

The mystery of the Finkelstein reaction

Henry Rzepa¹

¹Affiliation not available

April 17, 2023



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HENRY RZEPA

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CORRESPONDENCE:

h.rzepa@imperial.ac.uk

DATE RECEIVED:

June 10, 2015

DOI:

10.15200/winn.142795.56562

ARCHIVED:

April 02, 2015

CITATION:

Henry Rzepa, The mystery of the Finkelstein reaction, *The Winnower* 2:e142795.56562, 2015, DOI: [10.15200/winn.142795.56562](https://doi.org/10.15200/winn.142795.56562)

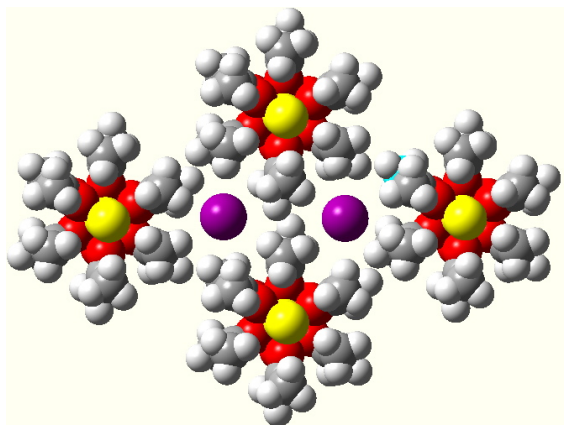
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This story starts with an organic chemistry tutorial, when a student asked for clarification of the [Finkelstein reaction](#). This is a simple SN2 type displacement of an alkyl chloride or bromide, using sodium iodide in acetone solution, and resulting in an alkyl iodide. What was the driving force for this reaction he asked? It seemed as if the relatively strong carbon-chlorine bond was being replaced with a rather weaker carbon-iodine bond. But its difficult to compare bond strengths of discrete covalent molecules with energies of ionic lattices. Was a simple explanation even possible?

All is not as it seems however. The traditional explanation, found by the quick Google search linked above, is that the reaction illustrates [Le Chatelier's principle](#), whereby an equilibrium is driven over to completion by removal of one of the products (in this case sodium chloride or sodium bromide, which crystallize out of solution). Well, we have replaced one possible (and probably complicated) explanation based on bond strengths and ionic lattices by another based on the solubilities of an ionic material in a moderately polar solvent. But all we have done is ask a different question, which now becomes why is sodium iodide highly soluble in acetone, whereas sodium chloride and bromide are not? The answer to this is less easily found using Google!

A good start would be the crystal structure of any complex formed between acetone and sodium iodide. Fortunately, one such does exist, and it is shown below (sodium=yellow, iodine=purple).

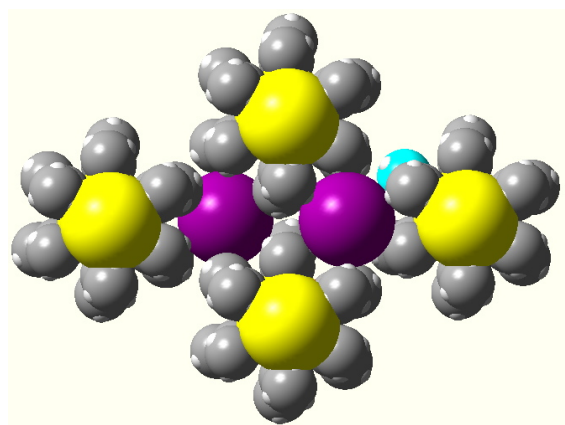


(Acetone)₃·NaI. Click for 3D.

