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Crystallisation of organic salts by sublimation: salt formation from the gas phase†

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Crystals of organic salts can be grown by sublimation in two systems: succinic acid with hexamethylenetetramine, and oxalic acid with 4,4′-bipyridine. Both systems also form co-crystals by sublimation. Additionally, salts and co-crystals are able to re-sublime once formed, allowing the separation of different multicomponent crystal forms using sublimation. Preliminary experiments indicate that ion pairs may be present in the gas phase during the sublimation of salts. Crystallisation by sublimation is compared to solution crystallisation and mechanochemical methods.

Introduction

Organic multicomponent crystals, such as co-crystals and salts, are of interest in various industries[1–4] due to the possibility that they will have improved physicochemical properties compared to their constituent species.[5] Co-crystals consist of two or more neutral molecules, whereas molecular salts contain ions, usually resulting from simple transfer of a hydrogen atom from one molecule to the other. Species containing both charged and neutral molecules also exist, often called co-crystals of salts.[6,7] While organic salts and co-crystals technically only differ by a change in the position of a hydrogen atom, they are distinct crystal forms,[1] often with different stoichiometries[8] and distinct physicochemical properties. It is important that these different forms can be prepared selectively in order to take advantage of whichever form has the more favourable properties. The use of different preparative techniques is one way of controlling the product of a crystallisation. Herein we demonstrate that organic salts and co-crystals can be selectively prepared, recrystallised and separated by sublimation.

Reports of sublimation of organic salts are rare, with only one paper mentioning re-sublimation of a molecular salt[9] (when pre-formed multicomponent materials are sublimed to re-crystallise the material, so that the same material is re-formed, we shall use the term re-sublimation, to distinguish this from subliming the individual molecular components together in order to form a multicomponent material, which we have called co-sublimation). In fact, salt formation has been used to prevent the sublimation of volatile compounds (for example the salt of mirtazapine[10]). Sublimation of salts generally involves high temperatures, and the material may degrade or dissociate in the process.[11–13]

There are no previous reports of crystallisation of organic salts from neutral starting materials by co-sublimation. It is known that proton transfer in the dilute gas phase is not favorable,[14] and isolated ions are not stable in the gas phase, so formation of salts from the gas phase by co-sublimation of neutral components is not anticipated. It has been reported that co-crystals can be formed by co-sublimation,[15–18] with one recent report from our group,[19] although this technique is not commonly used (see for example ref. 20, a review on preparative methods for co-crystals that does not mention sublimation). The re-sublimation of co-crystals is also rarely mentioned in the literature: the first report of this is a 2019 paper by Ye *et al.*[21] It is clear that the use of sublimation to prepare multicomponent organic crystals has not been well explored.

The use of different preparative techniques to selectively obtain different crystalline products is by no means a new idea. Losev *et al.* have used different crystallisation techniques to produce different polymorphs,[22] and in 2017 André *et al.* also showed that a particular hydrated multicomponent crystal can be selectively produced using mechanochemistry instead of solution methods.[23] However, the first mention of specifically selecting between salts and co-crystals using different preparative methods is in a 2018 study by Losev and Boldyreva.[24] They used mechanochemistry and several

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† Electronic supplementary information (ESI) available: Co-crystallisation procedures; mechanochemical conversions; re-sublimation procedures; crystal structure descriptions and crystallographic tables; hydrogen-bonding tables; crystallographic data for gas cell experiments; instrumental characterisation and analysis for all compounds (PXRD, TGA, DSC, FTIR) and TOF-MS data for **1a**. CCDC deposition numbers 1970253–1970262 contain the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ce01470b

variations of solution crystallisation (slow evaporation, fast and slow anti-solvent crystallisation, and slurry experiments) to control the rate of crystallisation and thereby select between a metastable salt and a stable co-crystal containing the same molecular components.[24] Jones *et al.* also mention systems where both a salt and a co-crystal can be obtained from the same components, and they investigated variations of solution crystallisation to establish the conditions resulting in selective isolation of the stable salt or the metastable co-crystal.[25] There is no mention in the literature of sublimation to obtain salts or co-crystals selectively.

