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A Possible Mechanism for the Formation of Oxiranes in Reactions of Singlet Molecular Oxygen with Olefins

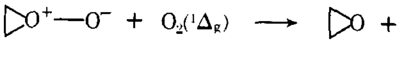
Sir:

Singlet ($^1\Delta_g$) molecular oxygen normally reacts with olefins to form either allylic hydroperoxides (ene reaction) or dioxetanes (1,2-cycloaddition). While both concerted pericyclic mechanisms and two-step processes involving intermediate peroxiranes have been suggested for these reactions,[1] most authors have tended to favor the former in view of failure[2] to detect peroxirane intermediates.

Recently, however, the photosensitized oxidation of 2,2′-biadamantylidene in pinacolone has been reported[3] to yield not only the corresponding dioxetane but also the oxirane and *tert*-butyl acetate. The formation of the latter two compounds was attributed to the trapping of a peroxirane intermediate in a Baeyer–Villiger type reaction with the solvent. Subsequently, the photooxidations of 7,7′-binornornylidene[4] and of norbornene[5] have likewise been shown to lead to the corresponding dioxetane and oxirane. In these cases, however, the products were obtained in a variety of solvents, including benzene[4] and acetonitrile[5], which are clearly incapable of Baeyer–Villiger type reactions. It was established in each case[4,5] that the oxirane was a genuine photooxidation product but no mechanism for its formation was suggested.

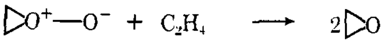
In order to derive a mechanism for these reactions[3-5] we have carried out MINDO/3[6] calculations for an analogous case, the reaction of ethylene with singlet molecular oxygen. An earlier MINDO/3 study[7] had led us to the conclusion that reactions of singlet oxygen with olefins always involve the initial formation of peroxirane intermediates (or, in the case of $-E$ substituted olefines, zwitterionic intermediates) which occupy shallow minima on the potential surface. We therefore decided to investigate the following reactions using theoretical techniques described previously[7]

(1)



$+ O_2(^1\Delta_g)$ $+ O_3$

(2)



$+ C_2H_4$

(3)

The closed-shell ground-state MINDO/3 calculations predict these reactions (1–3) to be exothermic by 49.4, 36.2, and 98.1 kcal/mol, with calculated activation energies of 34.1, 29.2, and 8.6 kcal/mol, respectively. The fully optimized structures for the three transition states are shown in Figure 1. The transition state for reaction 3 shows C_s symmetry and can be regarded as a weak π-complex between peroxirane and ethylene, similar to the C_s transition state found for the addition of singlet molecular oxygen to ethylene to form peroxirane.[7]

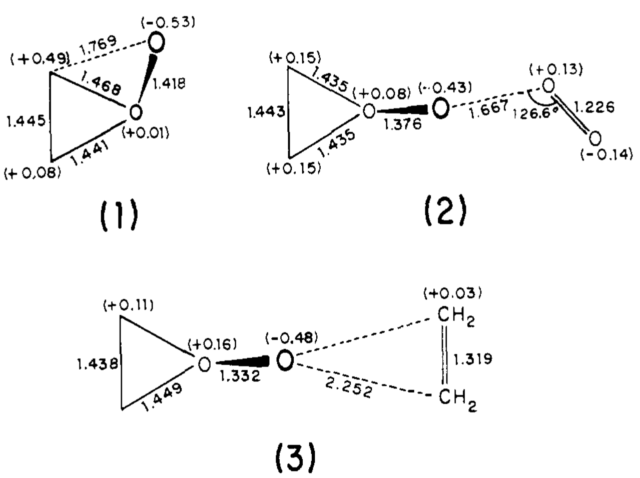


Figure 1. Calculated transition states for reactions 1–3. Bond lengths are given in Å, formal charges (in brackets) in electrons.

The calculated values for the heats of formation and activation energies are naturally subject to the errors of the MINDO/3 method which usually are less than 5 kcal/mol.[6] In our present case, however, we have to consider that oxirane is given too stable by MINDO/3, by 13.9 kcal/mol, and we expect a similar situation for peroxirane for which no experimental data are available. The calculated activation energies for eq 1 and 2 must therefore be too large, probably by similar amounts.[8] That for eq 3 should be little affected since the transition state closely resembles the reactants in structure (see Figure 1). All these reactions must in any case be exothermic. Several conclusions then follow.

For sterically nonhindered olefins, the reduction (eq 3) of an intermediate peroxirane by the olefin is predicted to be more facile than the reduction (eq 2) by singlet oxygen or the rearrangement (eq 1) to the dioxetane. The reaction between ethylene and singlet molecular oxygen (which has not yet been observed experimentally) should therefore yield oxirane as the main product, via mechanism 3, and not dioxetane or its cleavage product formaldehyde, as might have been assumed.

In the case of 2,2′-biadamantylidene,[3] 7,7′-binorbornylidene,[4] and norbornene,[5] the formation of the oxirane via route 3 is expected to be very unfavorable since the reduction of the peroxirane by the olefin is sterically inhibited. This is supported by the observation in the 7,7′-binorbornylidene system[4] that the ratio of oxirane to dioxetane in the product increased fourfold when the concentration of the olefin was reduced by a factor of 20. Our calculations indicate that in this situation the dioxetane and oxirane should be formed with similar ease via route 1 and 2, and concomitant formation of the two compounds is indeed observed.[3-5]

We therefore suggest that the formation of oxirane in these reactions involves the reduction of an intermediate peroxirane by singlet molecular oxygen. Detection of the ozone thus formed may be difficult since ozone reacts with olefins such as 7,7′-binorbornylidene to give oxiranes.[4] The most obvious test of the proposed mechanism would be provided by studies of the product ratio as a function of the concentration of singlet molecular oxygen. In a photooxidation experiment, we would expect the oxirane:dioxetane ratio to increase with increasing light intensity.

