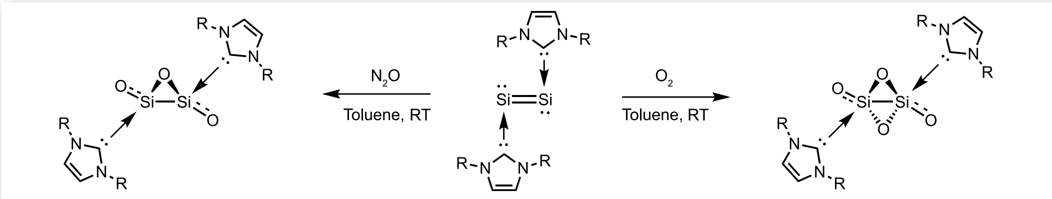
Souble sands boost silicon synthesis

Chemists stabilise silicon oxides with carbenes



Silicon and oxygen have been harnessed into previously unknown chemistry by US researchers, opening up a new 'world in a grain of sand'. From soluble disilicon molecules they previously showed helper compounds could stabilise, Gregory Robinson's team at the University of Georgia have isolated elusive small silicon oxide molecules. 'Utilising this carbene-stabilisation strategy, molecular silicon oxide moieties are synthetically approachable,' says Robinson.

When silicon and oxygen coexist it's usually in networks and chains, as in quartz and silicones. Because silicon–oxygen double bonds and low-oxidation-state silicon atoms are highly reactive, smaller silicon oxide molecules are generally unstable and rapidly form larger, typically insoluble, groupings.

Since showing that two *N*-heterocyclic carbenes can stabilise disilicon by donating electron pairs to it in 2008, Robinson's team has used the approach to isolate several other small inorganic molecules. Yet they harboured a lingering desire to oxidise disilicon. 'We were recently encouraged by the fact that stabilised diphosphorus was demonstrated in our laboratory to split molecular oxygen, yielding a stable molecule containing diphosphorus tetroxide,' Robinson explains.

But synthesising small silicon oxides proved to be 'arduously difficult from a synthetic perspective'. At first glance, adding nitrous oxide or oxygen to a stabilised disilicon solution in toluene at room temperature to make Si_2O_3 and Si_2O_4, respectively, looks straightforward. However, unlike air-stable diphosphorus tetroxide, the silicon oxides immediately decomposed when exposed to extra oxidant.

Despite that sensitivity, the Georgia chemists were able to isolate and retain enough for x-ray crystallography. Together with detailed structural calculations, the crystal structures showed the stabilised Si_2O_3 and Si_2O_4 molecules existed with central three-membered and four-membered ring structures, respectively.

The work amounts to making sand soluble, enthuses Herbert Roesky from the University of Göttingen, Germany, whose work also exploits carbene stabilisation. 'This is an amazing result, which will have a number of applications in depositing SiO_2 on surfaces of various materials,' he says.

Robinson now hopes to develop new reactions that swap the carbenes for other chemical groups, transferring individual silicon oxides. 'We also believe that other highly reactive main group oxides may be synthetically approachable using this strategy,' he adds.

This study will be one of the last to involve the University of Georgia's pioneering computational chemist Paul von Ragué Schleyer, who died in November 2014. 'Paul was very excited about this discovery and diligently worked with us right up to his passing,' Robinson says. 'His absence leaves a considerable void in us all.' *Andy Extance*

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Salt and flavour reach a compromise

Amylase triggers salt release in the mouth

Scientists in the UK have developed a water-in-oil-in-water (wow) emulsion that could cut salt levels in emulsion-based food by more than a fifth but maintain the same flavour.

Excess dietary salt can increase blood pressure – a risk factor for cardiovascular diseases. Processed foods, such as ready-made soups, often contain salt as a preservative and flavour enhancer. However, most of the salt in these emulsion-based foods is swallowed without us actually tasting it, and we often find ourselves adding even more.

Bettina Wolf and coworkers at the University of Nottingham, UK, have taken a microstructure approach to solve this problem. They trapped sodium chloride in the internal aqueous phase of an emulsion made from quinoa starch that had been modified with octenyl succinic anhydride. The salivary enzyme amylase will hydrolyse the starch. This means the salt is released immediately into the mouth, maximising its delivery to taste receptors.

'Wolf has successfully demonstrated how the interfacial layers of emulsion droplets can be engineered for the targeted release of salt or other tastants, over realistic timescales', comments food scientist Peter Wilde, from the Institute of Food Research in the UK. 'This could lead to rationally designed, lower salt foods requiring no artificial taste enhancers or salt replacers.'

Taste tests demonstrated that the salt content of the emulsions could be reduced by 23.7% without participants reporting any difference. In one test volunteers were given two liquid samples containing equal amounts of salt, one containing an orally-inert emulsion, the other, the starch-stabilised emulsion. Despite the samples containing the exact same amount of salt, a significantly greater number of volunteers said that the starch-based emulsion was saltiest.

'The idea is to remove salt that is not tasted but contributes to the negative health impacts of a high salt diet,' explains Wolf. 'The food industry has an opportunity here to develop a range of foods, such as sauces, salad dressings and soups, with reduced salt levels quite quickly using this strategy.' And by investigating the heating properties of the emulsion Wolf hopes to develop the technology for use in a wider-range of foods.

'Wow emulsions may prove to be a useful tool for designing emulsified food products with healthier nutrition profiles that still deliver the flavours and textures that consumers expect from traditional emulsified products', says food rheology expert Helen Joyner, from the University of Idaho, US.

Wolf plans to build on this research in a future collaboration with Wilde to apply this starch-stabilised emulsion to sugar.
Jessie-May Morgan

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