Unusual reactivity of acenaphthenone as an electron donor in sensitized photooxygenation

Shu-ping Wu, Ji-feng Liu and Zhi-qin Jiang*

Department of Chemistry, Tongji University, Shanghai 200092, Peoples Republic of China

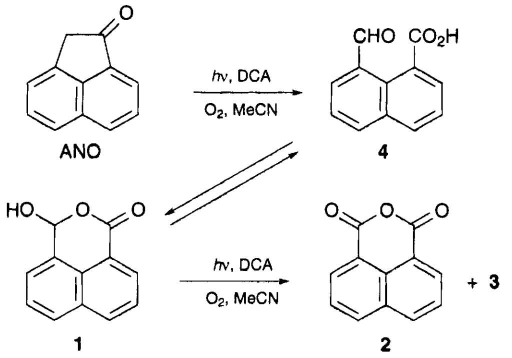
Acenaphthenone (ANO) is an effective electron donor and undergoes stepwise photooxygenation sensitized by 9,10-dicyanoanthracene, affording hydroxylactone and anhydride derivatives; the electron transfer mechanism *via* an enol intermediacy was verified by the enhancement effect of biphenyl, fluorescence quenching, exciplex emission and chemically induced dynamic nuclear polarization (CIDNP).

It has been widely acknowledged that most aromatic ketones behave as sensitizers or electron acceptor *via* their excited triplets, involving diradicals or ketyl radical anions ($C{-}O^{\cdot-}$), respectively.[1,2] However aromatic carbonyls acting as electron donors in photoinduced electron transfer (ET) reactions were reportedly rare due to their electron deficiency both in the ground and excited states. For a ketone to act as an electron donor, two situations should be considered, *i.e.* electron donation from either the excited or the ground state. K. P. Das measured the ET rate constants from aromatic ketone triplets to methyl viologen (MV^{2+}) by flash photolysis.[3] Tokumaru *et al.* has reported that cation carbonyl radicals were formed in the 2,4,6-triphenylpyrylium sensitized oxygenation of aryl–alkyl ketones.[4]

Here we report that one of the typical aromatic ketones, acenaphthenone (ANO), behaves as an effective electron donor in facile photooxygenation sensitized by 9,10-dicyanoanthracene (DCA). It was found that when an acetonitrile solution of ANO (2×10^{-2} mol dm^{-3}) and DCA (4×10^{-4} mol dm^{-3}) was irradiated ($\lambda \geqslant 400$ nm) under oxygen bubbling, the photooxygenation of ANO proceeded readily to afford the major products 1,8-(3-hydroxy)-δ-lactone naphthalene **1** and 1,8-naphthalenedicarboxylic anhydride **2** along with an oxidized oligomer mixture **3** ($m/z \geqslant 1000$).

For further examination of the reaction mechanism, pure **1**, prepared from acenaphquinone,[5] was subjected to photooxygenation under the same conditions and gave **2** and oligomer **3**. From this result, it can be concluded that **1** should be the initial product and the title reaction involves a stepwise process, *i.e.* ANO $\rightarrow$ **4** $\leftrightarrows$ **1** $\rightarrow$ **2** + **3** (Scheme 1).

When a solution of ANO in benzene (2×10^{-2} mol dm^{-3}) and DCA (4×10^{-4} mol dm^{-3}) was irradiated under an oxygen atmosphere no detectable product was observed. In the presence of rose bengal, a typical singlet oxygen ($^1O_2$) sensitizer, the photooxygenation of ANO also did not occur. These observations exclude the $^1O_2$ mechanism for the ANO/DCA system and based on this, an ET mechanism was proposed as shown in Scheme 2.

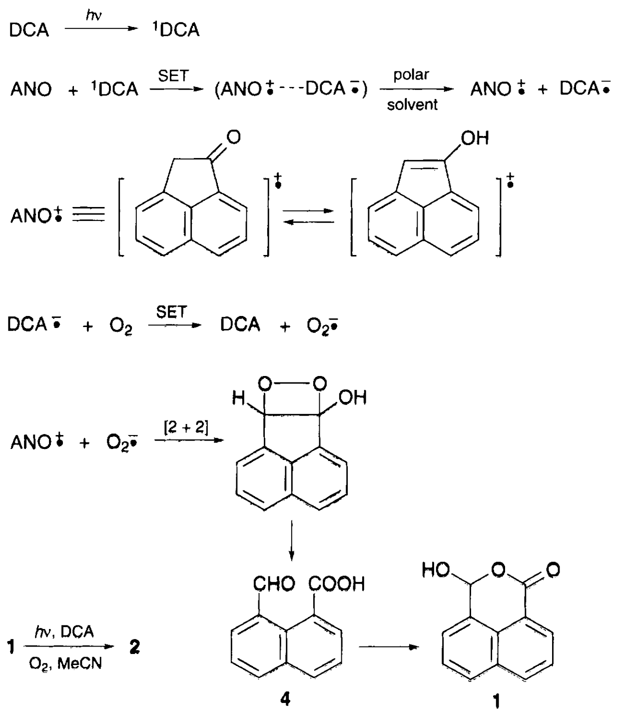


Scheme 1

The reaction involves a two-step single electron transfer. The radical cation $ANO^{\cdot+}$ dissociated from the exciplex (ANO···DCA)* is most likely to exist in the enol form since it is known to enolise easily in the ketone excited state.[6] Moreover, very slow DCA-sensitized photooxygenation of ANO in benzene could be attributed to the slow dissociation of the exciplex in non-polar solvent. The equilibrium between the carboxy aldehyde **4** and the hemiacetal **1** favours the formation of **1** in solution.[7]

