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THE ENE REACTION OF SINGLET OXYGEN WITH OLEFINS

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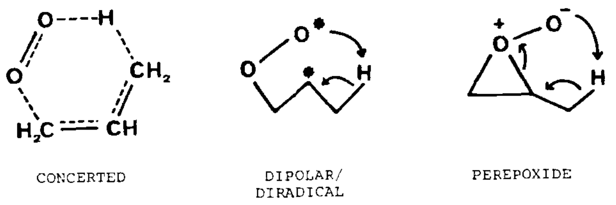
The reactions of singlet oxygen ($^1O_2$) with *cis* and *trans* butenes-1,1,1-d_3, at -80°C in Freon-11, show a product isotope effect (k_H/k_D) of 1.38 and 1.25 respectively. Isomerization of the starting materials or formation of dioxetanes were not observed during the course of the photooxygenation. Together with the isotope effects on the reactions of tetramethylethylene-d_6 isomers with singlet oxygen, these results require the reversible formation of a perepoxide or charge transfer intermediate.

KEY WORDS: Singlet oxygen, ene reaction, mechanism of *cis*-butene-1,1,1,-d_3, *trans*-butene-1,1,1,-d_3

Sensitized photooxidations have been studied for many years[1] not only for their mechanistic and synthetic interest but also because they have environmental and biological[2] significance. The ene reaction, which is the most common and important of the singlet oxygen reactions, has been extensively studied for the last twenty years.[1]

$$H_2C{=}CH{-}CH_3 \xrightarrow{^1O_2} HOOCH_2{-}CH{=}CH_2$$

The mechanism of this reaction is the subject of controversy, the main question being whether the reaction is concerted or involves intermediates. At least four mechanisms have been proposed for this reaction: 1) a concerted mechanism in which the characteristic bond shifts take place through a cyclic transition state; formation of a 2) diradical or 3) dipolar intermediate, in which the C–O bond forms first; and 4) a perepoxide intermediate are shown in Fig. 1.



CONCERTED

DIPOLAR/
DIRADICAL

PEREPOXIDE

FIGURE 1 Proposed mechanisms for singlet oxygen reactions.

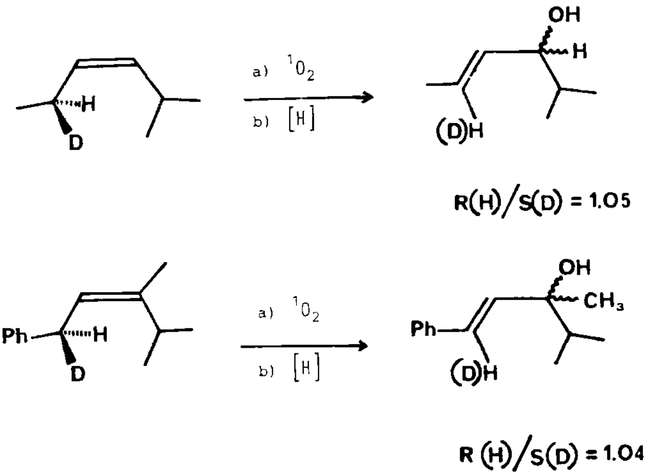


FIGURE 2 Stereospecificity of reactions of singlet oxygen with olefins.

