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Spotlights on Recent *JACS* Publications

FINALLY CAUGHT IN THE ACT: ATOMIC OXYGEN RADICAL ANIONS ESSENTIAL IN THE OXIDATION OF CARBON MONOXIDE

Carbon monoxide binds to hemoglobin more tightly than oxygen does, resulting in toxicity that could have fatal consequences. For this reason, the catalytic oxidation of CO is widely studied for applications in air purification systems used in submarines, for pollution control, and in catalytic converters for the cleanup of combustion engine exhaust. Now, Sheng-Gui He and co-workers report evidence for the existence of atomic oxygen radical anions in carbon monoxide oxidation reactions over titania and zirconia nanoparticles in a fast-flow reactor (DOI: 10.1021/ja311695t).

For many other catalysts, the exact mechanism of carbon monoxide oxidation remains poorly understood. This catalytic oxidation is thought to proceed via the generation of so-called reactive oxygen species (ROS), mainly superoxide radicals (O_2^-), peroxide species (O_2^{2-}), and highly reactive atomic oxygen radical anions (O^-). Among the ROS, the existence and role of atomic oxygen radicals (O^-) remained elusive.

By using time-of-flight mass spectrometry the researchers identify and characterize the short-lived O^- anions, supporting their involvement in oxidizing carbon monoxide molecules. The authors are confident that these gas phase results will help clarify reaction mechanisms involving solid-phase bulk catalysts. **Alexander Hellemans**

FLUORIDE IONS BEHAVE DIFFERENTLY IN S_N2 SUBSTITUTION REACTIONS

Bimolecular nucleophilic substitution (S_N2) reactions are of fundamental importance in organic chemistry, and are therefore frequently used as model systems both experimentally and computationally. In 2008, Roland Wester and co-workers made the surprising discovery that our understanding of the S_N2 reaction was incomplete (DOI: 10.1126/science.1150238). By analyzing the energies and scattering directions of the reaction products generated when a beam of neutral methyl iodide atoms was collided, in a vacuum, with a beam of chloride ions, they found that some of the substituted iodide ions left the collisions in a range of different directions. This observation was direct evidence for a yet unknown, indirect reaction mechanism involving rotation as part of the substitution.

Now Wester and his team have collided a beam of methyl iodide atoms with fluoride ions (DOI: 10.1021/ja308042v). To their surprise, another indirect mechanism, the formation of an intermediate complex, F^--HCH_2I—whereby the fluoride ion bonds to one of the hydrogen atoms of the methyl group—was found to be responsible for more than 50% of the observed substitution reactions. The large contribution of this indirect pathway is in strong contrast with similar substitution reactions with less reactive halogen ions, and also with the simple understanding of S_N2 reactions taught in introductory organic chemistry courses. **Alexander Hellemans**

PROTEINS SHAPE TRYPTOPHAN RADICALS' SPECTRA

Enzymatic reactions in living cells sometimes use tryptophan radicals to move electrons or protons. Now Adalgisa Sinicropi and colleagues have identified how certain proteins carrying such radicals affect the radicals' UV−vis, Raman, and EPR spectra (DOI: 10.1021/ja400464n). The results will enable scientists to better characterize enzymatic reactions such as DNA repair and even magnetic field detection.

The researchers create quantum-mechanics/molecular-mechanics computer models of a tryptophan radical in two different protein mutants. One mutant traps the radicals in its hydrophobic core, and the other exposes the radical to solvents. The team is able to compute how those proteins would affect features in the radicals' spectra. To this end, they use a powerful quantum-mechanical method known as CASPT2.

The team compares the properties computed for the protein-bound radicals with available experimental data obtained by different groups using several kinds of spectroscopy. In the ultraviolet and visible spectra, they clarify the nature of a distinctive pair of peaks for each protein-radical. They also interpret several other features of resonance Raman spectra and electron paramagnetic resonance spectra. The team reports that the combination of modeling and observation helps them better understand how the radicals interact with their distinctive host proteins at the molecular level. **Lucas Laursen**

LIGHT-POWERED MOLECULAR GLUE STOPS PROTEINS IN THEIR TRACKS

Kinesins are proteins that walk along and carry microtubules to the outer edges of a cell during cell division. Now Noriyuki Uchida, Kou Okuro, Michio Tomishige, Takuzo Aida, and their colleagues have built a light-powered "molecular glue" that can stop kinesin in its tracks (DOI: 10.1021/ja401059w).

The researchers design the branched molecule to have nine sticky feet, each tipped with a guanidinium ion and a benzophenone group. First, the glue molecule attaches to both kinesin and a microtubule—positively charged guanidinum ions stick to negatively charged areas of the protein surfaces. Ultraviolet light then triggers a photochemical reaction in which the benzophenone forms a reactive radical that eventually leads to the new covalent bond between the glue and the kinesin protein. Since the glue is covalently attached to each structure, the kinesin protein can no longer move along the microtubule.

Cancer cells have negatively charged surfaces too. This glue might be useful for light-controlled cancer therapy by accumulating in cancer cells and linking kinesins to microtubules, potentially stalling the excessive growth of tumor cells. **Melissae Fellet, Ph.D.**

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