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Disorder and Polymorphism of Tetramethylammonium Chloride

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The tetragonal (III)/rhombohedral (II) and rhombohedral/f.c.c. (I) transition lines of tetramethylammonium chloride were measured as functions of pressure. The III/II transition is reversible in the presence of trace amounts of solvents. Phase II has a configurational entropy of $\sim R\ln \frac{3}{2}$, and phase I a configurational entropy of $\sim R\ln 32$. It is suggested that this is due to orientational disorder of the cations, and that no major changes in proton disorder at the transitions are involved. A structure for tetramethylammonium chloride II, based on the space group *R3m*, is proposed.

Introduction

Chang and Westrum (*1*) measured the heat capacity of tetramethylammonium chloride [$N(CH_3)_4Cl$, to be called TMAC in the following] between 5 and 300 K, and found a first-order transition from a low-temperature phase V to a phase IV at 75.8 K, as well as a λ-transition at 184.9 K to the room-temperature phase III. TMAC III is tetragonal, space group D_{4h}^7-*P*4/*nmm*, with the PH_4I structure (*2*, *3*). The lattice constants of this phase appear to be somewhat variable (*2*–*7*). Dufourcq et al. (*6*) found that TMAC III, upon heating to ~413 K, irreversibly transformed to rhombohedral TMAC II, and concluded that TMAC II is the stable phase at room temperature, and that TMAC III is a hydrated phase which can only exist in the presence of a small amount of water. TMAC II reversibly transforms at 536 K (*7*) to TMAC I, which is face-centred cubic (*6*). TMAC II is piezoelectric (*4*, *8*). A proton magnetic resonance investigation (*4*, *8*) has shown that methyl-group reorientation occurs, with a fairly low activation energy even in TMAC IV, but without noticeable tunnelling. It was also found that the cations reorient with an activation energy which is somewhat higher, except in phase I. These reorientations will be disregarded in what follows since it may be argued, following Darmon and Brot (*9*), that they make little or no contribution to changes of entropy at phase transitions.

Experimental

Reagent grade tetramethylammonium chloride obtained from B.D.H. was washed with hot chloroform to remove any free amines or lower methylammonium chlorides present. Samples were then repeatedly recrystallized from dry methanol and heated to ~400 K in Pyrex ampoules for 25–30 hr to destroy any tetramethylammonium hydrogen dichloride present (*10*).

Pressure was generated in a piston-cylinder apparatus (*11*). Phase transitions were observed by means of differential thermal analysis (DTA), using Chromel–Alumel thermocouples. The detailed experimental procedure has been described before (*12*), but oven assemblies were constructed

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of Teflon instead of from talc as usual. Nonsymmetrical corrections (*13*) in this arrangement differed considerably from those observed in talc assemblies, and this effect had to be redetermined. The samples were contained in stainless steel capsules, with no evidence of contamination. Heating/cooling rates were in the range 0.8–1.3 K/sec. The results can be expected to be accurate within ±1 K and ±0.5 kbar.

Room-temperature X-ray diffraction patterns were obtained in a Philips high-angle diffractometer, while high-temperature photographs were obtained in a Pye Unicam high-temperature camera. In the latter case the samples were contained in evacuated 0.5 mm silica Lindeman tubes. Filtered Cu*Kα* radiation was used throughout. The high-temperature photographs were indexed and corrected using the Nelson–Riley correction method. Heats of transitions at atmospheric pressure were measured using a Perkin–Elmer Model 1B differential scanning calorimeter.

Results

High-Pressure Studies

The TMAC III/II transition yielded strong and sharp DTA signals [Fig. 1(i)] with a hysteresis of ~18–24 K between the transition temperatures observed upon heating and upon cooling. The transition was, however, completely reversible. The hysteresis depended strongly on the heating/cooling rate, and also on the previous thermal history of the sample. At atmospheric pressure our mean value for the III–II transition temperature was 409.7 K, and for the II–III transition temperature 389.0 K, yielding a mean "equilibrium" transition temperature of ~399.3 K. Tentative points on the transition line were obtained to ~6 kbar, with the DTA signals becoming progressively weaker until they were impossible to detect. The initial slope of the transition line is ~22 K/kbar. The line rises to 455.4 K at ~6.1 kbar.

