

DEPROTONATION OF ORGANIC RADICAL CATIONS. CHEMICAL EVIDENCE FOR PROTON TRANSFER BETWEEN 9,10-DIHYDROANTHRACENCE RADICAL CATIONS AND SUPEROXIDE RADICAL ANIONS

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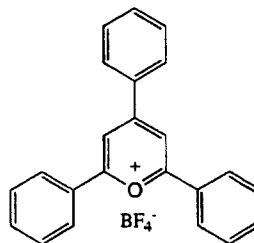
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Photoinduced electron-transfer oxygenation of 9,10-dihydroanthracene was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (TPP) and 9,10-dicyanoanthracene (DCA) as sensitizers. The time course of the oxygenation products was studied, and the results showed that anthrone was formed as a primary product in the DCA-sensitized oxygenation whereas in the TPP-sensitized oxygenation anthracene was the primary, major product which under the reaction conditions was converted to anthrone. A mechanism involving proton transfer in the radical ion pair consisting of 9,10-dihydroanthracene radical cation and superoxide radical anion, which cannot occur in the TPP-sensitized oxygenation, was proposed to rationalize the difference in the product distribution in the two sensitized oxygenation reactions.

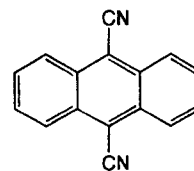
1. INTRODUCTION

We have recently shown that 2,4,6-triphenylpyrylium (TPP) salt-sensitized oxygenation of aralkyl hydrocarbons such as triphenylmethane and diphenylmethane gave the corresponding carbonyl compounds in modest to high yields, and proposed that the photooxygenation proceeded through deprotonation of their radical cations generated by the photoinduced electron transfer (PET).¹ Since it is well known that the superoxide radical anions ($O_2^{\cdot -}$) cannot be formed under the photooxygenation conditions with TPP,² comparative studies between 9,10-dicyanoanthracene (DCA)- and TPP-sensitized oxygenation of organic compounds may give an insight into the reactivity of radical ion pairs consisting of the organic radical cations and $O_2^{\cdot -}$. Although the participation of $O_2^{\cdot -}$ has been invoked to explain the products

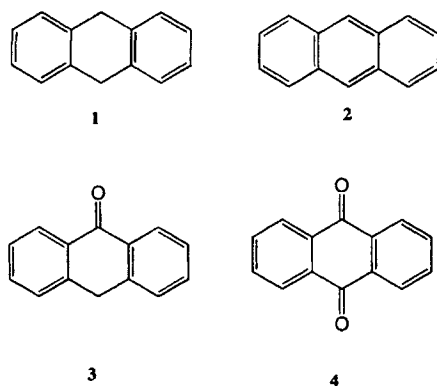
and their distribution in the DCA-sensitized oxygenation,³ little evidence supporting the direct involvement of $O_2^{\cdot -}$ in the initially formed radical ion pairs has been reported. In many cases, products and their distribution ascribed to the reactions of radical cations with $O_2^{\cdot -}$ in the DCA-sensitized oxygenation may also be explained in terms of the reactions of radical cations and/or radical species derived thereof with molecular oxygen.



Formula 1



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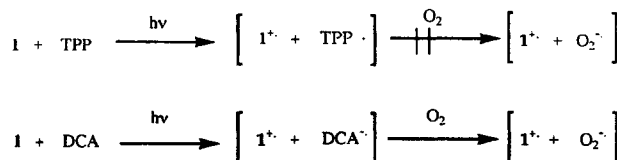
Formula 2

We report here chemical evidence for proton transfer in a radical ion pair consisting of 9,10-dihydroanthracene radical cation $1^{+\cdot}$, and $O_2^{\cdot-}$, generated by PET between **1** and the excited singlet state of DCA ($^1DCA^*$) (Scheme 1). Compound **1** may be an ideal substrate to probe the participation of $O_2^{\cdot-}$ in the proton transfer in the radical ion pairs since the following reactions can be expected to occur. Thus 9,10-dihydro-9-anthryl radical (**5**) (see below), derived from

deprotonation of $1^{+\cdot}$, may undergo rapid aromatization to give anthracene, which may decrease the amount of reaction of the radical with molecular oxygen. In the presence of $O_2^{\cdot-}$, however, rapid intermolecular proton transfer from $1^{+\cdot}$ to $O_2^{\cdot-}$ followed by their combination would lead to the formation of oxidation products. This was supported by the results.

