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SINGLET STATES OF MOLECULAR OXYGEN AND CYCLOADDITION MECHANISM IN OXYGENATION OF LINOLEATE SYSTEM

N.A. KHAN

P.C.S.I..R. Laboratories, Dacca 2

Initial oxygenation and formation of hydroperoxide only without decomposition, have been shown to be the actual process. The experimentations by singlet molecular oxygen from chemical source and chlorophyll sensitization compared to those of general oxygenation by visible light catalysis and lipoxidase catalysis, has brought out ample clues to possible mechanisms. The transitional cycloaddition by virtue of π-complexes earlier proposed by us has been shown to be the possible mechanism of oxygenation by active species of molecular oxygen towards formation of hydroperoxides as the independent step ahead of main autoxidation reactions. The *cis* attack keeping activated O_2-molecule and participating —CH in a plane perpendicular to olefinic centre, has been shown to be in the theories already proposed.[19–23] The stereospecificity evident from optical activity in products from both types (singlet and triplet states) under specific conditions, has established the fact that two types of singlet molecular oxygen are involved, one known as $^1\Delta g$ (22.5 kcals) and the other still uncertain about energy levels (possibly below 22.5 kcals with lesser activity).

The identity of hydroperoxide-forming step has been stressed in all our investigations[1–6] and now established by reactions of metastable singlet molecular oxygen $^1\Delta_g$. The application of singlet oxygen without any specific knowledge of its existence commenced with the dye-photosensitized autoxidation reactions.[7,8] However, in gaseous state, it has been shown and prepared by Foner and Hudson[9] and used for oxidation by Corey and Taylor.[10] The reaction of sodium hypochlorite and hydrogen peroxide has offered unique chemical means of obtaining excited singlet state of molecular oxygen.[11–14] Through comparative studies the excited singlet molecular oxygen has been established as intermediate in photo sensitized autoxidation.[15–17] It would be interesting to have investigations on oxygenation of methyl linoleate (ideal substance already shown for such processes[18]), by singlet molecular oxygen and also equivalent active species of molecular oxygen, particularly by chemically formed and chlorophyll-sensitized in the former cases and by lipoxidase and visual-light-catalysed in the latter. *cis*, *cis*-Methyl linoleate (spectroscopically pure) or, sodium linoleate[19] has been subjected to oxygenation under various conditions: (i) metastable singlet molecular oxygen oxygenation[12–16] at 0°C in three-necked flask containing stirred 1.0% neutral Na linoleate solution, with slow addition of H_2O_2 solution followed intermittently by Na hypochlorite solution[15,16] from two separatory funnels attached to the flask (Fig. 1) helping further control, (ii) chlorophyll-sensitized photooxidation at 0°C in simple arrangements (Fig. 2) (iii) visible-light-catalysed oxidation at 0°C; (iv) lipoxidase-catalyzed oxidation (Na Linoleate) at 0°C in suitable environments.[20] All precautions were taken to keep the environmental conditions, temperature, pH and concentration in particular, strictly maintained constant. In none of these oxygenation reactions, the peroxide level has been allowed to go beyond 5%. Only after careful neutralization by dilute hydrochloric acid in (i) and (iv) and in case of others without neutralization, the peroxides were

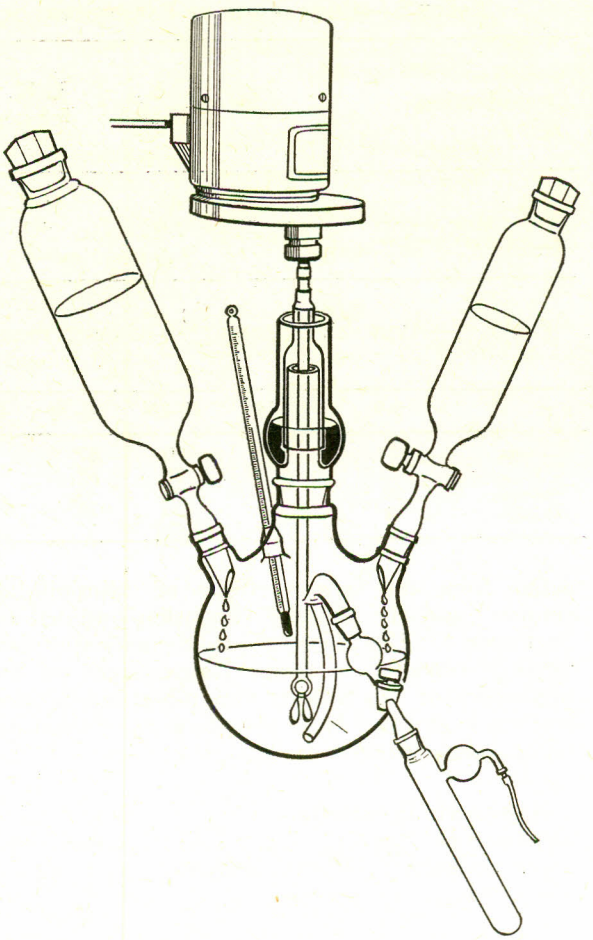

Fig. 1.—Singlet state molecular oxygen reaction vessel.