The TMAC II/I transition yielded extremely strong and sharp DTA signals [Fig. 1(ii)] with less than ~2 K thermal hysteresis. The transition was fully reversible, but after the II → I → II transition cycle has occurred, TMAC III could not be formed again, and TMAC II metastably persisted in the stability region of TMAC III. The II/I transition occurs at atmospheric pressure at 537.2 ± 1 K, and rises steeply with pressure with moderate curvature. The transition line was followed to 3.0 kbar, 653 K, beyond which explosive decomposition to a mixture of methyl chloride and trimethylamine consistently occur-

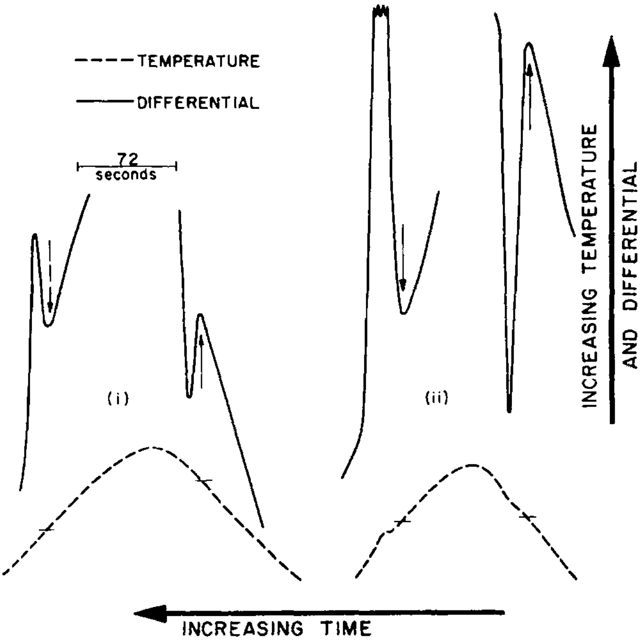

FIG. 1. Typical DTA signals obtained. (i) TMAC III/II transition at 0 kbar, 409.7 K upon heating, 389 K upon cooling. (ii) TMAC II/I transition at 0 kbar, 538 K upon heating, 536.4 K upon cooling.

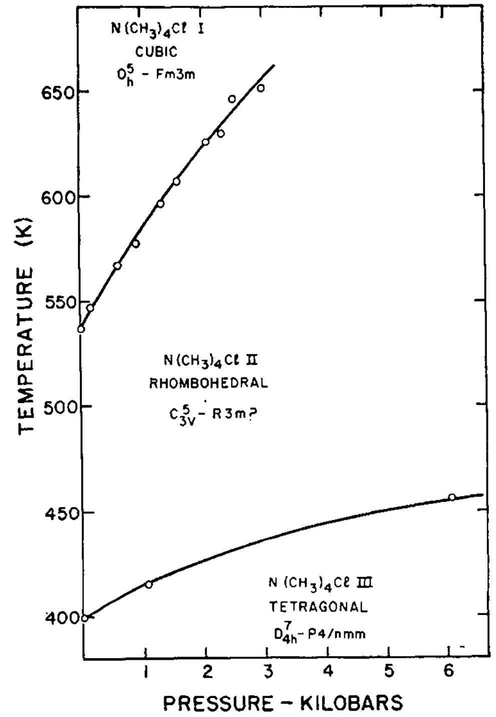

FIG. 2. Phase diagram of tetramethylammonium chloride (TMAC).

red. This decomposition was observed to occur at ~567 K under its own vapour pressure.

The P–T phase diagram of TMAC is shown in Fig. 2.

Entropies of Transitions

The TMAC III/II transition was found by means of DSC, to have an entropy of 3.8 J/mole-deg, i.e., ~*Rln* $\frac{3}{2}$, while the TMAC II/I transition had an entropy of 23.7 J/mole-deg, in close agreement with the value of 23.4 J/mole-deg obtained by Dufourcq et al. (*6*).

Using the initial slopes of the transition lines, viz., ~22 and 49.4 K/kbar, respectively, and applying the Clapeyron relation, it follows that

$$\Delta V_{\mathrm{III/II}} \simeq 0.8\ \mathrm{cm^3/mole}$$

and

$$\Delta V_{\mathrm{II/I}} = 11.7\ \mathrm{cm^3/mole}.$$

This value of $\Delta V_{\mathrm{III/II}}$ cannot be considered accurate in view of the limited number of tentative high-pressure points obtained on the III/II transition line.