Typically, irradiation (>360 nm) of dichloromethane solution of **1** ($ca\ 5 \times 10^{-2}$ M) with a high-pressure mercury lamp (400 W) in the presence of TPP ($ca\ 5 \times 10^{-3}$ M) under oxygen for 2 h gave three major products, anthracene (**2**), anthrone (**3**), and anthraquinone (**4**). Since **2** was found to be converted under the experimental conditions to **3**, and **4**, time course of the oxygenation products was studied, and the results are shown in Figure 1. Interestingly, neither **3** nor **4** was found to be a primary oxygenation product. As shown in Figure 1, a rapid increase in **2** was observed, and **3** and **4** were also formed with a concomitant decrease in **2**. The results clearly indicate that majority of **3** and **4** are derived from **2**. We note that **3** could not be observed at the early stage of the photooxygenation, and was significantly observed only after **2** began to decrease.

In sharp contrast, DCA-sensitized oxygenation of **1** gave different results. Most interestingly, formation of **3** as a primary product was observed. Thus, as shown in



Scheme 1

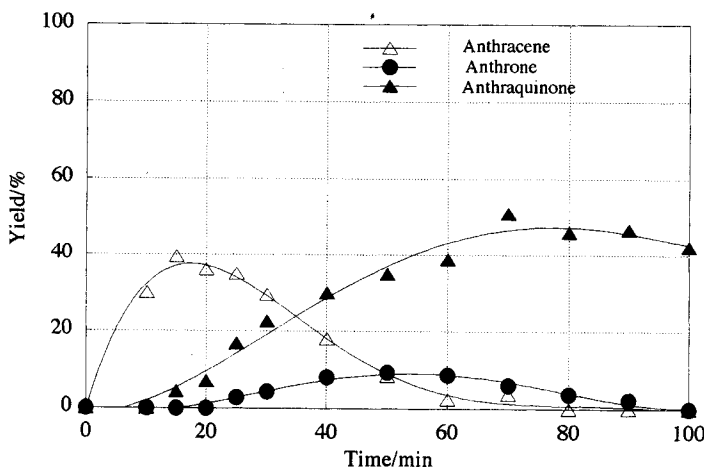


Figure 1. Time course of the product yields in the TPP (5×10^{-3} M)-sensitized oxygenation of **1** (5×10^{-2} M) in dichloromethane. Irradiation (>360 nm) was carried out with a 400 W high-pressure mercury lamp at running water temperature ($ca\ 20^\circ\text{C}$)

Figure 2, the time course of the products in the DCA-sensitized oxygenation of **1** indicates that both **3** and **2** were produced from the beginning of the photooxygenation.

We propose mechanisms involving PET for the product formation in the TPP and DCA-sensitized oxygenation of **1**, as shown in Scheme 2. PET in both cases was supported by the calculated free energy changes (ΔG) associated with the electron transfer from **1** to the excited singlet state of TPP ($^1\text{TPP}^*$) or to $^1\text{DCA}^*$ and the quenching of TPP or DCA Fluorescence by **1**.

Thus, $^1\text{TPP}^*$ undergoes electron transfer^{2c} with **1** to

give an 1^+ and a pyranyl radical, TPP^\cdot . 1^+ rapidly undergoes deprotonation to give **5**. Although the resulting radical **5** may undergo either hydrogen abstraction by molecular oxygen (aromatization, **path a**) to afford **2**, or the reaction with molecular oxygen (**path b**) giving a 9,10-dihydro-9-anthranlyldioxy radical **6**, which eventually may lead to **3**, the above results indicate that the predominant pathway of **5** is aromatization to afford **2** though the reaction of **5** with molecular oxygen as a minor pathway to afford **3** cannot be completely ruled out. Although **3** does undergo oxygenation reactions to give **4** under the experimental conditions, the almost complete absence of **4** at the early stage of

