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X-Ray Debye Temperatures in a Series of Organic Haloamines†

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Using the observed X-ray reflection intensities for eight organic haloamines, namely, chloramine-T, chloramine-B, bromamine-T, bromamine-B, dichloramine-T, dichloramine-B, dibromamine-T and dibromamine-B, we have determined Debye-Waller factors and hence Debye temperatures. The results have been compared and analysed in terms of molecular composition.

INTRODUCTION

Variety of reactions undergone by aromatic sulfonyl haloamines have attracted considerable interest. The lack of structural data on these compounds has been mentioned in review articles[1, 2] except for the crystal structure[3] of chloramine-T. The chemistry of these compounds is due to their ability to act as sources of halonium cations, hypohalite species and N-anions which act as both bases and nucleophiles. As a result, these reagents react with a wide range of functional groups effectively to induce an array of molecular transformations. Organic haloamines have received considerable attention as oxidimetric reagents.

In this paper, we report the Debye-Waller factors, Einstein temperature, specific heat and Debye temperature from X-ray studies of eight organic haloamines. Measurement of X-ray diffraction intensities for these organic haloamines was carried out with the object of extracting the X-ray Debye temperature θ_M using the Debye model where one does not distinguish between the accoustic and the optical branches of the dispersion curves. The Debye temperature is given by the expression

$$B = \frac{6h^2}{pm_a k_B \theta_M}\left(\frac{\phi(x)}{x} + \frac{1}{4}\right) \qquad (1)$$

where $\phi(x) = \frac{1}{x}\int_0^x y\,dy/[\exp(y) - 1]$ and $x = \frac{\theta_M}{T}$, p is the number of groups, m_a is

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the mean molecular weight, k_B is the Boltzmann constant, h is the Planck constant and T is the absolute temperature.

Using the Debye-Einstein model, where we have a Debye temperature and an Einstein temperature, the expression[4] for B is

$$B = \frac{6h^2}{pm_a k_B \theta_M}\left(\frac{\phi(x)}{x} + \frac{1}{4}\right) + \frac{2(p-1)h^2}{pm_a k_B \theta_E}\left(\frac{1}{\exp(x_E) - 1} + \frac{1}{2}\right) \tag{2}$$

In the classical limit, both have the same linear dependence and separation of these two temperatures is not possible, but it has been observed that Einstein temperature should be 2.5 times smaller than θ_M.

EXPERIMENTAL

Chloramine-T (CAT) (Aldrich, USA) was recrystallized from alcohol. Chloramine-B (CAB) was prepared by the partial chlorination of benzenesulphonamide (Aldrich, USA) in 4 M NaOH for 1 h at 70°C. CAB was recrystallized from methanol[5]. Dichloramine-T (DCT) and dichloramine-B (DCB) were prepared by the chlorination of CAT and CAB solutions respectively and were recrystallized from CCl_4.[6, 7] Dibromamine-T (DBT) and dibromamine-B (DBB) were obtained by the bromination of CAT and CAB respectively and were recrystallized from CCl_4.[8, 9]. Bromamine-T (BAT) and bromamine-B (BAB) were obtained by the partial debromination of DBT and DBB in NaOH and were recrystallized from methanol[10, 11]. The purity of all the compounds was checked by estimating the amounts of active halogen present in them, iodometrically. They were further characterized[12] by their IR spectra, ^1H and ^{13}C NMR spectra.

For recording the diffractograms, X-ray diffractometer RIGAKU, Model DMAX-IC (Japan) Cu K_α radiation was used. A current of 20 mA and voltage of 39 kV was used for all the samples.

RESULTS AND DISCUSSION

Care was taken for all the samples while recording the X-ray powder diffraction pattern. In all the samples a number of reflections were observed for a 2θ range of 5° to 50°. A typical result for DBB is given in Table-1.

To a first approximation, the Debye-Waller factor (B) was assumed to be same for all atoms in a given molecule, so that we can define a mean value of B for the molecule. With this approximation, the integrated intensity for the molecule is given by

$$I = KL_P\, P(\Sigma f)^2 \exp\left(-2B\frac{\sin^2\theta}{\lambda^2}\right) \tag{3}$$

Here K is a constant, L_P is Lorentz polarization factor, P the multiplicity factor, θ is the Bragg angle, λ is the wavelength of the X-rays and B is the mean Debye-Waller factor for the corresponding molecule. The atomic scattering factors given in International Table[13] have been used to compute $(\Sigma f)^2$. The average B factors are essential for further X-ray crystal structure analysis.