Crystallography

TMAC III at 20°C was found to be tetragonal, space group D_{4h}^7-*P4/nmm*, in agreement with earlier workers (*2–7*). However, a sample recrystallized from methanol yielded the cell constants

$$a_0 = 7.616 \pm 0.008\ \text{Å}$$
$$c_0 = 5.394 \pm 0.006\ \text{Å}$$

while another sample obtained by transforming TMAC II to III in the presence of traces of water vapour yielded the slightly different cell constants

$$a_0 = 7.583 \pm 0.008\ \text{Å}$$
$$c_0 = 5.388 \pm 0.006\ \text{Å}.$$

Vegard and Sollesnes (*2*) assigned the carbon atoms to the 8*i* positions of D_{4h}^7, yielding the same antiparallel arrangement of tetrahedra as in the tetragonal phase of ND_4Br (*14*). They also considered that the space group D_{4h}^7 requires the 24 protons in a unit cell to be divided into either three groups of 8 equivalent protons each, or into two groups, one of 8 and the other of 16. Only this latter arrangement is sterically acceptable to the cation at any temperature, and leads to a second moment in agreement with that observed at lower temperatures (*4*, *8*). Thus the methyl groups can contribute no configurational disorder, and phase III is ordered, in agreement with the small transition entropies of the V/IV and IV/III transitions.

Powder patterns of TMAC II at 473 K and 523 K are listed in Table I. These are in fair agreement with the patterns obtained by Dufourcq et al. (*6*) at 298 K and 518 K. The unimolecular rhombohedral lattice constants obtained are:

$$\text{At 473 K: } a_{rh} = 5.835\ \text{Å}$$
$$\alpha_{rh} = 70°31'.$$
$$\text{At 523 K: } a_{rh} = 5.857\ \text{Å}$$
$$\alpha_{rh} = 70°30'.$$

The selection rules (no restrictions) rule out the space groups *R3c* and *R$\bar{3}$c*. Since TMAC II is known to be piezoelectric (*8*), it must have a non-centrosymmetric space group. However, if TMAC III is assumed to be ordered, TMAC II must have a configurational entropy of ~*Rln* $\frac{3}{2}$. There does not appear to be any reasonable model yielding this particular entropy value, and it is more reasonable to assume TMAC II to

TABLE I

POWDER PATTERNS OF TMAC II (FILTERED CU$K\alpha$ RADIATION)

473 K		523 K			
d_{obs} (Å)	d_{calc} (Å)	d_{obs} (Å)	d_{calc} (Å)	*I*	*hkl* (*rh*)
5.30	5.326	5.36	5.345	8	001
4.350	4.350, 4.349	4.365	4.368, 4.365	10	111, 011
3.360	3.368	3.373	3.380	8	$01\bar{1}$
2.838	2.847, 2.847	2.862	2.858, 2.857	8	$121, 11\bar{1}$
2.656	2.663, 2.663	2.675	2.673, 2.673	8	012, 002
2.370	2.382	2.403	2.392	6	122
2.169	2.175, 2.175, 2.174	—	2.183, 2.183, 2.182	6	$222, 022, 01\bar{2}$
2.085	2.089	2.115	2.097	6	$12\bar{1}$
1.946	1.945, 1.945	1.949	1.952, 1.952	6	$131, 1\bar{2}1$
1.822	1.827, 1.827	1.834	1.834, 1.834	6	123, 013
1.772	1.776, 1.775, 1.775	1.781	1.783, 1.782, 1.782	4	$223, 1\bar{2}\bar{2}, 003$
1.682	1.684, 1.684	1.689	1.691, 1.690	6	$023, 02\bar{2}$
1.569	1.571, 1.571, 1.570, 1.570	1.572	1.577, 1.577, 1.576, 1.576	2	$233, 133, 13\bar{1}, 01\bar{3}$

