A Study of Photooxygenation of Cycloalkenes under 2,4,6-Triphenylpyrylium Tetrafluoroborate Sensitization

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2,4,6-Triphenylpyrylium tetrafluoroborate sensitized oxygenation of cycloalkenes to allylic hydroperoxides is described. This reaction appears to involve unusual electron transfer mechanism in the formation of observed products.

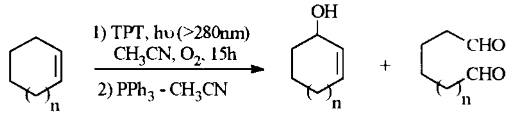
Photoinduced electron transfer (PET) oxygenations are receiving extensive study in recent years.[1] Cyanoaromatics such as 9,10-dicyanoanthracene and 9-cyanoanthracene are frequently used as sensitizers in these studies.[2] It has recently been confirmed that these excellent electron transfer sensitizers also generate singlet oxygen, which also is a good oxidant, by energy transfer to molecular oxygen.[3] Hence, application of these sensitizers involves singlet oxygen reaction as well as electron transfer oxygenation simultaneously causing ambiguity in identification of the actual reaction mechanism responsible for the formation of observed products. Earlier, Foote et al.[4] studied photooxygenation of cycloalkenes under cyanoaromatic sensitization and observed formation of their allylic hydroperoxides which is considered to be due to singlet oxygen reaction. In this, however, the possible reaction between molecular oxygen and cycloalkene radical cations generated under the reaction conditions remained dormant.

2,4,6-triphenylpyrylium tetrafluoroborate (TPT) is also a well known electron transfer sensitizer extensively in use. Recently, Akaba et al.[5] found that the energy transfer from excited TPT to molecular oxygen is a very inefficient process and hence, application of TPT is ideal[6] for electron transfer oxygenation studies as its use is devoid of singlet oxygen formation.

Photooxygenation of alkenes is an important and intensively studied subject which is mostly concerned with singlet oxygen reactions. However, there are only two reports in literature revealing electron transfer oxygenation of alkenes, viz., oxidation of stilbene, which is inert to singlet oxygen, to benzaldehyde under cyanoaromatic sensitization[7] and oxidative cleavage of adamantylideneadamantane to carbonyls under TPT sensitization,which is recently reported by Akaba et al.[5]

We envisaged that study of photooxygenation of cycloalkenes under TPT sensitization could give a way to observe the reaction between cycloalkene radical cations and molecular oxygen. For this, we chose simple cycloalkenes such as cyclohexene,**1a**, cycloheptene, **1b** and cyclooctene, **1c** to avoid complex product distribution. From Weller's[8] thermodynamic consideration, electron transfer from these alkenes to TPT is found to be exothermic[9] and hence is a feasible process. This study, however, gave a surprising result as these alkenes are efficiently converted to allylic hydroperoxides in good yields under TPT sensitization. We wish to present these results in this letter.

Photolysis[10] of cycloalkenes, **1a-c**(**1c** is cis-cyclooctene) in oxygenated acetonitrile under TPT sensitization formed allylic hydroperoxides in 70-80% yields (as estimated from iodometry) and corresponding allylic alcohols, **2a-c**(65-70%) were isolated after treatment with triphenylphosphine. In this reaction, the cleavage products, **3a-c** are obtained in trace quantities, Scheme 1.



1 **a** (n=1)
b (n=2)
c (n=3)

2 a-c
(65-70%)

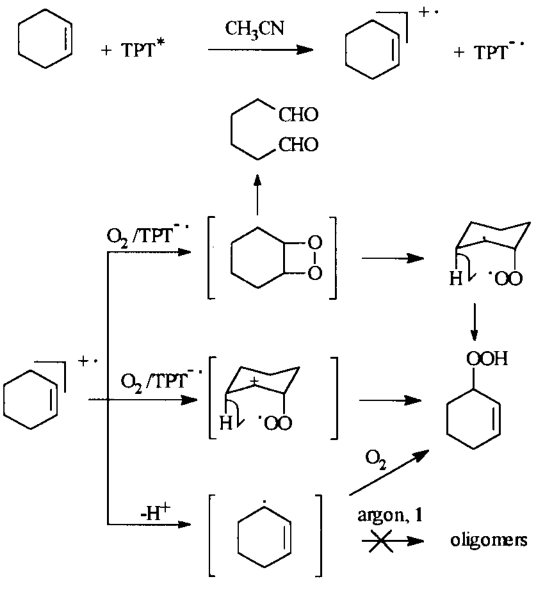
3 a-c
(1-3%)

Scheme 1.