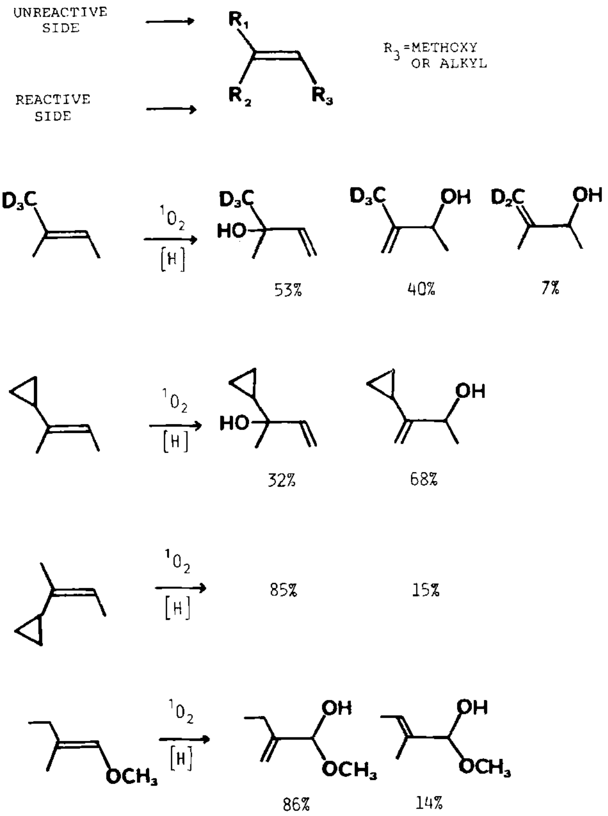


FIGURE 3 Regioselectivity of reactions of singlet oxygen with olefins and enol ethers.

Many stereochemical aspects of the ene reactions of singlet oxygen with olefins are well documented. For example, singlet oxygen reacts stereospecifically with olefins. This was shown with optically active di- and trisubstituted olefins.[3] (Fig. 2).

Singlet oxygen shows a high regioselectivity with enol ethers,[4] where oxygen adds on the same side as the alkoxy group. This unexpected regioselectivity has been shown to hold generally in simple trisubstituted olefins, where alkyl group exert a strong directing effect toward attack on the most crowded side (*cis*-effect).[5]

Isotope effect studies[6] have shown that a significant isotopic competition can be observed when the competing groups have a *cis* arrangement (*cis*-effect) and negligible (but not zero) when they have a *trans* relationship, Fig. 4. In a concerted mechanism, where CH and CD bonds are equally competitive, one would expect similar isotope effects in tetramethylethylene-d_6 isomers.

A dipolar or diradical intermediate shown in Fig. 5, in which the C–O bond forms first, should predict an identical and substantial isotope effect from (E)-2,3-*bis*-(trideuteriomethyl)-2-butene, **1**, and (Z-2,3-*bis*-(trideuteriomethyl)-2-butene, **2**, and negligible effect from 2,2-*bis*-(trideuteriomethyl)-2-butene, **3**, in contrast to the observed results.

If a perepoxide (or a charge-tranfer complex with a similar configurational structure) is formed irreversibly, then an isotope effect should be found when H and D are able to compete with each other in the *cis*-configuration but should be absent with *trans* or geminal olefins, where the isotopes are on opposite sides of the double bond.

Our recent results on the reaction of $^1O_2$ with *cis* and *trans*-butenes-d_3 show a substantial isotope effect for both the *cis* and *trans* isomers, equations (1) and (2). In the first entry, CH and CD bonds both have *cis* relationship and show an isotope

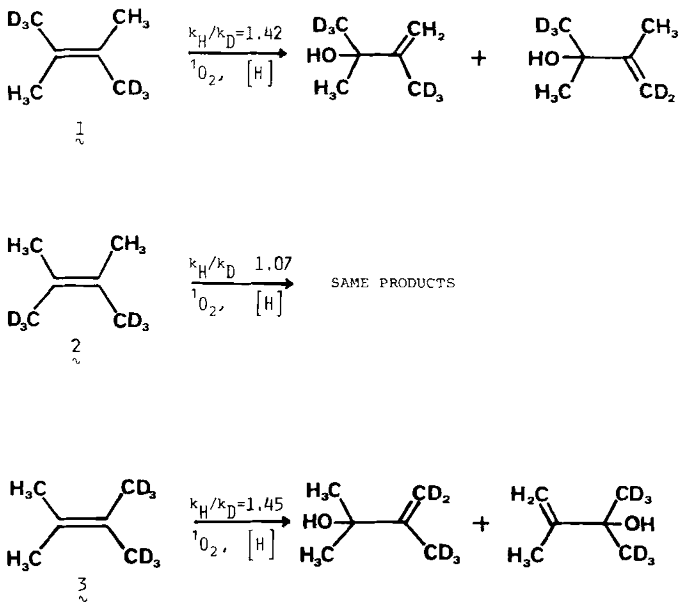
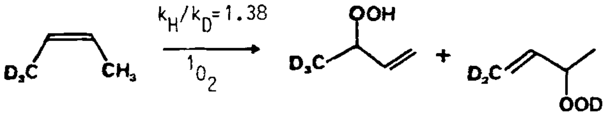