possess twofold disorder, i.e., to have a configurational entropy of $R\ln 2$ rather than $R\ln \frac{3}{2}$. This particular disorder can be obtained in the non-centrosymmetric space group $D_3{}^7$-$R32$ by placing the anion in the $1a(0,0,0)$ position, and allowing the nitrogen atom to randomly occupy the $2c \pm (x,x,x)$ positions with $x \sim \frac{1}{2}$. One carbon atom now occupies the $2c \pm (x,x,x)$ positions with $x \sim \frac{1}{4}$, while the other three carbon atoms occupy either one of the two staggered triplets of $6f(x,y,z;\ z,x,y;\ y,z,x;\ \bar{y},\bar{x},\bar{z};\ \bar{z},\bar{y},\bar{x};\ \bar{x},\bar{z},\bar{y})$ positions. This model involves exactly two equivalent distinguishable orientations of the cation tetrahedron. However, sterically it is difficult to understand how cation reorientation from one to the other of these positions can occur, since a large motion is required. A more acceptable model is based on the non-centrosymmetric space group C_{3v}^5-$R3m$ by placing the anion arbitrarily at the $1a(x,x,x)$ position with $x = 0$. The nitrogen atom is located at a $1a(x,x,x)$ position near $x \sim \frac{1}{2}$. One carbon atom is also on the threefold axis in a $1a(x,x,x)$ position near $x \sim \frac{1}{4}$. The other three carbon atoms of the cation tetrahedron can occupy either of the two triplets of $6c(x,y,z;\ z,x,y;\ y,z,x;\ y,x,z;\ z,y,x;\ x,z,y)$, centered at approximately $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$. This results in two distinct equivalent orientations of the cation and, therefore, a configurational entropy of $R\ln 2$. Furthermore, only slight motion is required to reorient. If the orientation of any given cation is not completely independent of the orientations of neighbouring cations, it is probable that the configurational entropy may be somewhat less than $R\ln 2$ just above the III/II transition, but that it reaches its full value of $R\ln 2$ at higher temperatures. At temperatures considerably below the stable III/II transition, quenched TMAC II may become either completely ordered, without any marked structural change, or the disordered arrangement may be "frozen in," i.e., a change from dynamic to static disorder.

The powder pattern of TMAC II can also be satisfactorily assigned on the basis of a cubic cell with $a_0 \sim 10.7$ Å, space group I*** and eight formula units per unit cell. The density in this case is essentially identical with that of the rhombo-

TABLE II

POWDER PATTERN OF TMAC I AT 543 K (FILTERED CU$K\alpha$ RADIATION)

d_{obs} (Å)	d_{calc} (Å)	*h k l*	*I*
4.54	4.555	2 0 0	10
3.22	3.221	2 2 0	8
2.74	2.747	3 1 1	6
2.623	2.630	2 2 2	4
2.089	2.090	3 3 1	4
2.048	2.037	4 2 0	2
1.857	1.860	4 2 2	2
1.750	1.753	511, 333	2

hedral cell. However, the transition behaviour of TMAC was studied in a hot-stage microscope under crossed Nicols, and this conclusively showed that TMAC II is not isotropic, whereas TMAC I is isotropic. A cubic indexing of the powder pattern of TMAC II can, therefore, not be correct.

The powder pattern of TMAC I at 543 ± 2 K is shown in Table II, and can be interpreted as f.c.c. with $a_0 = 9.11$ Å, in good agreement with Dufourcq et al.'s value (*6*). There are four formula units per unit cell.

The TMAC II/I transition entropy is 23.7 J/mole-deg. Previously, in dealing with the TMAC III/II transition, the tacit assumption was made that $\Delta S_{\text{vibr}} = 0$ in the expression (*15*)

$$\Delta S_{\text{tr}} = R \ln(N_2/N_1) + \Delta S_{\text{vibr}}.$$

This assumption is justified only if no major structural changes occur during the transition. However, the TMAC II/I transformation involves a change from a CsCl-like structure to an NaCl-like structure, and involves a change of coordination. An attempt must therefore be made to evaluate ΔS_{vib}. If all detail concerning the cation is neglected, TMAC I, on the one hand, and II, III, IV, and V, on the other, can be considered as analogous to the B_1 and B_2 phases, respectively, of the alkali halides. Bassett et al. (*16*) have shown that in that case, for which $R \ln(N_2/N_1) = 0$,

$$(\Delta S)_p \simeq \gamma_{01} C_{V1} \frac{\Delta V}{V_{01}} + (\Delta S)_v$$

where $(\Delta S)_p$ is the entropy difference at constant pressure, $(\Delta S)_v$ the entropy difference at constant volume due to structural reasons only, γ_{01} the Grüneisen constant of the B_1 phase, C_{V1} its specific heat at constant volume, and $\Delta V/V_{01}$ the relative volume change of the B_1/B_2 transition. Within their approximation, $(\Delta S)_V = 9.42$ J/mole-deg. If we assume $\gamma \simeq 1.5$, similar to the value for the alkali halides (*17*), and $C_{V1} = 50$ J/mole-deg (the Dulong–Petit value), the present value of the volume change (11.7 cm^3/mole) yields

$$(\Delta S_{\text{vib}})_{\text{II/I}} = +0.7\ J/\text{mole-deg}.$$

The configurational portion of the transition entropy is therefore

$$\begin{aligned} R \ln(N_{\text{I}}/N_{\text{II}}) &= (\Delta S_{\text{conf}})_{\text{II/I}} \\ &= 23.0\ J/\text{mole-deg} \\ &\simeq R \ln 16. \end{aligned}$$

