K with an enthalpy and an entropy of fusion of 18390 J mol^{-1} and 55.41 J K^{-1} mol^{-1}, respectively. Neither an ordering phase transition nor a glass transition was detected in the solid state, contrary to an expectation based on the apparent symmetry of the molecule at room temperature due to an orientational disorder. The calorimetric entropy of the gas was estimated using the vapor-pressure data. A comparison with spectroscopic entropy based on a quantum chemical calculation shows that the PBCB crystal has a residual entropy of about $R\ln 2$ (R: gas constant), which is compatible with the orientational disorder at room temperature. The absence of a sizeable anomaly due to a glass transition suggests two possibilities: an undetectably small thermal anomaly around the glass transition, or a glass-transition temperature higher than the temperature of fusion.

Some simple benzene derivatives have been regarded as compounds showing a "rigid disorder" in crystals concerning the molecular orientation.[1] It is widely assumed that a "rigid disorder implies" the absence of molecular reorientation in a crystal. In agreement with this implication, there rarely exist cases where molecular reorientation has been detected experimentally. From a thermodynamic point of view, the assumption of a "rigid disorder" is interpreted as a statement that assumes a glass transition at a higher temperature than room temperature.

In contrast to the assumption of "rigid disorder," the present authors recently provided concrete evidence of molecular reorientation at room temperature in a representative compound, *p*-chloronitrobenzene (PCNB),[2] which is just an example described in Kitaigorodtsky's textbook.[1] For PCNB, the glass transition due to orientational freezing is clearly detected at around 240 K. The motional mode responsible for the glass transition is deduced from the residual entropy, which was estimated from the calorimetric entropies of both the disordered and ordered crystalline phases.

The title compound, *p*-bromochlorobenzene (PBCB), belongs to a group of materials showing rigid disorder. Molecules crystallize in a monoclinic lattice with space group $P2_1/a$ at room temperature.[3] Since the number of formula units contained in the unit cell is 2, only half of the molecules are crystallographically independent. That is, the molecule sits on an inversion center. This requires, at least, the "head-to-tail" disorder concerning the molecular orientation. A broad linewidth in Cl-NQR[4] is compatible with this disorder. The possibility of molecular reorientation was recently suggested based on the temperature dependence of the relaxation time (T_1) of Cl-NQR,[4] though the possibility suggested together for PCNB contradicted the calorimetric results.[2]

For an orientational disorder in the crystal of a simple molecule, an entropic assessment is very powerful, because the possibility of a model for the disorder may be quantitatively discussed. This paper describes the results of precision heat-capacity calorimetry for crystalline PBCB. The residual entropy was estimated by combining the present calorimetric entropy, the vapor-pressure data reported previously, and a quantum chemical calculation of the molecular vibrations.

Experimental

Commercially available *p*-bromochlorobenzene (Aldrich Chemical Co.) was purified by fractional sublimation in a vacuum at room temperature. The purified specimen was sealed in a glass ampule, melted (at 338 K) in a nitrogen atmosphere under reduced pressure, and slowly cooled down to room temperature. The melting behavior of the sublimed-melted sample used for adiabatic calorimetry implied that the purity of the sample was better than 99.99 mol%.

The sublimed-melted sample was loaded into a calorimeter vessel and sealed with a small amount of helium gas (4 kPa at room temperature) to assist thermal equilibration within the vessel. The mass of the loaded sample was 5.3283 g (2.7830×10^{-2} mol) after buoyancy correction. The sealed vessel was set in a previously

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described adiabatic calorimeter.[5] The sample contributed to about half of the total heat capacity, which includes those of the vessel and helium gas. The working thermometer mounted on the vessel was a platinum resistance thermometer (MINCO S1059, $R_0 \approx 100$ Ω at 273.16 K), which was used even below 13.8 K. Its temperature scale was transferred from those of the calibrated platinum (Tinsley and the National Physical Laboratory at England) and germanium (Lake-Shore Cryotronics) resistance thermometers based on the ITS-90.

