THE ROLE OF A NOVEL DIRADICAL PATHWAY IN REACTIONS BETWEEN PEROXYL RADICALS AND NO

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The conversion of peroxyl radicals to organic nitrates via reaction with NO is of importance in atmospheric chemistry and biochemistry. The mechanism for nitrate formation is obscure; no previous theoretical results have been even vaguely consistent with the experimental evidence. We propose a simple valence bond argument to rationalize how an initially formed pernitrite, ROONO, can decompose to an alkoxy radical and NO_2 or rearrange to $RONO_2$. This qualitative mechanism, which involves the coupling of two valence bond states, is supported by coupled-cluster electronic structure calculations that predict a barrier of ca. 20-30 kcal mol^{-1}, that is provided by the radical/radical adduct. In addition to its obvious importance for atmospheric chemistry, it is likely that this mechanism is also responsible for chain termination of the oxygen-dependent oxidation of lipid membranes in biological cells. The mechanism can likewise be applied to the thermal decomposition of organic nitro compounds (explosives and solid propellants), RNO_2 + heat $\rightarrow$ products.