Another useful experiment suggested by our calculations is the photooxidation of a bulky olefin such as 2,2′-biadamantylidene in the presence of ethylene. We predict ethylene to trap the initially formed peroxirane of 2,2′-biadamantylidene via reaction 3, since the approach of ethylene is sterically feasible and since ethylene is a better reducing agent than singlet molecular oxygen.

Finally, we note that, in the transition state for reaction 2, the oxygen molecule is electronically polarized (see Figure 1). In cases for which reactions 1 and 2 are competitive,[3-5] the oxirane:dioxetane ratio in the product is expected to increase with increasing ability of the solvent to stabilize such a polarized oxygen molecule.

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Flash Photolysis Evidence for Metal-Metal Bond Cleavage and Loss of CO in the Photochemistry of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$[1]

Sir:

The photochemistry of metal-metal bonds appears to be extensive, although quantitative studies have begun to appear only recently.[2] The results of many reactions can be reconciled in terms of initial metal-metal bond cleavage (eq 1).[2b]

$$M\text{-}M \xrightarrow{h\nu} 2M \qquad (1)$$

However, several different types of photoproducts have been observed, and it is reasonable to suspect that alternate photopathways may exist. For example, the dimer, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$,[3] undergoes net light-induced substitution, disproportionation, and oxidation[4-7] with relatively high efficiencies.[8,9]

In the electronic spectrum of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ there are two well-defined absorption bands at 387 (ϵ 21,000) and 510 nm (ϵ 1870).[10] The band at 387 nm is probably the $\sigma \rightarrow \sigma^*$ transition of the metal-metal bond by analogy with the assignments made by Levenson, Gray, and Ceasar for the intense, near-uv bands of $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$.[11] The relatively low-intensity band at 510 nm is probably a d → d transition, since the spectra of related compounds without metal-metal bonds (e.g., $(\eta^5\text{-}C_5H_5)Mo(CO)_3Br$, $(\eta^5\text{-}C_5H_5)Mo(CO)_2Br_2^-$)[8] are qualitatively similar in the visible (ϵ ~500). Our work has shown that *either* uv (366 nm) *or* visible (546 nm) photolysis of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ in THF (tetrahydrofuran) can give efficient substitution, disproportionation, and oxidation reactions.[8,9]

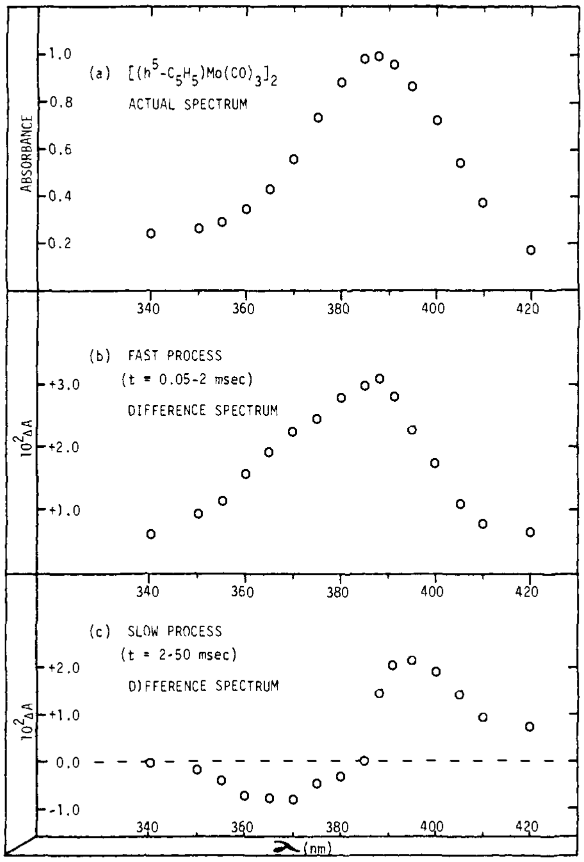

Figure 1. Comparison of the difference spectrum obtained by visible ($\lambda \geq 460$ nm) flash photolysis of 2×10^{-5} $M[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ *in* cyclohexane: (a) actual spectrum (2.5-cm pathlength) of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ taken before flash photolysis, (b) difference spectrum for the fast process (t = 0.05–2 msec) after being corrected for the slow process, and (c) difference spectrum for the slow process (t = 2–50 msec).

By applying conventional flash photolysis techniques to solutions of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ in cyclohexane, THF, and acetonitrile, we find direct evidence for the appearance of *two* distinct intermediates, immediately following photolysis. The intermediates subsequently react by independent thermal processes, which regenerate $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ quantitatively.[12] The intermediates are both present at the earliest experimental observation times ($t \geq 50$ μsec), and both appear following either uv or visible photolysis.[13]

One of the following thermal processes is ~50–100 times faster than the other, which has allowed us to resolve the difference spectra between regenerated $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and both intermediates (Figure 1). For the fast process (t ~0.05–2 msec), the difference spectrum (Figure 1b) closely matches the intense uv absorption band of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (Figure 1a) suggesting that in the intermediate, the metal-metal bond has been lost. For the slower process (t ~2–50 msec), the difference spectrum (Figure 1c) shows that the intermediate absorbs strongly in the $\sigma \rightarrow \sigma^*$ (Mo–Mo) spectral region, since there is an isosbestic point close to the uv λ_{max} for $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$.[14]