Probing electron-induced chemistry with X-rays

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In 1953 Miller and Urey fascinated the general public with their experiments that showed that an electrical discharge in a mixture of common gases causes reactions leading to important biological molecules that may have led to the genesis of life [1]. In more recent years the popular literature has showcased other approaches to produce biological molecules such as irradiation of ices found on interstellar dust grains [2, 3]. The great-unanswered question, though, is how does chirality arise. We hypothesized that a previously unconsidered chiral agent can play a significant role: low-energy spin-polarized secondary electrons produced by irradiation of a magnetic substrate [4, 5]. Our approach involved monitoring C-O bond cleavage of a model chiral molecule, (R)- or (S)-2-butanol ($CH_3CHOHC_2H_5$), adsorbed on a magnetic permalloy ($Fe_{0.2}Ni_{0.8}$) substrate, as a function of x-ray irradiation time. The chiral carbon on 2-butanol is bound to an –OH group. Experiments were carried out under UHV conditions using XPS to monitor the intensity of the chemically shifted C-O peak. We found that the intensity of the C-O peak decreases exponentially as a function of irradiation time as a result of cleavage of the C-O bond. Using the kinetic relationship, $I = I_0\exp(-t/\tau)$, where I = C-O peak area; I_0 = initial C-O peak area; t = time, we are able to extract the time constant, τ, of the reaction as a function of the chirality of the adsorbed molecule and spin polarization of the substrate secondary electrons. The results showed that there is an enhancement of ~10% in the rate of C-O bond cleavage that depends on the chirality of the molecule and the spin polarization of the substrate secondary electrons. This enhancement is well above that seen in most previous studies. Furthermore, this mechanism is more general in that it requires only a magnetic substrate and a source of ionizing radiation. Iron is one of the most common elements and is magnetic in many forms. Ionizing radiation and magnetic fields are ubiquitous throughout the universe. Therefore, this mechanism for inducing chirality should be viable in a wide variety of possible environments.

The exact nature of the chemical reaction that produces the dissociation is unknown. It is conjectured to involve dissociative electron attachment (DEA) to a transient negative ion (TNI) state with lifetimes between 0.01 to 10 psec [6]. The chiral enhancement may involve coherent excitation of many chiral centers by the low energy electrons. DEA and TNIs are also thought to be important contributors to electron-induced reactions that are thought to play major roles in a wide range of other scientific and technological areas including plasma chemistry [7], nuclear waste and reactor chemistry [8], radiation therapy [9], and atmospheric chemistry [10]. Having the ability to probe the dynamics of such reactions with elemental specificity would greatly enhance our understanding of this important class of chemical reactions. Chen and coworkers have utilized hard x-rays to probe the evolution of laser-induced chemical reactions [11]. Recent advancements in electron guns have produced pulsed sources with

temporal widths of picoseconds or less. Utilization of such sources as a pump and tunable, polarized x-rays from a third or fourth generation facility as a probe should produce unprecedented insight into the nature of DEA and TNI states and will have a major impact on our understanding of electron-induced chemistry. In this talk I will use our recent studies of secondary-electron initiated, chiral-specific chemistry as an example of a research area where such studies could provide an impact with the hope of engaging the community in discussions of broader areas of research.

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REFERENCES

1. Miller SL, (1953) A production of amino acids under possible primitive earth conditions. Science 117: 528.
2. Bernstein MP, Dworkin JP, Sandford SA, et al., (2002) Racemic amino acids from the ultraviolet photolysis of interstellar ice analogues. Nature 416: 401-403.
3. Munoz Caro GM, Meierhenrich UJ, Schutte WA, et al., (2002) Amino acids from ultraviolet irradiation of interstellar ice analogues. Nature 416: 403-406.
4. Rosenberg RA (to be published) Spin-polarized electron induced asymmetric reactions in chiral molecules. In: Naaman R (ed) Electronic and magnetic properties of chiral molecules and supramolecular architectures, Springer-Verlag, Berlin
5. Rosenberg RA, Abu Haija M, Ryan PJ, (2008) Chiral-selective chemistry induced by spin-polarized secondary electrons from a magnetic substrate. Phys. Rev. Lett. 101: 178301.
6. Bass AD, Sanche L, (2003) Reactions induced by low energy electrons in cryogenic films (review). Low Temp. Phys. 29: 202-214.
7. Morgan WL, Benjamin B, Herbert W (2000) Electron collision data for plasma chemistry modeling. in Advances in atomic, molecular, and optical physics, Academic Press, Volume 43, pp. 79-110.
8. Garrett BC, Dixon DA, Camaioni DM, et al., (2004) Role of water in electron-initiated processes and radical chemistry:,äâ issues and scientific advances. Chemical Reviews 105: 355-390.
9. Boudaffa B, Cloutier P, Hunting D, et al., (2000) Resonant formation of DNA strand breaks by low-energy (3 to 20 eV) electrons. Science 287: 1658-1660.
10. Lu QB, (2009) Correlation between cosmic rays and ozone depletion. Phys. Rev. Lett. 102: 118501.
11. Chen LX, (2005) Probing transient molecular structures in photochemical processes using laser-initiated time-resolved x-ray absorption spectroscopy. Ann. Rev. Phys. Chem. 56: 221-254.