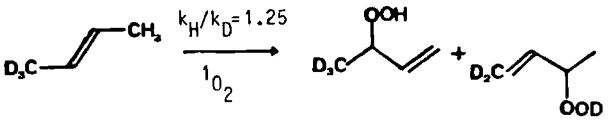
FIGURE 4 Isotope effect for tetramethylethylene-d_6 isomers.

effect $k_H/k_D = 1.38$ similar to the corresponding (E)-2-3-*bis*(trideuteriomethyl)-2-butene, **1**, $k_H/k_D = 1.42$ (*cis* competition).



(1)

In the second entry, where CH and CD bonds are in a *trans* relationship, there is an unexpected isotope effect, much larger than the corresponding effect observed with (Z)-2-3,-*bis*-(trideuterimethyl)-2-butene, $k_H/k_D = 1.07$



(2)

The only product detected during the photooxygenation of *cis* or *trans* butene-d_3 was the ene adduct. VPC analysis showed no isomerization of starting material or formation of any byproducts which could be the result of decomposed dioxetanes. Together with isotope effects on the reactions of tetramethylethylene-d_6 isomers with singlet oxygen, these results require the reversible formation of a perepoxide or charge transfer intermediate with similar structural requirements. The substantial isotope

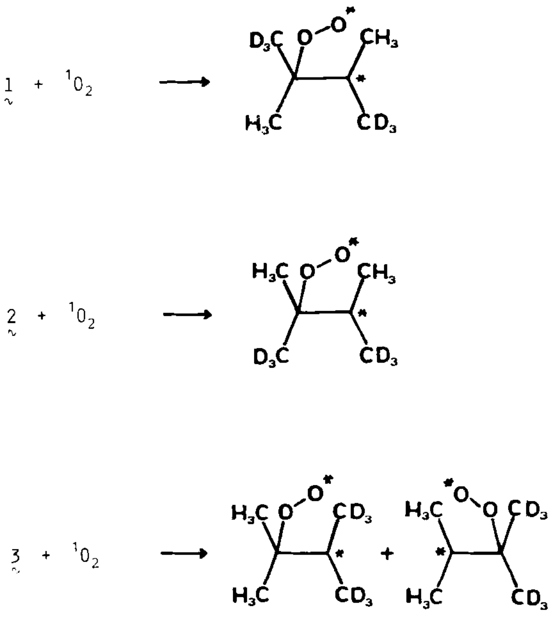


FIGURE 5 Dipolar or diradical intermediates of $^1O_2$ with tetramethylethelene-d_6 isomers.

