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SINGLET OXYGEN AND THE INITIATION OF FATTY ACID AUTOXIDATION

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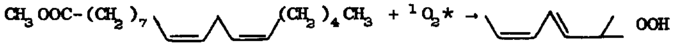
In fatty acid chemistry there has long been a gap in the complete understanding of the autoxidation process. This is because the initial presence of the unstable oxidation products - particularly hydroperoxides - which are necessary to supply free radicals for the autoxidation chain reaction, has not been adequately explained. There is neither sufficient energy nor the proper spin conservation in the reaction $^1RH + {}^3O_2 \rightarrow {}^1ROOH$ (RH is an unsaturated fatty acid and the superscripts refer to the spin multiplicity) to allow the reaction to take place in a simple way.

To overcome this difficulty we would like to propose that excited singlet oxygen ($^1O_2$), rather than ground state triplet oxygen ($^3O_2$) reacts directly with unsaturated fatty acids to produce unstable hydroperoxides. A mechanism which would supply such an excited O_2 molecule would serve to overcome both the energy and spin conservation requirements.

In order to see if this were the case, singlet O_2 from a radio frequency gas discharge (1,2) was passed over a thin film of methyl linoleate which had been highly purified. The progress of the oxidation was followed by the increase in absorbance at 234 nm, which is due to the formation of a conjugated hydroperoxide:



Assuming that this is a second order reaction (confirmed by rate studies), it was estimated from the results of the experiment that singlet O_2 reacted at least 1000 times faster than triplet O_2.

Later experiments showed that this figure might be as high as 10,000, the uncertainty being caused by uncertainties in the singlet O_2 concentration and the purity of the samples. It was found that the triplet O_2 oxidation rate decreased with increasing purity (as measured by the relative absorbance at 234 nm) while the singlet O_2 oxidation rate was either independent of, or far less dependent on, the initial purity.

Due to its great reactivity, then, singlet O_2 could serve to initiate autoxidation by forming unstable hydroperoxides - provided that it could be supplied to the system. A wealth of indirect evidence (2-5) indicates that singlet O_2 is the reactive intermediate in a number of photosensitized oxidation reactions. Since all fatty acids originate in either plant or animal products where natural pigments abound, a photosensitization mechanism in which these pigments serve as the light absorbing sensitizer (S) can reasonably be visualized:

$$^{1}S + h\nu \rightarrow {}^{1}S^{*} \rightsquigarrow {}^{3}S^{*}$$

$$^{3}S^{*} + {}^{3}O_2 \rightarrow {}^{1}O_2^{*} + {}^{1}S$$

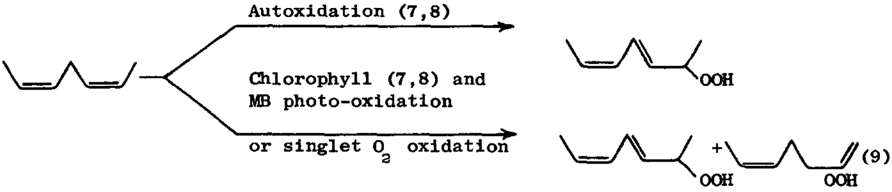
$$^{1}O_2^{*} + {}^{1}RH \rightarrow {}^{1}ROOH$$

$$\mathrm{ROOH} \rightarrow \text{free radical products}$$

The only necessary ingredients are visible light, triplet O_2 and a light absorbing sensitizer.

The direct observation of a singlet O_2 intermediate is rather difficult. However, two indirect methods have recently been used to confirm the presence of this species: comparison of products formed in two different reactions, a similar product distribution indicating a common reactive intermediate (3); and inhibition experiments using molecules known to react strongly with singlet O_2, an inhibition indicating competition for the reactive intermediate (5).

Using chlorophyll a, pheophytin a, protoporphyrin dimethylester and methylene blue (MB) as sensitizers, methyl linoleate was photo-oxidized and the products compared with singlet and triplet O_2 oxidation products by thin-layer chromatography and infrared analysis. The pattern of separated spots shown by TLC was essentially the same in all cases, only minor differences being noticeable among the secondary products. The primary oxidation products appear (6) as a single spot (mono-hydroperoxides). This was removed from the TLC plate and analysed by IR spectroscopy. The singlet O_2 and MB photo-oxidized samples were found to contain both nonconjugated and conjugated hydroperoxides, as is known (7,8) to occur in chlorophyll photo-oxidized methyl linoleate. Oxidation by triplet O_2 (air autoxidation), however, is known (7,8) to produce only conjugated hydroperoxides as the primary oxidation products. Thus we can conclude that:



Since, in the process of initiating autoxidation, any nonconjugated hydroperoxides initially present would soon be changed into secondary products, it is not expected that they would be found among the primary oxidation products in systems where free radical autoxidation is the predominate mechanism.

Inhibition studies gave further evidence for singlet O_2 involvement in the photo-oxidation of methyl linoleate. In these experiments tetramethylethylene and tetraphenylcyclopentadienone - both known (3,5) to react strongly with singlet O_2 - inhibited photo-oxidations catalysed by all four sensitizers.

Our present evidence for the involvement of singlet O_2 in autoxidation, then, consists of three parts:

1) it does react directly with methyl linoleate at a very high rate to form unstable hydroperoxides;
2) there is an indication of common product formation between singlet and photo-oxidation, especially for the important sensitizer chlorophyll;
3) Photo-oxidation is inhibited by molecules known to react strongly with singlet O_2.

The evidence thus supports the conclusion that the photosensitized production of singlet O_2 must play an important role in the formation of the initial hydroperoxides which are necessary for the initiation of autoxidation. Work is currently underway to further define this process and a more detailed report will be published elsewhere.

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