Enhanced Nucleophilicity and Depressed Electrophilicity of Peroxide by Zinc(II), Aluminum(III) and Lanthanum(III) Ions

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Z. Naturforsch. **56 c,** 138–143 (2001); received August 7/September 11, 2000

Peroxide Ion, Zinc(II), Lanthanum(III)

The binuclear zinc(II) complex, $[Zn_2(HPTP)(CH_3COO)]^{2+}$ was found highly active to cleave DNA (double-strand super-coiled DNA, pBR322 and ϕ×174) in the presence of hydrogen peroxide. However, no TBARS (2-thiobarbituric acid reactive substance) formation was detected in a solution containing 2-deoxyribose (or 2′-deoxyguanosine, etc); where (HPTP) represents N,N,N′-N′-tetrakis(2-pyridylmethyl)-1,3-diamino-2-propanol. These facts imply that DNA cleavage reaction by the binuclear Zn(II)/H_2O_2 system should be due to a hydrolytic mechanism, which may be attributed to the enhanced nucleophilicity but depressed electrophilicity of the peroxide ion coordinated to the zinc(II) ion. DFT (density-functional theory) calculations on the peroxide adduct of monomeric zinc(II) have supported the above consideration. Similar DFT calculations on the peroxide adducts of the Al(III) and La(III) compounds have revealed that electrophilicity of the peroxide ion in these compounds is strongly reduced. This gives an important information to elucidate the fact that La^{3+} can enhance the growth of plants under certain conditions.