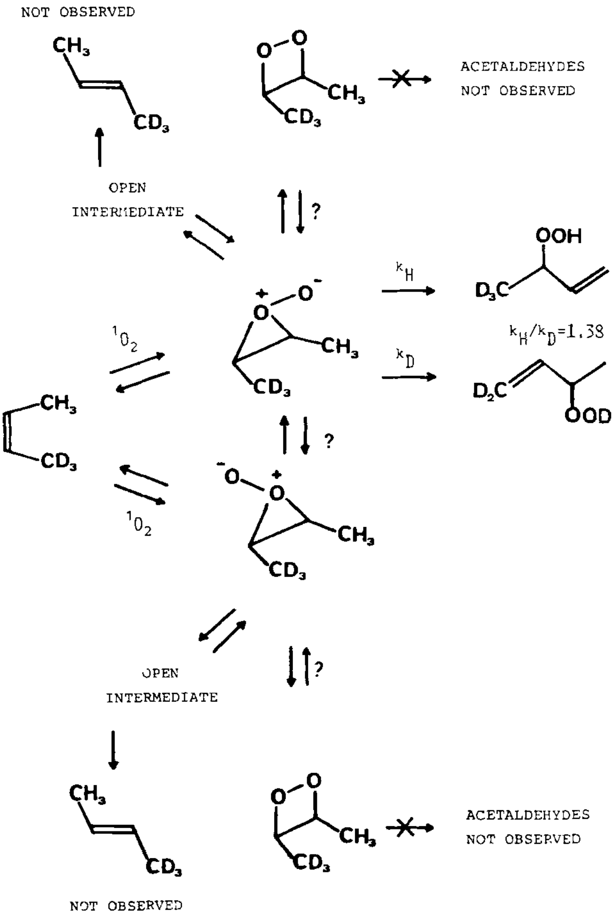


FIGURE 6 Possible mechanism of photooxidation of *cis*-butene-1,1,1, d_3.

effect observed for *trans*-butene-d_3, (1.25) could be the result either of partial reversion of the intermediate complex to the starting materials or isomerization of the perepoxide intermediate by opening to a zwitterion or diradical, or by some other mechanism. However, if there is an open intermediate, it cannot return to starting material, since no isomerization of the starting olefin was observed during the photooxygenation reaction, Figs 6, 7. If one or both of these processes operate to a significant extent, an isotope effect is expected even for methyl groups on opposite sides of the double bond.

It is also interesting that, although the *trans*-isotope effects for the tetramethylethylenes with $^1O_2$ are very small, they are also not zero, and an interconversion process is required for these olefins as well. The magnitude of the effect should be dependent on the relative contribution or the direct reaction and the isomerization. If the intermediate reverts to starting material, this process should be more efficient with the butenes than with the more electron-rich olefins, where the bonding should be

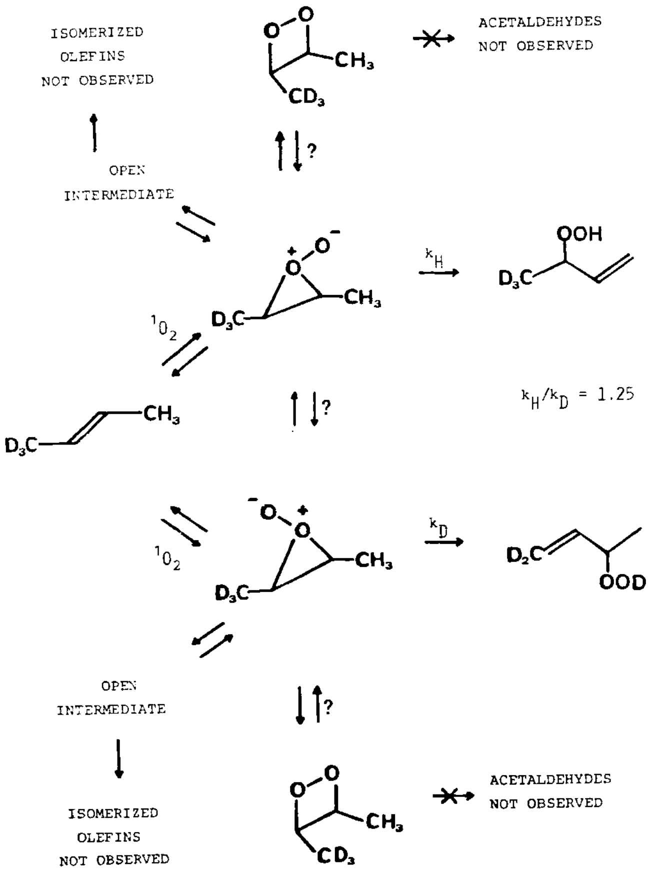


FIGURE 7 Possible mechanism of photooxidation of *trans*-butene-1,1,1-d_3.

stronger. A larger *trans* isotope effect would therefore be expected for the butenes than tetramethylethylenes, as observed.

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