We therefore set out to investigate sublimation as a method to selectively form organic salts or co-crystals. We hypothesised that, due to the absence of solvation, neutral molecules would be more stable in the gas phase, leading to preferential formation of co-crystals by co-sublimation. As proof of concept, we selected two systems known to form multicomponent crystals: the combination of succinic acid (SA) with hexamethylenetetramine (HMT), and oxalic acid (OA) with 4,4′-bipyridine (BPY) (Chart 1). The ΔpK_a in both systems suggests that either a salt or a co-crystal could form in both cases.[27] The combination of SA and HMT gave a salt (**1a**) and three co-crystals (**1b**, **1c** and **1d**), while the combination of OA and BPY gave one salt (**2a**), and one co-crystal (**2b**) (Table 1). The structures of **1b**, **2a**, and **2b** have been reported previously (CSD refcodes: TOZTIN01,[28] EZECOC[29] & XEZDIQ[30]).

Results and discussion

Co-crystallisation of both acid–base combinations was attempted from solution, by mechanochemical grinding using a ball mill and *via* vacuum sublimation. Full experimental details are given in the ESI.† Products were identified using a combination of single-crystal and powder X-ray diffraction. All crystal structures were re-determined for this study in order to confirm the position of the acidic hydrogen atom, *i.e.* to confirm whether the material is a salt or a co-crystal. All details, as well as descriptions of the crystal structures, are given in the ESI.†

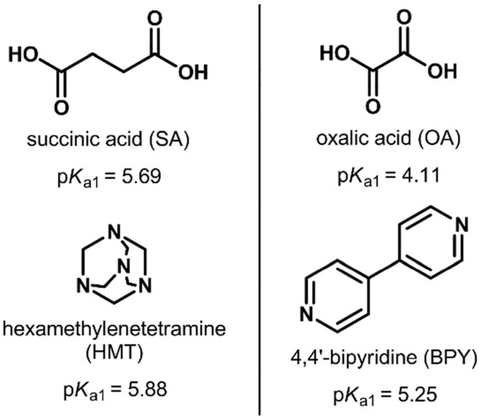


Chart 1 Molecules used in this study with predicted pK_a values for the first ionisation.[26]

Table 1 Summary of the stoichiometry of the multicomponent crystals investigated in this study[a]

	Salt or co-crystal?	Stoichiometry (acid : base)
1a	Salt	2 : 1
1b	Co-crystal	1 : 1
1c	Co-crystal	1 : 2
1d	Co-crystal	1 : 2
2a	Salt	2 : 1
2b	Co-crystal	1 : 1

[a] All multicomponent crystals can be made from solution, mechanochemically and by sublimation, with the exception of **1d**, which can only be made mechanochemically.

Multicomponent crystals by sublimation

Crystalline **1a**, **1b** and **1c** could all be formed from both solution crystallisation and mechanochemistry, although solution crystallisations did not give predictable products. Mechanochemistry could be used to convert between **1a**, **1b** and **1c** by adding the extra equivalents of acid or base to give the required stoichiometry and continuing the milling process.[15,31–33] An additional kinetic form, co-crystal **1d**, was obtained by mechanochemistry only.

Sublimation of a 1 : 1 mixture of SA and HMT at 90 °C yielded crystals of the co-crystal **1b**. At higher temperatures (110 °C) the salt **1a** also started to crystallise in a thin band below the co-crystal. Careful observation of sublimations of HMT and SA at 110 °C (Fig. 1) revealed that only HMT crystallised initially (it has the higher vapour pressure). As the glass heated up, the HMT crystals re-sublimed higher up the sublimation tube, and the co-crystal **1b** started to crystallise in a separate band. After about 2 hours, crystals of HMT and the co-crystal had shifted further up the tube, and crystals of the salt started to form in a third band. The clear separation of crystallisation zones allows separate collection of the products. Pure **1b** can be collected if the experiment is stopped before **1a** starts to sublime.

Solution crystallisation experiments and mechanochemistry could be used to form **2a** and **2b**, with co-crystal **2b** crystallising less often from solution. Again, solution crystallisation was unpredictable in terms of the

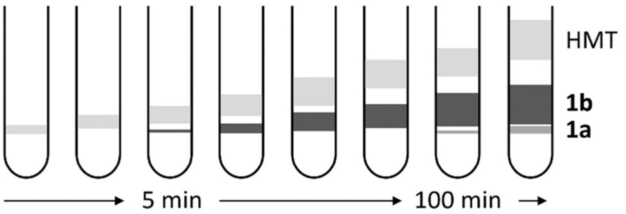


Fig. 1 Product distribution on the sides of the tube during the co-sublimation of succinic acid with HMT at 110 °C.

stoichiometry of the product obtained. Formation of **2b** mechanochemically did not go to completion and a small amount of **2a** always formed concomitantly. Salt **2a**, the seemingly less stable form, could be converted to co-crystal **2b** by milling with an additional equivalent of BPY, while **2b** only partially converted to **2a** upon milling with additional oxalic acid.

