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Publication Date

1978-03-01

Submitted to Journal of Chemical Physics

LBL-7535
Preprint

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March 1978

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

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Calorimetric Studies of Choline Chloride, Bromide, and Iodide

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(Received

A long standing question regarding the remarkable ionizing-radiation sensitivity of crystalline choline chloride, $[(CH_3)_3NCH_2CH_2OH]^+Cl^-$, is the extent to which the chain-decomposition depends on the crystal structure.¹

The unique radiation sensitivity is shown by only one of the two known crystallographic polymorphs (α) which exists below 78°C (351°K).^{1,2} At about 351°K the crystal undergoes a crystallographic transition to a radiation stable, high temperature phase (β). Detailed radiolysis data (G values) have not been reported, so far, for temperatures lower than ambient. It is known, however, that the α form is radiation stable at $\sim 200^\circ K$,¹ and this radiation stability seems to extend up to $\sim 250^\circ K$.¹

In search of a possible phase transition, which might act as a low temperature boundary to the radiation sensitivity of α -choline chloride, we have recently carried out calorimetric studies below room temperature. Moreover, since similar studies have not been reported, we extended our measurements to higher temperatures and to two more choline salts: the choline bromide, which is also radiation sensitive, and the choline iodide, which is radiation stable.

The measurements were obtained with a Perkin-Elmer model DSC-2 differential scanning calorimeter supplied with a subambient accessory (range $\sim 203^\circ K$ to $\sim 1000^\circ K$). The instrument was calibrated by indium (m.p. $429.78^\circ K$) and water (m.p. $273.15^\circ K$) standards. The baseline flatness was carefully optimized in the temperature range of interest ($\sim 203^\circ - 480^\circ K$) to within 0.2 millicalorie/second. All thermograms, including the choline

samples, were repeatable within 0.02 in millicalorie/second. The transition peak areas were transformed into millicalories by comparison with the indium heat of fusion data.³

The results of the measurements (summarized in Table I) are as follows:

1) Choline Chloride

The thermogram showed a broad phase transition at $\sim 351^\circ\text{K}$, which was identified as the α to β form transition. Beyond this transition no other peak appeared with sample quantities up to ~ 7 mg. A phase transition at the lower end of the temperature scale might have been masked, however, by hysteresis effects. Approximate measurements at lower temperatures than 203°K were performed by means of a simple calorimetric experiment. A large quantity (a few gm) of choline chloride folded in aluminum foil, in order to achieve thermal homogeneity, was placed in a pyrex tube which was sealed. After the sample was cooled to $\sim 77^\circ\text{K}$ it was allowed to reach ambient temperatures, slowly, inside a dewar. The temperature of the sample was recorded as a function of time with the aid of a thermocouple embedded in the choline chloride powder. An isothermal transition should appear as a second order change (step change) in the temperature vs. time curve. Repeated scans showed a very smooth baseline without indication of a transition in the range $\sim 77^\circ$ to $\sim 290^\circ\text{K}$. On the contrary, the curve showed a considerable change when the sample was heated slowly through the α to β form transition temperature. It is, therefore, very unlikely that choline chloride undergoes any other transition, except the α to β , in the temperature interval 77° to 475°K .

Thermograms of samples of different purities and masses showed little variation in the transition energy. The transition temperature varied, however,

over a range of a few degrees. Average values and errors are listed in Table I.

2) Choline Bromide

Infrared,¹ electrical conductivity,¹ and NMR studies^{4,5} indicate a possible phase transition at 364°K for this compound. This transition appeared in our measurements as a broad peak similar to the one of the α to β form^{transition} in choline chloride. The transition temperature and energy averaged over two samples and various scanning conditions are listed in Table I. In addition to the large peak starting at ~363°K the thermograms indicated the presence of a very small broad peak centered around 270°K. This peak became more pronounced with larger samples. It is not clear if this peak represents a new phase transition in choline bromide.

3) Choline Iodide

In addition to the evidence for a possible phase transition at 364°K,^{1,4} McDowell et al. recently reported NMR measurements that indicate another phase transition at 430°K for this compound.⁵ Our measurements demonstrated clearly both transitions. One occurs around 367°K and the other at 436°K. The respective transition energies are listed in Table I.

All transitions that were recorded by increasing the temperature also appeared on cooling, with a hysteresis of approximately 10-20 degrees.

It is interesting to note in Table I that choline chloride and bromide have similar transition energies. This, combined with the similarity in their infrared¹ and NMR spectra,^{4,5} indicates that the choline bromide transition is also of the order-disorder type, as is the case for choline chloride.⁶ In many respects, therefore, including radiation sensitivity, these two salts have very similar properties. In contrast to the chloride

and bromide, the iodide has much lower transition energies. The NMR data for this salt support a diffusion of the choline ion in the temperature range between the two phase transitions.

The results of this study show that there is no low temperature crystallographic boundary to the radiation sensitivity of choline chloride. Therefore, the fact that the choline chloride exhibits radiation sensitivity only above approximately 250°K should be attributed to the onset of non calorimetrically detectable thermodynamic processes. Graham and Hannon⁴ and McDowell et al.⁵ have concluded from proton NMR studies of choline chloride and some analogs that there is a successive onset of rotations of various groups in the molecule as the temperature is raised from 77°K. It has been suggested^{4,6} that the isotropic reorientation which occurs at the α to β phase transition of choline chloride might inhibit the decomposition chain mechanism through protonic conductivity.¹

In order to elucidate further the possible rotation mechanism in the choline salts we are presently pursuing high resolution ¹³C and ¹⁵N NMR studies of the above choline analogs in the solid state.

The authors are indebted to Professor Ian Carmichael for the use of his DSC-2 apparatus. The research was supported by the Biomedical and Environmental Division of the U. S. Department of Energy.

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Table I

Transition Temperatures and Energies of the Three Choline Salts*

Compound	Trans. Temp. °K	$\Delta H \frac{\text{Cal}}{\text{gr}}$	$\Delta H \frac{\text{Kcal}}{\text{mole}}$	$\Delta S = \frac{\Delta H}{T} \frac{\text{cal}}{\text{mole} \cdot \text{deg}}$
Chol. Cl	351(3)	28.3(7)	3.95(5)	11.3(2)
Chol. Br	363(2)	21.1(5)	3.88(5)	10.7(2)
Chol. I	367(3)	13.2(4)	3.05(5)	8.3(2)
	436(3)	6.45(10)	1.49(2)	3.4(1)

* Numbers in parentheses represent estimated errors in the last significant digit.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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