CHEMICAL REACTIVITY, MOLECULAR OXYGEN AND THE MODERN GENETIC CODE

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Abstract

The origin of the genetic code and its choice of amino acids (AAs) have remained enigmatic. We have analyzed the quantum chemistry of all proteinogenic and various prebiotic AAs and find that the energetic HOMO-LUMO gap, a correlate of chemical reactivity, becomes incrementally closer in modern AAs, reaching the level of specialized redox-cofactors in the last two AAs, tryptophan and selenocysteine. We show that the prediction of higher reactivity of the more recently added AAs is true for various free radicals, particularly oxygen-derived peroxyl radicals, and we demonstrate an immediate survival benefit conferred by AA-mediated radical scavenging in living cells using model compounds. Our data indicate that in demanding building blocks with more versatile redox-chemistry, biospheric molecular oxygen triggered the selective fixation of the last AAs in the genetic code.