The unexpected formation of salts by co-sublimation in both systems investigated led us to question when proton transfer between acid and base is occurring. A mixture of SA and HMT was heated together in the bottom of a test tube at ambient pressure. No multicomponent crystals were observed to form under these conditions, suggesting that multicomponent crystal formation occurs after the molecules enter the gas phase. In a separate series of experiments, solid HMT and SA were kept physically separate from one another during sublimation. Both **1a** and **1b** were observed to crystallise, even though the starting materials were not in physical contact with one another. In these experiments, the two coformers could only encounter one another in the gas phase, and crystals of the salt were observed to form, suggesting that proton transfer is either occurring in the gas phase, or after the neutral components crystallise in an arrangement analogous to that observed in **1a**. Such a ‘neutral’ form of **1a** would be a co-crystal of different stoichiometry to **1b**, not observed under any other conditions.

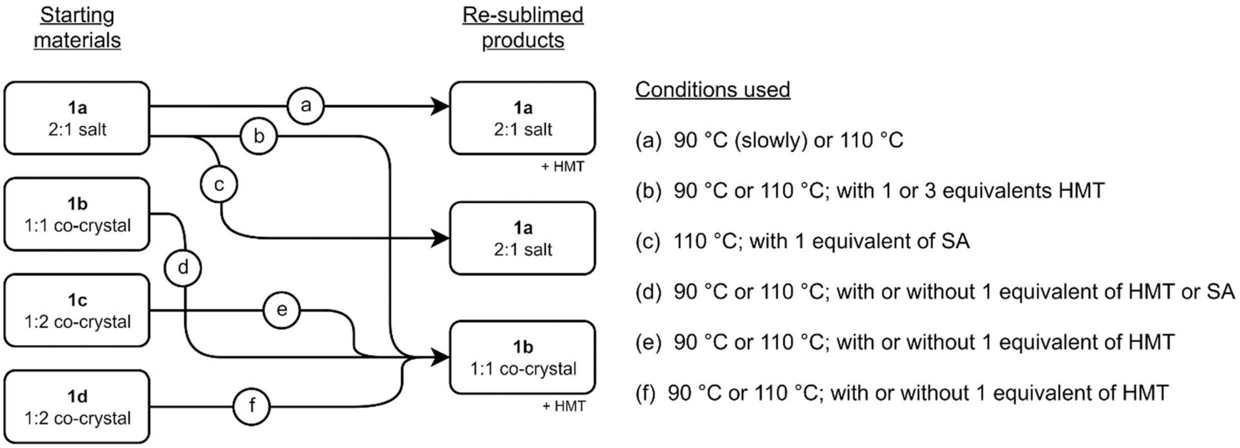
Heating OA and BPY together in a test tube at atmospheric pressure, at either 125 or 150 °C, resulted in formation of a mixture of **2a** and **2b**, showing that in this case both the salt and co-crystal form in the solid state before sublimation. However, both **2a** and **2b** could also be crystallised by vacuum sublimation when the starting materials were not in physical contact with one another, confirming that formation of both the salt and the co-crystal from the gas phase is occurring (as with **1a** and **1b**). These experiments also show that, in the case of **2a** and **2b**, the multicomponent materials can be formed by heating and then re-sublimed. This led us to investigate the re-sublimation of all six multicomponent crystals.

Re-sublimation of salts and co-crystals

Re-sublimation experiments were carried out in a similar manner to the original sublimation experiments, *i.e.* in a Schlenk tube heated in an oil bath, *in vacuo* (~0.6 mbar). We found that most of the multicomponent crystals in this study (with the exception of **1c** and **1d**) can be re-sublimed (Scheme 1).