Taking the configurational entropy in TMAC II to be $\sim R \ln 2$ or slightly less, this demands a configurational entropy in TMAC I of $\sim R \ln 32$ or slightly less. There are a number of possible arrangements in the space group O_h^5-$Fm3m$ yielding configurational entropies of this order, and, in the absence of highly accurate diffraction intensities, it is not at this stage possible to make a definite choice.

Conclusions

If proper allowance is made, by extrapolation, for thermal expansion, the present high-temperature X-ray diffraction results yield a value of 9.6 cm^3/mole for the volume change of the TMAC II/I transition, in reasonable agreement with the value of 11.7 cm^3/mole derived from the observed initial slope of the transition line and the observed entropy of transition.

Dufourcq et al. (*6*) discussed the cation configurational disorder in TMAC I on the basis of its supposed equivalence to NH_4I, and concluded that the disorder in this phase will not exceed $R \ln 6$, and could well be less. It is clear now that this is not the case, and that the cation disorder in TMAC I is, in fact, not similar to the cation disorder occurring in NH_4I I or ND_4Br I, one reason being the absence of hydrogen bonding in TMAC^5. Although the configurational entropy terms are similar in disordered cubic ND_4Br II and in rhombohedral TMAC II, the II/I transition entropy is $\sim R \ln 3^{18}$ for ND_4Br, while it is $\sim R \ln 16$ for TMAC.

Dufourcq et al. (*6*) further concluded that TMAC III is a hydrated phase, and that TMAC II is the stable phase at ambient conditions. It is true that TMAC II will not revert to TMAC III below ~380 K in the absence of traces of solvents, but Gibson and Raab (*8*) found that as little as 0.5% by volume of water, or small amounts of dry methanol, ethanol and butan-1-ol, caused the transformation to occur, while chloroform (which is not a solvent) had no effect. It must be concluded that the solvent simply acts as a mineralizer, and that TMAC II below ~400 K is metastable with respect to TMAC III. Heating to ~540 K also prevents the II–III transition on cooling, probably by removing all traces of solvent by solvolysis as in the alkali halides. The thermal hysteresis observed for the TMAC III/II transition, as well as the DTA signals corresponding to this transition [Fig. 1(i)], shows that the transition must be of the first order, as is obvious from its crystallography.

It can be concluded that the TMAC III/II and II/I transitions involve discontinuous increases of the cation configurational entropy, but that the methyl groups make no important contribution at these transitions. We tentatively suggest that TMAC IV and V may have structures derived or related to those of the ordered low-temperature and high-pressure forms of NH_4Br (*19*). There are indications that TMAC IV may be tetragonal (*20*) with unit-cell constants close to those of TMAC III.

If this is the case, one can expect the phase diagram of TMAC to be somewhat similar to those of the ammonium halides, even though the exact degree of disorder in some pairs of corresponding phases may differ. The question now arises why no phase similar to disordered NH_4Br II (space group O_h^1-$Pm3m$) is encountered for TMAC. A possible explanation may be found in the generalized phase diagram of the ammonium halides (*19*, *21*), which shows the D_{4h}^7 phase to be a low-pressure phase relative to both ordered (T_d^1) and disordered (O_h^1) CsCl-type cubic phases and also relative to the new ordered phase of NH_4Br (*19*). If the analogy holds, one would therefore expect disordered CsCl-type cubic TMAC to occur at somewhat elevated pressures. It is possible that the disappearance of the DTA signals corresponding to the TMAC III/II transition near $\sim$6 kbar may have been due to the intervention of such a phase at a possible O_h^1/III/II triple point. The rhombohedral phase TMAC II would appear to be unique.

This hypothesis could also account for the absence of phases similar to TMAC II and I for $N(CH_3)_4Br$ and $N(CH_3)_4I$, at least at atmospheric pressure. The generalized phase diagram for the ammonium halides (*19*, *21*) shows that the stability region of the tetragonal phase increases markedly with increasing anionic radius. This suggests that the phase diagrams of $N(CH_3)_4Br$ and $N(CH_3)_4I$ may be similar to that of TMAC only at elevated pressures. At ambient pressure decomposition occurs before any high-temperature phases appear.

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