Results and Discussion

Calorimetric measurements on PBCB were performed from 6 to 350 K. The results for the entire temperature range are shown in Fig. 1 in terms of the heat capacity. The crystal melts at around 338 K with an enthalpy of fusion of (18390±4) J mol^{-1}. By dividing the enthalpy of fusion by the temperature of fusion, a precise determination of which is described below, the entropy of fusion is determined as (54.41±0.01) J K^{-1} mol^{-1}. Those are generally in good agreement with previous values.[6] They are believed being the most accurate values because only the present experiment utilized adiabatic calorimetry.

The purity of the sample was estimated by the standard fractional melting method, which utilizes the so-called melting temperature depression. To obtain the equilibrium temperature, the temperature reading of the thermometer was monitored several hours under an adiabatic condition. The fraction melted (f) was deduced from the enthalpy of fusion and the electric energy supplied to the vessel including the sample. The good linearlity of the plot supports the assumption of a liquid soluble-solid insoluble impurity. The temperature of fusion of the sample within the vessel was determined to be (337.990±0.002) K as the equilibrium temperature at $f^{-1} = 1$. The temperature of fusion of an ideally pure compound was deduced to be (337.994±0.002) K from the equilibrium temperature corresponding to infinite dilution ($f^{-1} = 0$). From the slope of the plot, the purity of the specimen within the vessel is estimated to be 99.991 mol%.

The molecular orientation should be highly disordered so as to fulfill the space-group symmetry at room temperature. The assumption of thermal equilibrium is equivalent to that of the dynamical nature of the orientational disorder. Then, two scenarios are possible concerning cooling down to absolute zero. The first possibility is the occurrence of an ordering transition to fulfill the third law of thermodynamics. The other is the presence of a glass transition. Namely, the ordering is kinetically forbidden within a practical time duration. In reality, however, there is no thermal anomaly corresponding to the ordering transition and/or the glass transition, as can be seen in Fig. 1. Indeed, the obtained heat capacities are smooth within 0.5% below 20 K and 0.1% above 20 K.

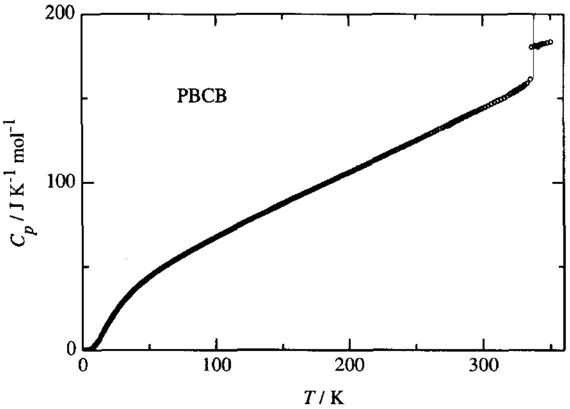

Fig. 1. Measured molar heat capacities of p-bromochlorobenzene.

At this stage, one may be inclined to believe that the disorder reported from diffractometry is incorrect. This is, however, not the case. First the broad linewidth in Cl-NQR[4] is only rationalized by assuming a disordered structure, though it is open as to whether the disorder is dynamical or static in nature. Besides, the following analysis of the present result also supports disorder in the crystal. The presence of disorder is surely confirmed from the magnitude of the residual entropy.

To obtain thermodynamic functions, including the calorimetric (third-law) entropy, the heat-capacity curves of a solid and a liquid were smoothed out, and integrated in appropriate ways to yield the enthalpy and entropy. The contributions from the temperature region below 6 K were estimated by a smooth extrapolation of the heat-capacity curve, matching the Debye model in the low-temperature limit. The Gibbs energy was obtained by the standard relation, $G = H - TS$. The resulting standard functions are tabulated at round temperatures in Table 1.