Both **1a** and **1b** re-sublime at 90 °C, but the salt does so to a lesser extent, after a longer time and will only re-sublime optimally at higher temperatures than the co-crystal (*i.e.* 110 °C). In fact, the co-crystal **1b** can be isolated from a mixture of **1a** and **1b** by re-sublimation at 90 or 110 °C if the apparatus is removed from heat after 2 hours (*i.e.* before **1a** starts to crystallise). If one or three additional equivalents of HMT are added to **1a** in a Schlenk and the mixture heated under vacuum (to 90 or 110 °C), crystals of **1b** are isolated (along with unreacted HMT). This conversion of **1a** to **1b** requires proton transfer. Conversely, when an extra equivalent of SA or HMT is added to **1b** and the mixture heated under vacuum, no conversion to **1a** is observed, and **1b** crystallises. During re-sublimation, co-crystals **1c** and **1d** convert to **1b**. This is probably because **1b** is the favoured product (it is also observed to form preferentially during co-sublimation). Adding extra succinic acid to **1a** during re-sublimation leads to this salt recrystallising in larger amounts, with very small amounts of HMT crystallising separately, making this the preferred method for crystallising pure **1a**. The product obtained appears to be, to some extent, dependent on the relative amounts of coformer present in the gas phase.

Salt **2a** and co-crystal **2b** can both be re-sublimed at the same temperature (for example 170 °C), but in all experiments crystals of both forms recrystallise, irrespective of whether **2a** or **2b** is present initially. The same physical



Scheme 1 Summary of the main re-sublimation pathways for crystals consisting of HMT and SA. All experiments were carried out for roughly 18 hours, the first two hours under dynamic vacuum, and the remainder under static vacuum. Starting the experiment using dynamic vacuum allowed for better separation of the different bands of products inside the tube.

distribution of products is observed as with direct co-sublimation, *i.e.* a band of **2b** above a band of **2a**. The two products can easily be separated due to this difference in deposition region.

When does proton transfer occur?

It is clear that salts can be formed by co-sublimation of the neutral components, and also that salts are able to re-sublime. This is contrary to our original hypothesis that sublimation would selectively produce co-crystals, because ions are not stable in the gas phase. It is also clear that proton transfer reactions are occurring during both co- and re-sublimation. During co-sublimation, our experiments clearly indicate that this proton transfer occurs *after* the molecules enter the gas phase. One possibility is that during co-sublimation, neutral molecules are entering the gas phase and crystallising as a co-crystal, and that the hydrogen atom transfer to form the salt is only occurring in the solid state after the product has crystallised. Similarly, during re-sublimation, it is possible that heating a salt causes this same shift of the acidic hydrogen atom before the neutral molecules enter the gas phase. It is known that proton migration can occur in a strongly hydrogen-bonded co-crystal on changes in temperature.[34] To explore this possibility in system **1**, a salt re-sublimation experiment was carried out inside an environmental gas cell[35] mounted on a single-crystal diffractometer. Our aim was to determine the crystal structure of the bulk material as it is heated under vacuum, to confirm that no shift in the hydrogen atom position is observed before sublimation. A crystal of salt **1a** was placed under static vacuum (~0.9 mbar) inside a glass capillary on a gas cell, which was mounted on a diffractometer. The temperature was gradually increased from room temperature, and the structure was determined *in vacuo* at 20° intervals. The structural data collected at 90 °C show that the salt has remained essentially unchanged on heating, and that the acidic hydrogen atoms remain attached to the HMT cations (Tables S3 and S4†). Hydrogen atoms were placed on peaks in the electron density map that were clearly evident, and their positions were not fixed in any way (Fig. S28–S31†). Further heating of the crystal above 90 °C caused it to re-sublime. These results show that it is unlikely that a bulk neutral co-crystal similar to **1a** exists right before re-sublimation, although it is possible that proton transfer occurs on the surface of the crystal to yield small numbers of neutral molecules which then sublime, and then de-sublime, after which proton transfer once again occurs to yield the salt.

