A HISTORY OF OXYGEN ACTIVATION: 1773-1993

R.A. Sheldon

Delft University of Technology
The Netherlands

INTRODUCTION

Controlled partial oxidation of hydrocarbons (alkanes, alkenes and aromatics) is the single most important technology for converting petrochemical feedstocks to industrial organic chemicals [1]. For economic reasons, these processes predominantly involve the use of molecular oxygen (dioxygen) as the primary oxidant. The success of these processes depends largely on the use of metal catalysts to promote both the rate of reaction and the selectivity to partial oxidation products. Both gas phase and liquid phase oxidations, employing heterogeneous and homogeneous catalysts, respectively, are practiced industrially. In biological systems a broad range of selective oxidations of hydrocarbon substrates by dioxygen are catalyzed by metalloenzymes, appropriately known as oxygenases [2,3]. A common feature of most of these processes is the involvement of a multivalent transition metal ion.

Structure and Reactivity of Dioxygen

The ground state of dioxygen is a triplet with two unpaired electrons with parallel spins. The first two electronically excited states are both singlets, formed by relocation and/or pairing of the unpaired electrons in the $2p\pi$ antibonding orbitals. The half-filled antibonding molecular orbitals of $^3\text{O}_2$ can accommodate two additional electrons. The addition of one electron affords the superoxide anion ($\text{O}_2^-$) and two-electron reduction gives the peroxide ion ($\text{O}_2^{2-}$).

The complete oxidation of organic materials by dioxygen, to give carbon dioxide and water, is thermodynamically very favorable. Fortunately, unfavorable kinetics preclude the spontaneous combustion of living matter into a puff of smoke. Thus, the direct reaction of $^3\text{O}_2$ with singlet organic molecules to give singlet products is a spin-forbidden process with a very low rate. One way of circumventing this energy barrier is via a free radical pathway. The reaction of a singlet molecule with $^3\text{O}_2$ (reaction 1) forming two doublets (free radicals) is a spin-allowed process. Reaction 1 is, however, highly endothermic (up to 50 kcal.mol$^{-1}$) and is observed at moderate temperatures only with very reactive substrates that form resonance stabilized radicals, e.g. reduced flavins (reaction 2). This is a key step in the activation of $^3\text{O}_2$ by flavin-dependent oxygenases.
A second way to overcome the spin conservation obstacle is for $^{3}O_2$ to combine with a paramagnetic transition metal ion (reaction 3). The expectation that the resulting metal-dioxygen complex may react selectively with organic molecules at moderate temperatures forms the basis for the extensive studies of oxygen activation by metal complexes during the last three decades [4-6]. The various oxygenated species that may play a role in metal-catalyzed oxidations with dioxygen are depicted in Figure 1.