Alkene having allylic hydrogens is known to form allylic hydroperoxide upon singlet oxygen reaction.[11] However, formation of the same product under electron transfer oxygenation is hither to unknown. The singlet oxygen reaction on **1a-c** under methylene blue sensitization in dichloromethane gave their allylic hydroperoxides in very low yields (<5%). It can not be ruled out that this observed reaction also could be due to electron transfer oxygenation induced by methylene blue[12]. Further, *cis*-cyclooctene, **1c** is known to be unreactive with singlet oxygen[13] which has reacted well under TPT sensitization forming its allylic hydroperoxide in good yield. In order to look further into the possibility of singlet oxygen generation under the reaction conditions, we have carried out irradiations of cholesterol as well as tetramethyl ethylene, which are good singlet oxygen probes, under TPT sensitization in oxygenated acetonitrile. These substrates, however, did not produce their singlet oxygen reaction products (allylic hydroperoxides) indicating the absence of singlet oxygen under TPT sensitization. From these results it can be concluded that the formation of allylic hydroperoxides from **1** under TPT sensitization involves a non-singlet oxygen mechanism, possibly[14] electron transfer oxygenation as shown in Scheme 2.

The other conceivable route for formation of hydroperoxides of **1** is oxygenation of alkene radicals. These radicals, under high concentration of **1** and in the absence of oxygen, are expected to give oligomeric products of **1**. In our study, however, **1** has not shown any reaction and recovered as such when irradiated in presence of TPT under argon atmosphere which indicates lack of formation of alkene radicals in this reaction.

In conclusion, this work is the first observation of oxygenation of cycloakenes to allylic hydroperoxides through a non-singlet oxygen pathway, possibly involving oxygenation of cycloakene cation radicals.



Scheme 2.

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9 ΔG_S values calculated for **1a**, **1b** and **1c** using Rehm and Weller equation[8] are -9.19, -12.4 and -12.8 kcal mol^{-1} respectively.

10 The general procedure used for the oxygenation of cycloalkenes, **1a-c** under 2,4,6-triphenylpyrylium-tetrafluoroborate sensitization is as follows: The solution of cis-cyclooctene, **1c** (3 g, 2.7 x 10^{-2} M) and **TPT** (0.25 g, 6.3 x 10^{-4} M) in acetonitrile (300 ml) was irradiated for 15 h with 450 W Hanovia medium pressure mercury lamp surrounded by Pyrex jacket with cold water circulation at 10°C. Irradiation is carried out under oxygen bubbling and reaction is monitored by glc using 10% OV-17 column which showed formation of only one major product. Irradiation is stopped when reaction is nearly complete and the photolysis mixture is concentrated to about 25 ml under reduced pressure and keeping bath temperature below 10°C. To this 7 g of triphenylphosphine is added in portions and finally the mixture is stirred for 1h. The remaining acetonitrile is also removed under reduced pressure and purification of the mixture by normal column chromatography furnished **2c** (2.2 g, 70%) and **3c** (50 mg, 1.3%). Spectral data obtained for **2c**: ^{1}H NMR (CDCl$_3$) : δ 5.5 (m, 2H), 4.6 (m, 1H), 2.5-1.2 (m, 10H); Mass : 126 (M$^+$); for **3c** : δ 9.8 (s, 2H), 2.4 (m, 4H), 1.8-1.2 (m, 8H); Mass : 142 (M$^+$).

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14 The rationale for the mechanism is as follows : i) Formation of **3** in the reaction indicates that dioxetane is produced as intermediate and its formation through electron transfer oxygenation is a well understood subject.[15] ii) Formation allylic hydroperoxide of **1** through intramolecular hydrogen abstraction is a thermodynamically favourable process since incorporation of double bond in the cyclic structure could lower its strain energy by 2-4 kcal mol^{-1}.[16]

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