TABLE-1
2θ AND OTHER PARAMETERS FOR DIBROMAMINE-B

Peak	2θ	I(cps)	$\sin\frac{\theta}{\lambda}$	$\log\left(\frac{I}{L_p(\Sigma f)^2}\right)$
1	9.281	1232	0.0525	–2.0195
2	13.764	478	0.0778	–2.2209
3	14.341	728	0.0810	–2.0153
4	15.300	346	0.0864	–2.3026
5	16.187	315	0.0914	–2.3096
6	17.655	297	0.0996	–2.2857
7	18.316	432	0.1033	–2.0983
8	19.306	614	0.1088	–1.9098
9	19.644	642	0.1107	–1.8785
10	20.181	492	0.1137	–1.9776
11	21.407	596	0.1206	–1.8523
12	21.906	420	0.1233	–1.9889
13	23.433	535	0.1318	–1.8453
14	23.446	567	0.1319	–1.8101
15	24.077	401	0.1354	–1.9394
16	26.837	623	0.1506	–1.6658
17	27.582	3277	0.1547	–0.9235
18	28.334	951	0.1589	–1.4375
19	29.274	575	0.1640	–1.6286
20	30.962	952	0.1733	–1.3619
21	31.794	436	0.1778	–1.6775
22	32.880	490	0.1837	–1.5967
23	34.253	624	0.1912	–1.4546
24	35.956	447	0.2004	–1.5512
25	36.702	551	0.2044	–1.4417
26	37.075	422	0.2064	–1.5482
27	37.631	430	0.2094	–1.5253
28	38.800	535	0.2156	–1.4023
29	40.637	344	0.2254	–1.5483
30	42.983	485	0.2378	–1.3417
31	43.804	378	0.2421	–1.4292
32	45.642	342	0.2518	–1.4287
33	48.168	419	0.2649	–1.2854

It follows from equation (3) that a graphical plot of $\log \left[\frac{I}{KL_pP(\Sigma f)^2}\right]$ against $\frac{\sin^2\theta}{\lambda^2}$ is a straight line and the least square method has been used to determine the slope and also the standard deviation from which the temperature factor B is obtained. Using this value in equation (1) and the published value[14] of W(x) for various x, we have determined θ_M for the Debye model, θ_E for Einstein model and specific heat Debye temperatures θ_D. These are given in Table-2.

TABLE-2
TEMPERATURE FACTORS FOR ORGANIC HALOAMINES

Compound	B in 10^{-16} cm^2 ($\pm$ 0.01)	W(x)	x	θ_M	T_m	$\theta_{Theo.}$	θ_E	θ_D
CAT	18.67	68.61	0.1210	36.30	442	44.65	25.67	51.34
CAB	10.56	33.16	0.1740	52.20	445	51.08	36.91	73.82
BAT	20.80	88.53	0.1065	31.95	443	39.55	22.59	45.18
BAB	10.61	39.33	0.1595	47.85	452	44.82	33.83	67.67
DCT	15.75	49.36	0.1420	42.60	346	45.12	30.12	60.25
DCB	22.43	66.18	0.1230	36.50	347	47.50	25.81	51.62
DBT	19.99	85.86	0.1080	32.40	383	37.84	22.91	45.82
DBB	12.83	52.76	0.1375	41.25	366	35.68	29.17	58.33

Temperature factors in K.

Using cell parameters (V) (obtained from a multidimensional FTN 77 programme SIMPLEX which fits all the observed reflections to within 1% of the mean value) and mean molecular weight (m_a), the Debye temperature, employing the relation[15]

$$\theta_{Theoretical} = C\left(\frac{T_m}{m_a V^{2/3}}\right)^{1/2} \qquad (4)$$

for all the samples have been estimated and these are also given in Table 2. T_m is the melting temperature. It is to be noted that the theoretically estimated Debye temperature ($\theta_{Theoretical}$) is in agreement with the Debye temperature θ_M obtained from the Debye model. The similarities in these compounds are however due less to the crystal structure than to the similarities in the relative magnitudes of the forces between atoms or ions, which is a natural outcome of the results reported here even within the limitations of averaged Debye-Waller factors for the molecule in all the samples.

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