DPhil Calum Patel

Shaking up fluorine chemistry

Q: Is the introduction of fluromix into aromatic compounds different to that of aliphatic compounds?

A: For the aromatic compounds we are breaking a carbon-chloride bond and forming a carbon-fluorine bond, whereas in the aliphatic compound we are breaking a carbon-bromine bond and forming a carbon-fluoride bond. However, for the aromatic compound the reaction goes via nucleophilic aromatic substitution (SNAr) and for the aliphatic compound the reaction proceeds via bimolecular nucleophilic substitution (SN2).

Q: Are there any other shapes that are more effective than a ball, at grinding the CaF2?

A: No other shapes were tried in the project! For mechanochemistry, spherical-shaped objects, like ball bearings, are used because the ball moves (oscillates) in a figure of eight during the shaking process and collides the with the solids and walls of the milling vessel (jar) to initiate the reaction. The oscillation and movement of the object, and thus the reaction, may be less effective with non-spherical objects.

Q: Are there any other notable ideas for circumstances where this method could be applied?

A: Absolutely! There are lots of materials, minerals, salts that are insoluble in most solvents and thus remain unreactive in traditional solvent based chemistry. Mechanochemistry, or solid-state chemistry, may provide new opportunities to break down materials or unlock unseen reactivity of insoluble salts. This may greatly reduce solvent usage in industrial chemical processes, serving as a greener alternative to reactions that rely on solvents and thus product solvent waste.

Q: Are there some and if so what types of molecules that can't be formed using fluoromix without a lot of processing of it?

A: Fantastic question! There are plenty of fluorochemicals that, currently, cannot be formed with Fluoromix directly. For example, there is a whole group of fluorochemicals prepared from fluorine gas called electrophilic fluorinating reagents. Fluoromix is a nucleophilic fluorine source, so accessing those electrophilic fluorinating reagents represents another chemical challenge.

Q: What is the process of x-ray diffraction?

A: In X-ray diffraction, a sample made up of many crystals is illuminated with X-rays. Each crystal is made up of a periodic arrangement of atoms separated by well-defined distances. Each atom is made up of a nucleus surrounded by a cloud of electrons. X-rays are high energy light with a wavelength that is on the same order of magnitude as the distance between the atoms in the crystal. When an X-ray encounters an atom, its energy is absorbed by the electrons and some energy is re-emitted. X-rays are scattered by the regularly spaced atoms. The X-ray signals are amplified at very specific angles where the scattered waves constructively interfere. This is called "diffraction". We can record the diffracted X-ray signals from the sample to give an X-ray diffraction pattern. The pattern tells us about the atomic structure of the crystals in the powder.

Q: When looking at the X-ray diffraction spectra of fluoromix, how did you separate the spectra of each chemical? Wouldn't the spectrometer show you an overlap of all the spectra?

A: Indeed, the diffraction pattern recorded by the diffractometer (not spectrometer) of Fluoromix contained many overlapping peaks. We could make various salts in the lab, each with their own diffraction pattern and peaks, and carefully match those peaks to the recorded diffraction pattern of Fluoromix, thereby deconvoluting what salts were contained within Fluoromix.

Q: Is it specifically important that the wavelength of the x-rays is similar to the distance between the atoms in the lattice?

A: Yes, it is very important. The wavelength of the X-ray ranges between 0.01 to 10 nanometres, which is approximately of the same order of magnitude as the distance between the planes of atoms in a solid crystalline lattice. A mathematical relationship called Braggs law relates the X-ray wavelength to the distance between the atomic planes. Braggs law is very important because it can be used to measure the distance between atoms in a crystalline lattice and help scientists work out the structure of a solid lattice of crystals, materials, battery electrolytes etc.

Q: Are there any other reactions that solid state chemistry could be used for?

A: Plenty! There is enormous potential to use mechanochemistry, and solid-state chemistry in general, to synthesise new battery electrolytes, drug compounds, to break-down waste for upcycling, and to break-down solids into useful gases (such as ammonia). Traditional chemistry has relied on solvents for hundreds, perhaps even thousands, of years. If we can do chemistry without relying on the solubility of chemicals then we greatly increase the number of possible chemical reactions!

Q: Would the material used to create the ball baring be made of an inert solid?

A: In the case of Fluoromix yes, we chose to use stainless steel balls. However, today mechanochemical reactions using balls made of catalytic metals have been developed to trigger mechanochemical catalytic reactions.

Q: What is the most effective way to make two compounds react?

A: Grinding fluorspar (calcium fluoride) together with a phosphate salt using a stainless steel jar and stainless steel ball at 35 Hz (the milling frequency) for 3 hours was certainly effective. However, this doesn't necessarily mean it's the best system for calcium fluoride activation.