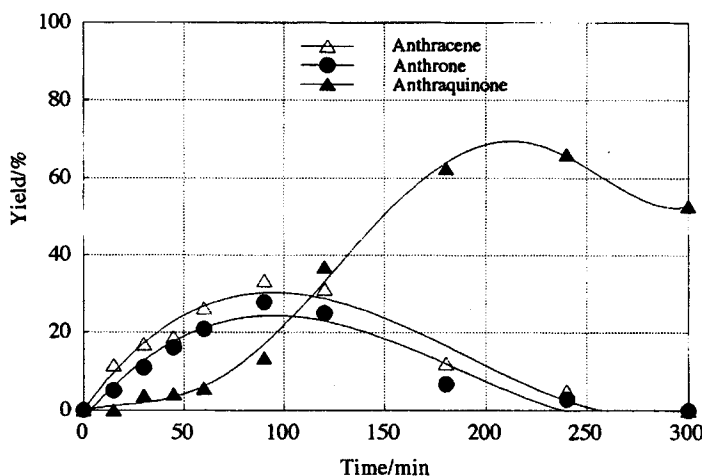
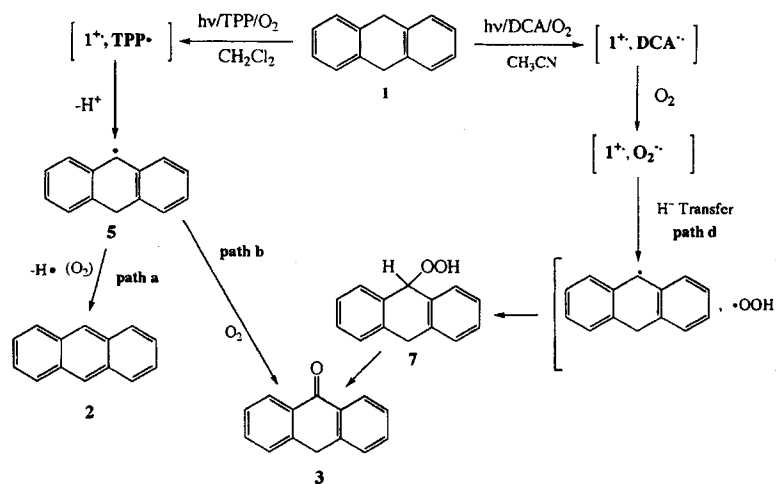


Figure 2. Time course of the product yields in the DCA (1×10^{-4} M)-sensitized oxygenation of **1** (5×10^{-2} M) in acetonitrile. Irradiation conditions, as in Figure 1



Scheme 2

the reaction indicates that the absence of **3** in the TPP-sensitized oxygenation cannot be ascribed to this mechanism.

In the DCA-sensitized oxygenation, however, the direct participation of $O_2^{\cdot -}$ to accept a proton from $1^{\cdot +}$ to form **5** and hydroperoxy radical followed by their recombination may explain the formation of **3** as a primary product. Thus, electron transfer from **1** to $^1DCA^*$ affords $1^{\cdot +}$ and DCA radical anion, $DCA^{\cdot -}$, the latter undergoing rapid electron transfer to molecular oxygen to give $O_2^{\cdot -}$.^{2a} The electron transfer from $DCA^{\cdot -}$ to molecular oxygen was also supported by our observation of the disappearance of the absorption band due to $DCA^{\cdot -}$ in the presence of molecular oxygen (results from laser flash photolysis experiments; unpublished work). The radical ion pair thus formed undergoes either diffusion to give a free $1^{\cdot +}$, (path c)(not shown), which finally affords **2** through the deprotonation, or intermolecular proton transfer (path d) to give a radical pair consisting of **5** and a hydroperoxy radical. Since **3** was not formed as a primary product in the absence of $O_2^{\cdot -}$, the recombination reaction of **5** and the hydroperoxy radical followed by the decomposition of the resulting hydroperoxide **7** under the reaction conditions gives initially formed **3**. The low yield (<5%) of **3** in the DCA-sensitized oxygenation of **2** is also consistent with the above mechanism. In both sensitized reactions, anthraquinone **4** was formed from **2** and/or **3** under the experimental conditions.

Finally, we note that molecular orbital calculations also support that, as other hydrocarbon cation radicals such as diphenylmethane cation radical and triphenylmethane cation radical give the corresponding carbonyl compounds through deprotonation,¹ $1^{\cdot +}$ may also be acidic enough to undergo deprotonation to give **5**. Thus, PM3 calculations³ indicate that upon electron removal from **1** the dihedral angle θ between the two benzene rings in $1^{\cdot +}$ ($\theta = 179.4^\circ$) becomes much larger than that in **1** ($\theta = 149.50^\circ$). A similar structure was also obtained in **5** ($\theta = 179.9^\circ$), suggesting that the deprotonation from $1^{\cdot +}$ to give **5** may be rapid because of the absence of structural changes during the deprotonation.

In conclusion, we have demonstrated that the proton transfer between $1^{\cdot +}$ and $O_2^{\cdot -}$ gives an important route

to the formation of **3**, which does not occur in the TPP-sensitized PET oxygenation because of the absence of $O_2^{\cdot -}$. It should also be pointed out that this work was first made possible by the simultaneous use of both sensitizers, and that the concept should be applicable to elucidating the reactivity of organic radical cations generated by PET reactions in general.

ACKNOWLEDGMENT

Part of this work was supported by Grants-in-Aid for Scientific Research to R.A. (Nos. 06640708 and 05640622) from the Ministry of Education, Science and Culture.

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