

molecules, but now a team led by John Yates Jr from the University of Virginia has uncovered exactly where the reaction occurs and how the reactants are delivered to the reactive site. Infrared spectroscopy experiments indicated that the reaction did not occur solely on a gold site and that the titania–gold interface was indeed important. Density functional theory calculations strongly supported a mechanism in which oxygen preferentially adsorbs by straddling the interface, attached to both a gold atom and a titanium atom. This activated oxygen molecule can then react with carbon monoxide.

Infrared spectroscopy also showed that during the reaction the number of carbon monoxide molecules adsorbed on titania decreased significantly whereas the number on gold hardly changed — supporting the idea that the carbon monoxide that takes part in the reaction is initially supplied by the titania surface. GA

GAS-PHASE KINETICS

Analysing the α -effect

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The α -effect is the empirical observation that nucleophiles with a second lone-pair-bearing atom adjacent (α) to the nucleophilic centre exhibit anomalously high reactivity. Generally, the reactivity within a series containing the same nucleophilic atom correlates well with basicity, but some nucleophiles, such as hydroperoxide and hydrazine, do not fit the pattern well. Experimental studies of the α -effect can be difficult to interpret because a number of different phenomena that can enhance or attenuate it can be convoluted. There has, therefore, been much debate as to whether the α -effect is an intrinsic result of structure or just a solvent-induced phenomenon.

Now, Veronica Bierbaum and co-workers from the University of Colorado have performed gas-phase studies that compared the reactivity of an α -nucleophile (hydroperoxide, HOO^-) with a series of related normal oxygen nucleophiles (HO^- , CH_3O^- , $\text{C}_2\text{H}_5\text{O}^-$ and *i*- $\text{C}_3\text{H}_7\text{O}^-$) with three different electrophiles (methyl fluoride, anisole and 4-fluoroanisole). A gas-phase study eliminates any solvent effect, but more importantly this study also investigates reactions with relatively small enthalpy changes (large enthalpy changes can mask the α -effect) and takes into account the different reaction pathways that can be followed.

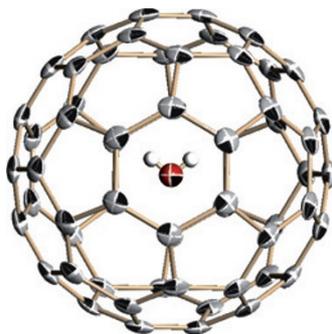
Even in the simplest system — comparing the reactions of methoxide or hydroperoxide with methyl fluoride — Bierbaum and co-workers observe a rate enhancement of 3.7 when using the α -nucleophile. In these

reactions both nucleophiles have similar proton affinities, the reactions involve similar enthalpy changes, and only one reaction pathway ($\text{S}_{\text{N}}2$) is possible, so the measured rate enhancement confirms that the α -effect is intrinsic to the nucleophile structure. SD

ENDOEDRAL FULLERENES

Water behind walls

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Atoms and molecules can be trapped inside the hollow interiors of fullerenes using either physical or chemical methods. For example, high pressures and temperatures can be used to force noble gases into these cage-like compounds. Alternatively, chemical reactions can be used to open windows in the carbon framework that are large enough for small molecules to pass through under ambient conditions. In some cases, the original fullerene framework can be restored by another sequence of reactions, resulting in guest molecules being trapped inside.

Now, Kei Kurotobi and Yasujiro Murata from Kyoto University in Japan have used the latter strategy to make bulk quantities of $\text{H}_2\text{O}@C_{60}$ — a compound in which a single water molecule is trapped inside each C_{60} cage. Water molecules have been put inside fullerenes before, but the openings in the cages were not closed and the water was free to escape. Kurotobi and Murata made a 16-membered-ring opening — through which a water molecule can pass — in C_{60} in just a few steps. Sealing up the hole restored the original carbon cage and trapped a water molecule inside.

X-ray crystallography confirms that the structure of the C_{60} cage is unaffected by the encapsulated water molecule and UV-visible spectroscopy is unable to detect any electronic interactions between the two species. The inclusion of a water molecule in its cavity is, however, expected to make $\text{H}_2\text{O}@C_{60}$ a polar molecule — unlike C_{60} itself, which has a zero dipole moment. SC

Written by Gavin Armstrong, Stuart Cantrill, Steven Davey, Anne Pichon and Neil Withers

blogroll

Angry chemists

Funding woes spark indignation and ire, but excellence sparks inspiration.

The release of the new research portfolio of the UK's Engineering and Physical Sciences Research Council (EPSRC) in July dismayed many chemists (see <http://go.nature.com/MKxmjz> for some of that dismay) but it angered synthetic organic chemists the most. They are due to be among the first to feel the pinch of reduced funding. Rather than take this lying down, Paul Clarke of York University started off with a blog post at Sheer Lunacy (<http://go.nature.com/GgGGb7>) that soon ended up with letters to national newspapers (<http://go.nature.com/DipiC3>), cabinet ministers (<http://go.nature.com/m8Ghbg>) and the prime minister (<http://go.nature.com/NeCOUY>).

In response, EPSRC chief executive David Delpy argues that organic synthesis has received “a greater proportion of EPSRC support than most other areas in [its] physical sciences portfolio” and that this will be reduced so they can increase funding in other important areas (<http://go.nature.com/z4WykA>). But of particular annoyance to Clarke and other organic chemists was the lack of consultation: it seems the EPSRC's definition of ‘consultation’ is different from, among others, the RSC's, with president David Phillips writing to Delpy outlining his concerns (<http://go.nature.com/Xp8rGX>). The issue is so contentious that the Periodic Table of Videos crew made a video called *Angry Chemists* (<http://www.youtube.com/watch?v=op3w7GI83mU>).

From angry organic chemists to inspirational ones... Dr Freddy, on Synthetic Remarks, implores Phil Baran (Scripps) to “Slow down, Phil” (<http://syntheticremarks.com/?p=1328>). Poor Dr Freddy offers this plea, because “mortals have no chance to keep up with you” and they “need a break” from Baran's relentlessly high-profile publications! Dr Freddy suggests Baran should ‘do a Heck’: “Invent an awesome reaction, publish, disappear from the face of the Earth for some 20+ years, only to return to pick up the Nobel prize.” In a nice post-script, Baran himself commented on the post, humbly suggesting that it was his students who deserve the credit.