An estimation of the residual entropy requires some "ordered" state, the entropy of which is safely assigned. In the case of PCNB, the ordered crystalline phase is used as a reference.[2] For PBCB, however, since such an ordered phase is not known, another reference state is necessary. The residual entropy is usualy estimated by comparing the experimental (calorimetric) entropy of the vapor and the entropy calculated on the basis of statistical mechanics. There is no direct measurement of the enthalpy and entropy of sublimation, which can be deduced from the temperature dependence of vapor pressure according to the Clapeyron formula. The vapor pressure of solid PBCB was reported between 294 and 338 K.[7] The enthalpy and entropy of sublimation were estimated to be 70.00 kJ mol^{-1} and 221.5 J K^{-1} mol^{-1}, respectively, at 316 K, the midpoint of the reported temperature range, where the vapor pressure is 172.1 Pa. Ignoring the non-ideality, which would be small for PBCB, because of no special intermolecular interaction, compression to 10^5 Pa lowers the entropy by 52.9 J K^{-1} mol^{-1}. The calorimetric entropy of the PBCB solid is 190.83 J K^{-1} mol^{-1} on the basis of the present heat-capacity data. The calorimetric entropy of the ideal PBCB gas is thus estimated to be 359.4 J K^{-1} mol^{-1} at 316 K and 10^5 Pa, as summarized in Table 2.

It is thus necessary to evaluate the absolute entropy of an ideal PBCB gas statistical mechanically. To this end, molecular parameters, such as the molecular moment of inertia and the vibrational frequencies of all (30) intramolecular normal modes, should be available. Although experimentally

Table 1. Standard Thermodynamic Quantities of *p*-Bromochlorobenzene

T K	C_p° $\mathrm{J\,K^{-1}\,mol^{-1}}$	$[H^\circ(T)-H^\circ(0)]/T$ $\mathrm{J\,K^{-1}\,mol^{-1}}$	$S^\circ(T)-S^\circ(0)$ $\mathrm{J\,K^{-1}\,mol^{-1}}$	$-[G^\circ(T)-H^\circ(0)]/T$[a] $\mathrm{J\,K^{-1}\,mol^{-1}}$
		Crystal		
10	3.91	1.02	1.34	0.32
20	17.25	5.67	7.95	2.28
30	28.73	11.55	17.24	5.69
40	37.35	16.97	26.74	9.77
50	44.02	21.74	35.82	14.08
60	49.62	25.93	44.35	18.42
70	54.59	29.67	52.38	22.71
80	59.20	33.08	59.97	26.89
90	63.55	36.23	67.20	30.97
100	67.74	39.17	74.11	34.95
110	71.80	41.95	80.76	38.81
120	75.76	44.60	87.18	42.57
130	79.66	47.15	93.40	46.25
140	83.50	49.61	99.44	49.83
150	87.30	52.00	105.33	53.34
160	91.07	54.32	111.09	56.77
170	94.82	56.59	116.72	60.13
180	98.57	58.82	122.25	63.43
190	102.34	61.01	127.68	66.66
200	106.10	63.17	133.02	69.85
220	113.54	67.41	143.48	76.07
240	121.06	71.57	153.69	82.11
260	128.81	75.67	163.68	88.01
280	136.49	79.74	173.51	93.76
298.15	143.43	83.41	182.29	98.89
300	144.14	83.78	183.18	99.40
320	151.96	87.80	192.73	104.94
330	156.01	89.80	197.47	107.67
337.99	159.33	91.41	201.24	109.84
		Liquid		
337.99	180.90	145.82	255.66	109.84
340	181.26	146.03	256.73	110.70
350	183.47	147.06	262.02	114.95

a) This entry is $-[G^\circ(T)-H^\circ(0)]/T-S^\circ(0)$ in reality because $S^\circ(0)$ is non-vanishing due to the orientational disorder.

Table 2. Calculation of the Residual Entropy of Crystalline *p*-Bromochlorobenzene

	$S^\circ/\mathrm{J\,K^{-1}\,mol^{-1}}$
Calorimetric entropy by adiabatic calorimetry at 316 K	190.83
Sublimation at 316 K (172.1 Pa)	221.5
Compression to 10^5 Pa	−52.9
Calorimetric entropy of gas at 316 K and 10^5 Pa	359.4
Translational entropy at 316 K	175.60
Rotational entropy at 316 K	120.9
Vibrational entropy at 316 K	68.6
Spectroscopic entropy at 316 K	365.1
Residual entropy	5.7

determined values are not available, in spite of the simple molecular structure, the simplicity enables us to calculate them quantum chemically. It is noted that the calculated vibrational entropy is rather insensitive to each calculated frequency because the vibrational entropy is given as the sum of the entropy contributions of each vibrational mode. The vibrational entropy calculated in the same procedure for a benzene molecule is within 2 $\mathrm{J\,K^{-1}\,mol^{-1}}$ of that based on