It is also possible that material enters the gas phase as ion pairs or clusters that have an overall neutral charge. This may also be relevant during co-sublimation: hydrogen-bonded clusters of molecules in the gas phase may allow for proton transfer to occur prior to de-sublimation if a stable ion pair is formed as a result. It has been reported that gas-phase proton transfer can take place for strong Brønsted acids and bases where the product of the reaction is an ion-pair complex,[36] and experimental evidence for the existence of such ion pairs in the gas phase has been reported.[37] Other reports have shown that a cluster of molecules is needed for proton transfer to occur.[38,39]

In order to investigate the possible existence of clusters in the gas phase, we turned to mass spectrometry. Attempts were made to carry out measurements on solid samples vaporised using an atmospheric solids analysis probe (ASAP), however samples degraded before sublimation as a vacuum could not be applied. Similar experiments were carried out under vacuum using an in-house-assembled mass spectrometer. However, crystals of the salt or co-crystal deposited inside the cooler instrument tubing, as heat could not be applied uniformly throughout the instrument. Finally, crystals of salt **1a** were dissolved in methanol and analysed using time-of-flight mass spectrometry. A peak was observed at m/z 257 (Fig. S32†), indicating the presence of a hydrogen-bonded adduct of HMT and SA. Although not a replication of the conditions in the sublimation experiment, this does indicate the stability of such hydrogen-bonded adducts.

Conclusions

In conclusion, we have shown that both salts and co-crystals of organic components can be crystallised from the gas phase by co-sublimation. The re-sublimation of both salts and co-crystals was also observed. Preliminary gas-cell and TOF-MS experiments indicate the possibility that ionised molecules are entering the gas phase on re-sublimation, probably as neutral ion pairs or clusters. During co-sublimation, we have shown that proton transfer to form the salt takes place after the neutral coformers enter the gas phase. The formation of small clusters of molecules in the gas phase may allow proton transfer to take place, resulting in a stable ion pair or cluster. This would explain why salts are only observed to crystallise from sublimation at higher temperatures: at higher temperatures there are more molecules in the gas phase, and clusters are more likely to form. However, it is also possible that proton transfer occurs in the solid state after deposition of neutral molecules, and only neutral molecules are present in the gas phase. In this case it is unclear why both a salt and a co-crystal should form from sublimation. Investigations to probe both possibilities are ongoing.

In contrast to solution crystallisation, the outcome of sublimation crystallisation is predictable and can be controlled with temperature and time. Mechanochemical co-crystallisation is arguably more predictable, but does not result in single crystals. Co-sublimation results in the crystallisation of multiple products in distinct bands, which can be separated to obtain pure material. The efficacy of re-sublimation for the separation of mixtures of multicomponent crystals has been demonstrated. Sublimation can thus be used to selectively prepare salts or co-crystals.

It is clear from this work that sublimation is a powerful tool for the controlled crystallisation of both organic co-crystals and salts. We hope that this report, highlighting the ease with which organic salts can be prepared by sublimation, will result in increased interest in this surprisingly versatile technique.

Experimental

All chemicals and solvents were obtained from Sigma Aldrich South Africa and used without further purification. Full details of all experimental procedures are given in the ESI.†

Solution crystallisation

Solution crystallisation experiments were carried out in small 10 ml vials using the slow-evaporation method. Starting materials were dissolved in the appropriate solvent or solvent system, with heating, and the resultant solution left to crystallise at room temperature in the capped vial. Crystals formed within a few days.

Mechanochemistry

Mechanochemical milling experiments were carried out using a FTS1000 Shaker Mill from Form-Tech Scientific. Samples were loaded into 15 ml steel SmartSnap™ grinding jars containing two 6 mm steel grinding balls (~900 mg each). Samples were milled for 20 minutes at a frequency of 25 Hz (1200 rpm). A total sample mass of roughly 100 mg was used with solvent volume (where applicable for LAG) corresponding to $\eta = 0.25\ \mu l\ mg^{-1}$ (approximately 25 μl).

Sublimation

Sublimation experiments were carried out in thin Schlenk tubes under either static or dynamic vacuum (0.6 mbar line pressure). Tubes were inserted in an oil bath pre-heated to the desired temperature, and sublimation took place onto the sides of the tube within a few hours. For comparison, these experiments were also carried out in a larger Schlenk tube fitted with a water-cooled cold finger as crystallisation surface. To determine the role played by the heat applied during sublimation, selected experiments were repeated in a test tube with similar dimensions as a thin Schlenk tube. Here the starting materials were heated in an oil bath and the powder tested to determine how the composition changes due to heat. Finally, sublimation experiments were also carried out in a flat-bottomed Schlenk tube fitted with a cold finger which allowed placement of the starting materials into separate cut-off glass vials. This was done to ensure the starting materials would not come into contact with each other while in the solid state.

Conflicts of interest

There are no conflicts to declare.

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