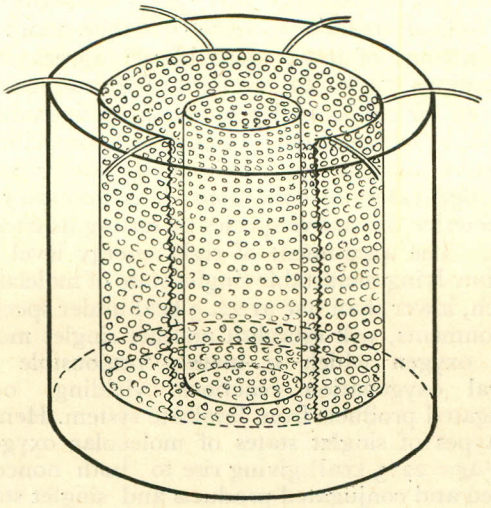

Fig. 2.—Cooling system with ice chips in annular space containing suitable openings.

concentrated by usual methods[19,21] and reduced by stannous chloride.[22] In both the chlorphyll-sensitized photooxidation and oxygenation by chemically produced singlet molecular oxygen of (ii) and (i) respectively, the products are identical, having both conjugated and nonconjugated isomers with the accompanying remarkable phenomena of optical activity in each. The others (iii) and (iv) showed only conjugated products. However, the products from (iv) lipoxidase catalysis showed optical activity and the rest racemic. This establishes the selective nature of oxygenation by (i) metastable singlet molecular oxygen, (ii) chlorophyll-sensitized photooxidation and (iv) lipoxidase-catalysed oxidation. These three processes (i, ii and iv) involve rapid oxygenation also. Moreover, with *cis*, *cis*-linoleate system, the oxygenation has become stereospecific, highly so in (i), (ii) and (iv) giving rise to specific products and new phenomena of optical activity not recognized so far in this dienoic system. The proposal of cyclic mechanisms did incorporate

