

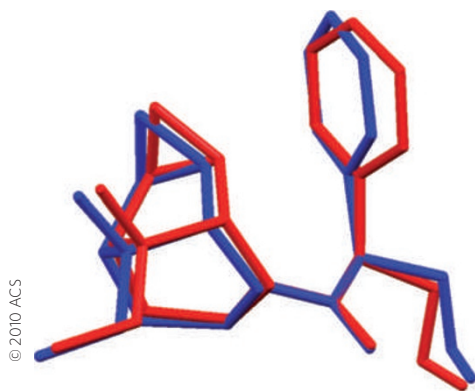
aluminium — suggest that more oxidized phases may be more stable in general.

Understanding these relationships can help to explain observed nanoparticle behaviour; for example, the ability of nanosized Co_3O_4 to oxidize carbon monoxide at high CO/CO_2 ratios with low oxygen supply. Furthermore, a calculated phase diagram for nanosized iron oxides shows no stable region for $\text{Fe}_{0.947}\text{O}$, tallying with observations of their spontaneous oxidation to form materials useful for memory applications.

THERMOSALIENT EFFECT

Jumping crystals

J. Am. Chem. Soc. **132**, 14191–14202 (2010)



The thermosalient phenomenon is also known as the jumping crystal effect, an apt name to describe crystals that undergo phase transitions that cause them to literally jump. The movement is caused by anisotropic changes in the crystals' shape and in some cases can be several centimetres. Although most examples known so far have been discovered serendipitously — usually on hot-stage microscopes — crystals with this interesting property could find use as actuators. The stress put on the crystal to make it jump, however, also causes extreme difficulty in making a full structural analysis of the subsequent phase, and thus the thermosalient effect remains poorly understood.

Now, Panče Naumov, Joel Berstein and colleagues from Osaka University and Ben-Gurion University in Israel have fully studied the phenomenon in crystals of oxitropium bromide (OXTB), a compound originally developed to treat bronchial diseases. On heating to 328 K, crystals of OXTB were seen to jump. Heating them rapidly through this temperature resulted in disaggregation, but slower heating retained the crystallinity. This allowed the structures of both phases to be fully determined using single-crystal X-ray diffraction.

Although the team found that the changes in unit cell and atomic positions did not

seem to be strikingly large, they did discover a conformational difference between the oxitropium molecules in the two phases. Although the rigid tricyclic part of the molecule changes little, the flexible ester linkage allows different orientations of two other terminal groups. The thermal strain built up on heating transfers through this ester bridge and triggers the phase transition.

BECKMANN REARRANGEMENT

Catalyst or initiator?

Chem. Sci. doi:10.1039/c0sc00421a (2010)

The Beckmann rearrangement is the reaction of an oxime to form an amide by migration of an alkyl group. The mechanism involves a dehydration step, and traditionally the reaction has been catalysed by strong Brønsted or Lewis acids. Recently, however, several reports of the reaction being catalysed by small organic molecules have appeared. Following on from earlier work that uses the energetically favourable formation of an aromatic cation to perform a variety of dehydration reactions, Christine Vanos and Tristan Lambert from Columbia University have now turned their attention to this famous and useful reaction.

They soon found that they could efficiently promote a variety of Beckmann rearrangements at room temperature by the addition of a dichlorocyclopropene. A mechanistic investigation, however, resulted in some intriguing conclusions regarding both this reaction and several previously reported 'organocatalytic' variants of the Beckmann rearrangement. Vanos and Lambert realized that there were two possible ways in which their cyclopropene reagent mediated the reaction — it could be catalytic, or it could simply initiate a self-propagating cascade. The distinction is an important one, particularly if future efforts are directed towards controlling the reaction by changing the catalyst structure.

The initial evidence points towards a self-propagating cascade at elevated temperatures. Unlike the previously reported reactions, the cyclopropenium-activated rearrangement is still rapid at lower temperatures where a key step in the self-propagating cascade is slow. This suggests that a truly organocatalytic version of the Beckmann rearrangement is possible and might ultimately lead to the development of an enantioselective variant.

The definitive versions of these Research Highlights first appeared on the *Nature Chemistry* website, along with other articles that will not appear in print. If citing these articles, please refer to the original web version.

blogroll

We don't like blogs...

...we love them — but not everyone shares our opinion.

In a post on Everyday Scientist titled 'caveat grumpton' (<http://go.nature.com/f45SuZ>), Sam alerted the blogosphere to an editorial in *Analytical Chemistry* (<http://dx.doi.org/10.1021/ac102628p>) and lit a fire that burned long and wide. Royce Murray, the journal's editor, "casts science blogging in a very unfair light" according to Paul Bracher on ChemBark (<http://go.nature.com/mCrsw>) when Murray "believe[s] that the current phenomenon of 'bloggers' should be of serious concern to scientists". Derek Lowe agrees on In the Pipeline (<http://go.nature.com/VCT781>) that there "is indeed a lot of inaccurate nonsense on the internet", but points out that it exists in newspapers, magazines and "in the peer-reviewed literature, too". Lowe also takes issue with the notion that bloggers are unqualified: "the most widely read ones are all written by chemists", and suggests that the editorial itself might have benefited from some of the fact-checking or peer-reviewing that Murray is worried is missing from blogs.

David Kroll, at the ACS's own CENTRAL Science Terra Sigillata (<http://go.nature.com/3xLurC>), also responds — he is concerned "that not enough scientists are bloggers" and "that a scientist of [Murray's] stature and influence holds negative views of science blogs". Kroll stands up for blogs, as they allow scientists to "communicate effectively to the public". The final word goes to the commenter on Kroll's post, identified only as 'J', who pointed out that Murray is "a sort of blogger and he doesn't know it [...]" The difference is that his 'blog' is monthly, has appeared mostly in print until the past few years and there is no place for others to comment."

Ever shaken your head at some of the more ingenious examples of table-of-contents graphics? Now you can see some choice examples and suggest your own at TOC ROFL (<http://tocrofl.tumblr.com/>) — we must admit that a couple of *Nature Chemistry's* own graphics have made the list.