The formula shows three acetone molecules for each sodium iodide. The carbonyl oxygen has two lone pairs of electrons, and each of these is used to coordinate a (different) sodium cation. This allows each sodium to be coordinated by a total of six lone pairs, giving it octahedral coordination. This sets up what in fact is quite a rigid scaffold, with the unusual feature of an approximately triangular shaped

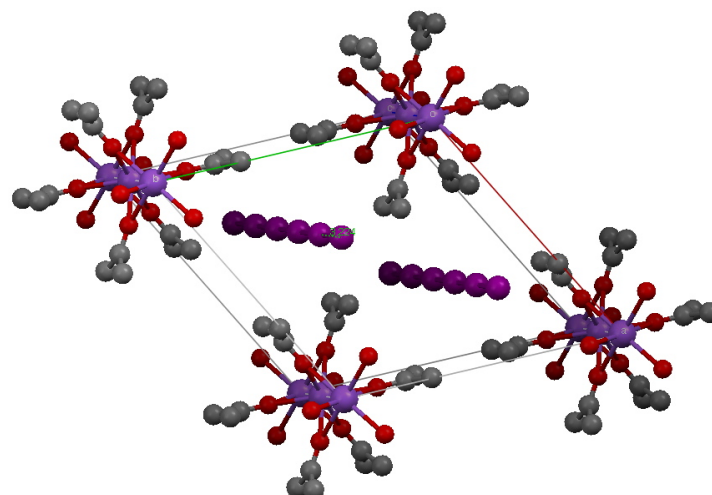
channel running down the lattice (two such are shown above). The size of this hole is determined by the methyl groups of the acetone, and it is into this cavity that the halide ion must fit.

As it happens, the iodide anion is exactly the right size to produce a perfectly snug fit up against those methyl groups (click on the image above to view this). If a chloride or bromide anion were to be fitted into the cavity, there would be empty space surrounding it. The cavity itself is too rigid to collapse around the halide anion to absorb this space. This means these halide anions are further away from the positively charged sodium than they would like to be such that they **minimize their ionic lattice energies**. Instead they avoid fraternizing with the acetone at all, and form a pure sodium chloride or sodium bromide lattice (where the two oppositely charged ions CAN approach at optimal distances). The result is that sodium chloride crystallizes out of solution, and the Finkelstein reaction proceeds to completion!



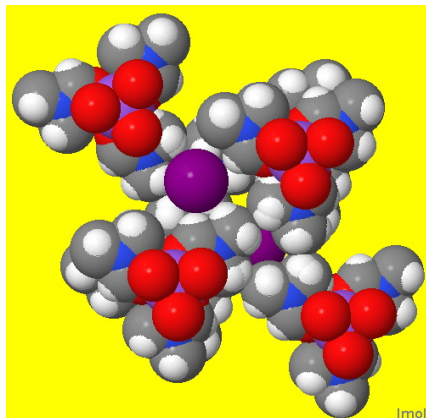
Acetone. NaI in spacefill mode. Click for 3D.

But that is not quite the end of the story. If you view the acetone.NaI lattice sideways (click on the diagram above to view this aspect), you will find that in fact there is still space in the scaffold after all! Each iodide anion has room above or below it, with space for exactly one more iodine atom to fit without having to change the shape of the scaffold. And indeed such a molecule has **been reported**, but it is an odd one! The stoichiometry is now (acetone)₃.NaI₂, which implies that the iodide anion has been joined by an iodine atom. I₂⁻ is called a radical anion, and as such has an unpaired electron. Just like two iodine atoms can couple their unpaired electrons to form a covalent bond, so can two I₂⁻ radical anions, forming I₄²⁻ [or I₃.I] or on to infinity as a linear iodine polymer, of formula n[I₂⁻], with all the I...I distances equal at 3.224Å (a system with no **Peierls distortion**). Straight rod-like polymeric chains of a single element might appear highly unusual, but curiously, another class of elements that exhibits this behaviour is Cu/Ag/Au and Ga (DOI: [10.1002/anie.200601726](https://doi.org/10.1002/anie.200601726), the ultimate in thin wires!).



Acetone. NaI₂. Click for 3D.

Finally, it is worth noting that the same phenomenon occurs with the [dimethylformamide.NaI](#) complex. In this example, only the NaI and not the NaI₂ complex has been reported.



DMF. NaI. [Click for 3D.](#)