Table 3. Calculated Intramolecular Vibrational Frequencies (in cm^{-1}) of *p*-Bromochlorobenzene

A_1	A_2	B_1	B_2
267	362	82.7	174
503	844	258	321
760	979	479	637
1008		658	1101
1064		858	1189
1125		993	1324
1292			1526
1551			1798
1766			3061
3062			3075
3078			

the experimental vibrational frequencies at 298.15 K. The package used here was MOPAC97.[8] All calculations were made assuming the PM3 Hamiltonian. The molecular geometry was optimized and then a vibrational analysis was performed. As expected, the optimized structure has a point group symmetry of C_{2v}. The resulting harmonic vibrational frequencies are given in Table 3. The entropies of the ideal PBCB gas were calculated assuming standard formulae for the translational, rotational, and intramolecular vibrational degrees of freedom. For the vibrational entropy, the normal modes were assumed to be harmonic. Each contribution has magnitudes of 175.60 $\mathrm{J\,K^{-1}\,mol^{-1}}$, 120.9 $\mathrm{J\,K^{-1}\,mol^{-1}}$, and 68.6 $\mathrm{J\,K^{-1}\,mol^{-1}}$ for the translational, rotational and vibrational degrees of freedom. The total "theoretical" entropy is 365.1 $\mathrm{J\,K^{-1}\,mol^{-1}}$.

The residual entropy of a PBCB solid is given by the difference in the calorimetric and calculated entropies, 5.7 $\mathrm{J\,K^{-1}\,mol^{-1}}$, as summarized in Table 2. This is surprisingly close to the expected residual entropy, $R\ln 2$ (≈ 5.8 $\mathrm{J\,K^{-1}\,mol^{-1}}$), corresponding to the "head-to-tail" disorder reported from diffractometry. This coincidence may be accidental, because the present estimate of the spectroscopic entropy relies on a quantum chemical calculation utilizing a commercial package without a deep insight concerning it. Considering that the residual entropy is smaller than one-tenth of the calculated total vibrational entropy, however, it is plausible that the PBCB crystal has a residual entropy comparable to $R\ln 2$.

The presence of a residual entropy comparable to $R\ln 2$ implies that the reported disorder at room temperature is surely frozen-in without a detectable glass transition at some temperature above absolute zero. Such situations had been previously encountered, for example, in hexagonal ice (H_2O) and carbon monooxide (CO), for which the presence of glass transitions was demonstrated by high-precision heat-capacity calorimetry.[9,10] The resolution of the appartaus used in this study was better than those previously utilized. This put the PBCB crystal at a special position.

Since the PBCB crystal under consideration is in the disordered state, i.e., the high-temperature phase of a virtual order-disorder transition, the thermal effect may be undetectably small due to the effective centrosymmetry of the molecular structure. On the other hand, if a marginal glass transition temperature is located above the melting temperature, there arises a question concerning chemical thermodynamics. Is the temperature of fusion defined for such a system? The temperature of fusion determined by the fractional melting method thus has no theoretical basis, but merely means a specific property of a sample. The temperature of fusion of such systems would depend on the sample history (the detailed situation under which the crystal was grown). In any case, the direct and reliable assessment is strongly desired concerning the molecular reorientation and static (or dynamical) nature of the orientational disorder in crystalline PBCB.

Conclusion

The "rigid disorder" in substituted benzenes suggested by Kitaigorodsky still remains unsolved from a thermodynamic point of view. The crystal of the title compound (PBCB) belongs to materials showing solid disorder. The heat capacity of solid and liquid PBCB was measured by adiabatic calorimetry. Neither an ordering phase transition nor a glass transition was detected in the solid state in contrast to the expectation based on the high apparent symmetry of the molecule at room temperature due to an orientational disorder. The existence of a residual entropy of the order of $R\ln 2$ was demonstrated. Some thermodynamic consequense is briefly discussed.

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