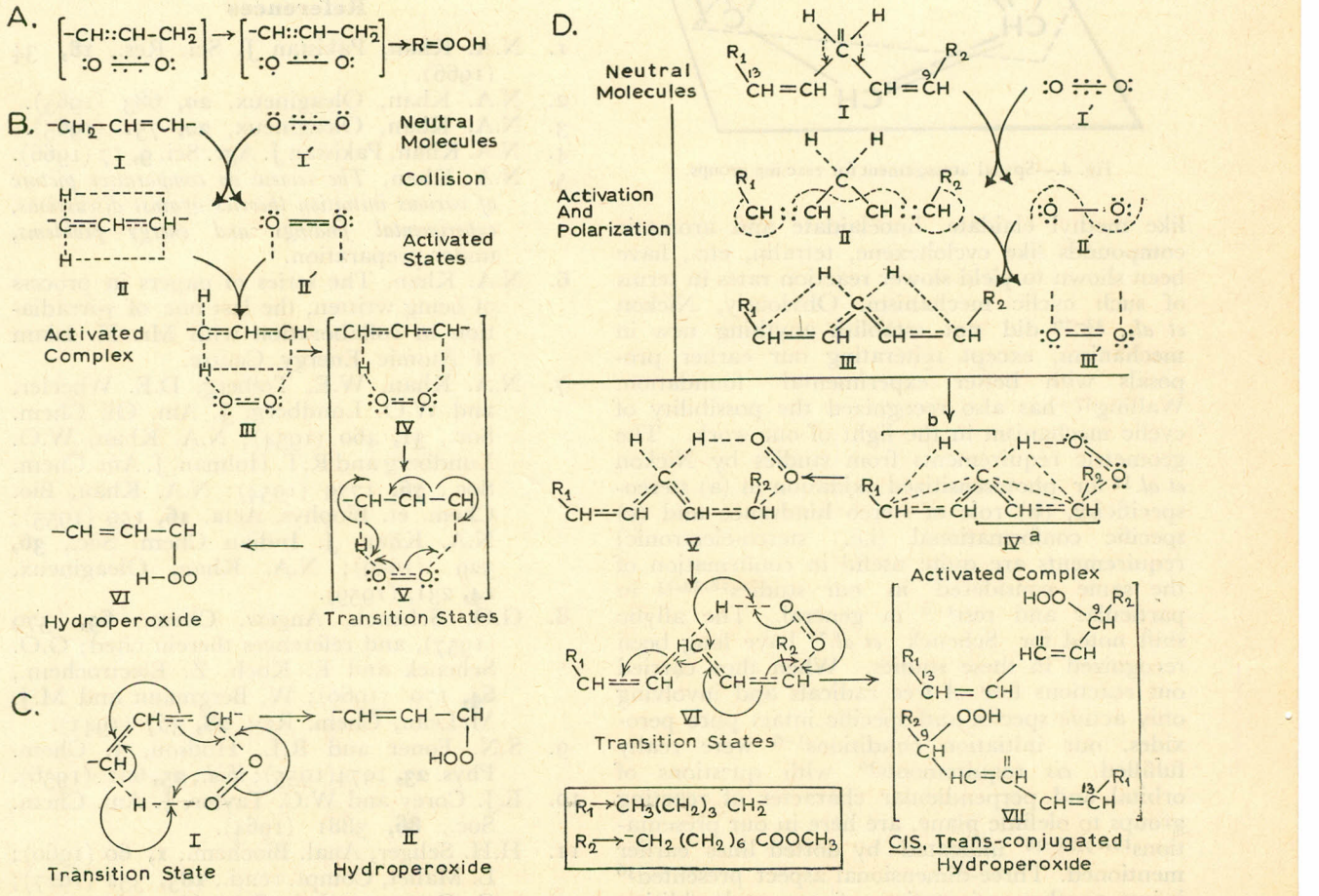

Fig. 3.—Cycloaddition mechanism.

the idea of such specificity in our earlier publications.[18,19,22,23–28] The whole concept centres round one pivotal point of separate identity of hydroperoxidation[1–6] by excited molecular oxygen free of decomposition and free radicals against the rest of autoxidation reactions involving complicated systems of decompositions, scission polar products, free radicals, so on and so forth.[29–31] In all our mechanism proposals, (Fig. 3), the cycloaddition of active oxygen molecule did face *cis* structure, i.e.,O_2-molecule and C—H are in separate plane compared to that of—C=C— double bond, the links in the former being indicated by dotted lines, perpendicular to each other (Fig. 4). The hindered systems in *trans* structure,

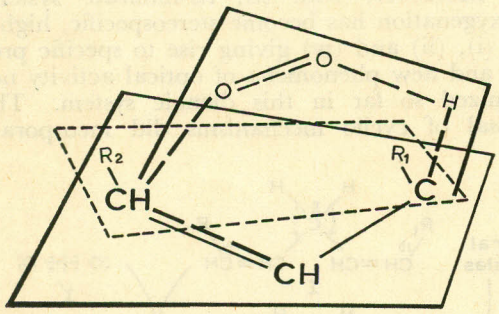

Fig. 4.—Spatial arrangement for reacting groups.

like methyl elaidate, linoelaidate and aromatic compounds like cyclohexene, tetralin, etc., have been shown to yield slower reaction rates in terms of such cyclic mechanism. Obviously, Nickon *et al.*, [32–36] did not establish anything new in mechanism, except reiterating our earlier proposals with better experimental foundation. Walling[37] has also recognized the possibility of cyclic mechanism in the light of our work. The geometric requirements from studies by Nickon *et al.*[32] for photosensitized oxidation in (a) stereospecificity, (b) role of stereo hindrance and (c) specific conformational (i.e. stereo-electronic) requirements are quite useful in confirmation of the same considered in our studies[18,22,23] in particular and rest[1–6] in general. The allylic shift noted for Schenck *et al.*[33] have long been recognized in these studies. When they carried out reactions free of free radicals and involving only active species and specific intact pure peroxides, our initiation conditions[1–6] were really fulfilled. *cis* requirements[36] with questions of orbital and perpendicular character of reacting groups to olefinic plane, are here in our presentations[18,19,22–28] indicated by dotted lines earlier mentioned. Three-dimensional aspect presented[36] is just another orientation of our cycloaddition process noted. The very idea that active species of oxygen molecule has no similarity to free radical reactions and resembles more or less reactions of intact peroxides,[38] agrees with our findings.[1–6,19] In the light of optical activity observed for conjugated products from lipoxidase-catalysed oxygenation giving stereospecificity to active oxygen species involved under such controlled catalytic conditions, it is necessary to characterize this active species by setting its energy levels. The assignment of right energy level for such low-lying metastable singlet state of molecular oxygen, lower than one at 22.5 kcal under specific environments, will establish another singlet molecular oxygen which is mainly responsible for general oxygenation reactions, yielding only conjugated products from linoleate system. Hence, two types of singlet states of molecular oxygen, one ($^1\Delta g$=22.5 kcal) giving rise to both nonconjugated and conjugated products and singlet state (energy levels lower than $^1\Delta g$ to be established), yielding only conjugated products, are in volvedin oxygenation indicating scope for further work.

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