

Why Does Tetramethylammonium Oxalate Exhibit Sublimation?

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Solid state features of the ionic compound $[\text{NMe}_4]_2[\text{C}_2\text{O}_4]$ are used to explain its unexpected sublimation behaviour.

Usually, decomposition of organic solids is irreversible. During experiments with $[\text{NMe}_4]_2[\text{C}_2\text{O}_4]$ in solid state reactions, we made the unexpected observation that the salt decomposed at temperatures above 260 °C and recrystallized in cold parts of the reaction vessel. At temperatures above

294 °C decomposition was irreversible. To understand this behaviour, we have analysed the properties of tetramethylammonium oxalate and investigated the mechanism of the sublimation.

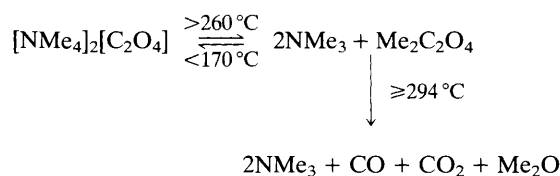
The substance was synthesized from $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and

$\text{NMe}_4\text{OH}\cdot\text{H}_2\text{O}$.¹ The crystalline material obtained was shown to be pure by IR and Raman spectroscopy and elemental analysis. The observed powder diffraction pattern could be simulated by a calculated pattern based on a structural model derived from the fluorite-type (face-centred cubic, $a = 1114.22$ pm). In this model it is assumed that the cations $[\text{NMe}_4]^+$ as well as the anions $[\text{C}_2\text{O}_4]^{2-}$ are rotationally disordered around their centres of gravity ($[\text{NMe}_4]^+$: $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and $\frac{3}{4}, \frac{1}{4}, \frac{1}{4}$; $[\text{C}_2\text{O}_4]^{2-}$: $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, 0$). This assumption was confirmed by cooling the substance. Two phase transitions at -14 and -27°C were recorded using low temperature Guinier powder diffraction. These phase transitions take place with loss of symmetry and are accompanied by thermal effects as measured by low temperature difference thermal analysis. The observations indicate that the phase transitions are associated with the freezing of the rotational degrees of freedom.

The decomposition behaviour was investigated by high temperature difference thermal analysis and high temperature Guinier powder diffraction. Total and irreversible decomposition of $[\text{NMe}_4]_2[\text{C}_2\text{O}_4]$ took place at 294°C (atmospheric pressure). In this case no solid residue was obtained and the gas phase consisted of carbon monoxide, carbon dioxide, dimethyl ether and trimethylamine, as proved by high resolution mass spectroscopy. Earlier, the same decomposition products had been assumed without proof by Lawson and Collie,² who reported the title compound's decomposition but did not observe its sublimation. The residue of an interrupted decomposition procedure was analysed by IR spectroscopy. The material consisted of dimethyl oxalate and $[\text{NMe}_4]_2[\text{C}_2\text{O}_4]$. Based on these observations, we derive the sublimation mechanism in Scheme 1.

In an independent experiment we were able to confirm the recombination of the ester and the amine. The recombination resembles the reaction of methyl halides with amines observed in mass spectroscopic experiments. The high synthetic potential of this reaction from methyl esters and amines to tetramethylammonium compounds is evident.

Why does the ionic compound $[\text{NMe}_4]_2[\text{C}_2\text{O}_4]$ sublime by decomposing reversibly to the molecular entities ester and



Scheme 1

amine and back to the salt, a process not known for other tetramethylammonium salts? We believe that this macroscopically observable behaviour is only possible because of the microscopic properties of the salt: the flexibility due to the rotation of the molecular ions allows an intermolecular methyl group transfer in the solid. Thus, in this case an otherwise crucial requirement for (topochemical) reactions in the solid state³ becomes unnecessary: the structural arrangement of the reacting partners along the reaction coordinate in the crystal. The orientational disorder allows decomposition at a temperature which is low enough to guarantee the stability of the ester which is formed. At lower temperatures the ester and the amine may react back to the salt which is favoured by the contribution of the lattice energy to the free energy.

In conclusion, the molecular chemical reaction responsible for the sublimation behaviour, the methylation of an anion by the tetramethylammonium ion, is made possible by the substance's topological and dynamical properties in the solid state. In support of our explanation for the observed effect we will later report on high temperature solid state NMR spectroscopic investigations.

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References

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