

1 was then determined from a combination of experimental and theoretical deductions that looks much like a detective story.

Firstly, oxidation of dimethylene cyclopropane **2** led to a compound that gave ESR, IR and optical spectra quite similar to those derived from oxidation of **1**, which means that removal of one electron from either **1** or **2** leads to the same cation. Secondly, abstraction of a proton from this cation (by thermal annealing) gave a radical containing an allylic fragment. Finally, near-IR photolysis of the same cation led to a vinylidene cyclopropane radical cation **4**^{•+} (which can also be formed independently from the neutral species **4**), very possibly generated by ring closure of the allylic moiety. Together, these observations led to the assignment of the species obtained after ionization of **1** and **2** to the Y-shaped radical cation **3**^{•+}. This is further confirmed by the excellent agreement between the observed and calculated IR, optical and ESR spectra.

How can a tricyclic cage molecule such as **1** break three bonds (shown in green in Fig. 1) to yield an open Y-shaped species after a mere one-electron oxidation? The mechanism of this extensive rearrangement was investigated by high-level *ab initio* quantum chemical computations of the reaction path leading from **1** all the way to **3**^{•+} (via **5**^{•+} and **2**^{•+}). These calculations revealed a successive cleavage of three bonds as depicted in Fig. 1, in which each step involves a barrier of less than 3 kcal mol⁻¹.

The next question is, qualitatively speaking, why does the primary radical cation **1**^{•+} undergo such a facile cascade

of rearrangements? The first step of this process turns out to be favoured by vibronic coupling — which accounts for the interactions between electronic and nuclear motions of a compound. This coupling was found to reduce the molecular symmetry of **1**^{•+}, thus allowing mixing of orbitals of the ground state (²A₁') and an excited state (²E''). This results in a deformation and a significant stabilization of the ground state. Combined with the low energy gap between the two states (1.56 eV), this leads to the formation of the first intermediate **5**^{•+}. Therefore, although this may be counter-intuitive, this process is not driven by strong exothermicity. Remarkably, this vibronic coupling had already been invoked long ago by Heilbronner and Wiberg in a different situation — to explain the unusual vibronic structure in the first band of the photoelectron spectrum of **1** (ref. 7). Further rearrangements are subsequently facilitated by the stabilizing effect of allylic resonance of the open-ring structures **5**^{•+} and **2**^{•+}, eventually leading to **3**^{•+}.

A most remarkable aspect of the above radiolytic oxidation experiment is that a mere one-electron ionization ends up opening a tricyclic cage molecule by breaking no less than three lateral bonds in a short sequence. Also unexpected is the fact that the weak bridgehead bond between the two inverted carbon atoms in [1.1.1]propellane (shown in red in Fig. 1) is considerably reinforced and eventually even gets some double-bond character in the radical cation **3**^{•+}, the detailed electronic structure of which might be

investigated further in future studies. Three resonance structures and their mirror images can be drawn for **3**^{•+}, some of which are shown in Fig. 1. An interesting question is what are their respective weights? A calculation of valence bond type would provide a direct answer.

It would be fascinating to run similar calculations and/or experiments whenever possible on analogues of [1.1.1]propellane, where the CH₂ groups at the wings would be replaced by substituents such as NH, O, CF₂, BH and OH⁺. Such compounds have been shown⁵ to display a bridgehead bond that has even more charge-shift character than **1**. Would these hetero-propellanes also lead to acyclic cations on oxidation? Finally, the same question applies to the heavier analogues E₃H₆ (E = Si, Ge, Sn). In any case, the influence of vibronic coupling on chemical reactivity should not be underestimated. □

Philippe C. Hiberty is at the Physical Chemistry Laboratory, Theoretical Chemistry Group, CNRS UMR 8000, University of Paris-Sud, 91405 Orsay Cédex, France.
e-mail: philippe.hiberty@u-psud.fr

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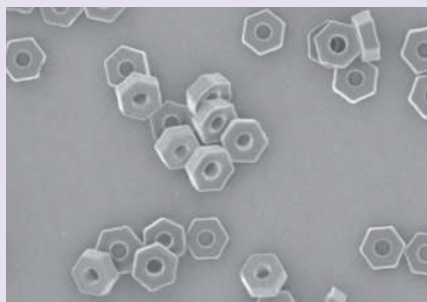
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BIOMATERIALS

Silyl ether linkers

Silyl ether groups, typically used to protect alcohol functions in organic synthesis, offer good control over the rate and mechanism of their cleavage through judicious choice of silicon substituents. Now, Joseph DeSimone and co-workers from the University of North Carolina have used this tunable stability to prepare acid-sensitive materials that show promise for medical devices (*J. Am. Chem. Soc.* **132**, 17928–17932; 2010).

Four bifunctional silyl ethers (CO–Si(R)₂–OC, where R is a methyl, ethyl, isopropyl or *tert*-butyl group) bearing a terminal acrylate moiety on each side chain were crosslinked and subsequently moulded into particles



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with well-defined morphologies. The particles degraded in acidic conditions — known to exist in 'unhealthy' tissue — and the rate of degradation could be influenced significantly by using different

alkyl substituents; bulkier groups slow the rate of degradation. DeSimone and co-workers used this concept to control the rate of release of the drug Rhodamine B from cubic microparticles. They also visualised *in vitro* degradation with transmission electron and laser scanning confocal microscopies using 'hexnut'-shaped nanoparticles (pictured), which were easily recognizable in cellular environments.

ANNE PICHON

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