In order to demonstrate the proposed ET mechanism further experiments were carried out. The oxidation potential of ANO was measured by cyclic voltammetry, E_{ox} = 1.78 V *vs.* SCE in acetonitrile. The reduction potential and the excited state energy of DCA are −0.97 and 2.89 V, respectively.[8] Hence the free energy change ΔG was calculated to be −4.7 kcal mol^{-1} (1 cal = 4.184 J) according to the Rehm–Weller equation,[9] which indicates that the primary electron transfer is thermodynamically favoured. In addition, the secondary electron transfer generating superoxide anion ($O_2^{\cdot-}$) was also known to be exothermic ($\Delta G \sim -5$ kcal mol^{-1}).[10]

The fluorescence of DCA was effectively quenched by ANO in a variety of solvents. The transient quenching was also



Scheme 2

Table 1 DCA sensitized photooxygenation of ANO in MeCN[a]

[ANO]/ mol dm^{-3}	[BP]/ mol dm^{-3}	Irradiation time/h	Conversion (%)	Quantum yield Φ^{b} (%)	Product distribution (%) 1	2	3
0.025	0	20	95	0.05	32	8	60
0.025	0.025	9	94	0.18	35	5	60

[a] [DCA] = 4×10^{-4} mol dm^{-3}. [b] The consumed quantum yield Φ was measured by potassium ferrioxalate actinometer at a conversion of ANO $\leqslant$ 10%.

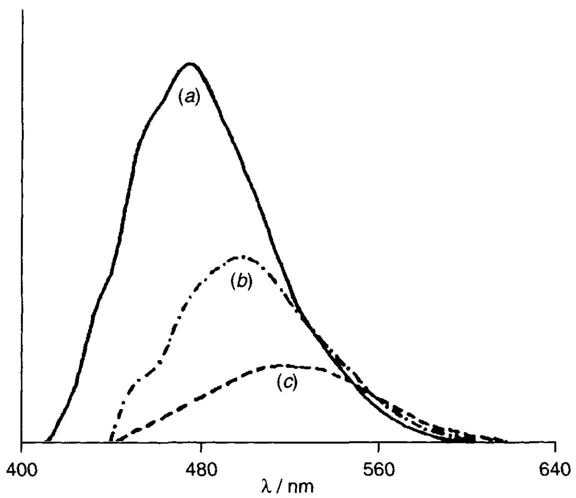
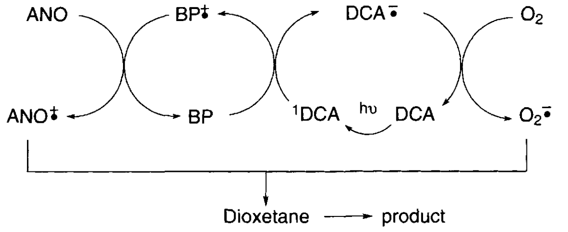


Fig. 1 Exciplex emission spectra and solvent effect (*a*) cyclohexane; (*b*) chloroform; (*c*) acetonitrile



Scheme 3

measured by single photon counting on a nanosecond fluorimeter. Both steady state and transient quenching in MeCN followed the Stern–Volmer equation and the quenching constants were $k_q(s) = 1.17 \times 10^{10}$, $k_q(t) = 1.05 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, respectively. Both values are close and in the order of diffusion controlled rates which implied that the quenching is characteristic of ET process and the interaction of ANO and DCA in their ground states is negligible.

After normalization of the ANO-quenched fluorescence of DCA, its difference spectrum with DCA fluorescence gave a weak and structureless emission band (λ_{max} = 477 nm) which could be assigned to the ANO/DCA exciplex emission. In addition, the emission (Fig. 1) shows a red shift (*ca.* 45 nm) and a decrease of intensity with increasing solvent polarity, presumably due to the exciplex dissociation into solvent-separated radical ions in polar solvent.[11] The observation of the ANO/DCA exciplex emission also provide evidence for the interpretation of the ET process.

Some aromatic compounds can behave as a relay *via* secondary ET to accelerate the desired ET reaction.[12] The enhanced action of biphenyl (BP) on the DCA-sensitized photooxygenation of ANO was observed. The results listed in Table 1 showed a similar product distribution in the absence and presence of BP. Therefore the nature of the ET reaction should remain the same in both cases. However, the quantum yield and reaction rate were substantially increased. This enhancement effect of BP on the DCA-sensitized ET photooxygenation was attributed to its role as an ET relay chain *via* the secondary ET from ANO to $\text{BP}^{+\cdot}$ (Scheme 3).

In summary the chemically induced nuclear spin polarization (CIDNP)[13] was studied for the photoinitiated ET reaction of ANO and DCA. During irradiation of DCA/ANO in [$^2H_3$]acetonitrile, the ^{1}H NMR spectrum exhibited emission (δ 3.7; $-CH_2-CO$) and enhanced absorption (δ 7.8–8.2) along with a new emission (δ 5.9). This effect was ascribed to the generation of the radical-ion pair ($\text{ANO}^{+\cdot}\cdots\text{DCA}^{-\cdot}$) by ET from ANO to the ^{1}DCA. The signal at δ 5.9 can be assigned to the alkenic proton of the enol which cannot be detected either in the dark or under irradiation of ANO alone. These facts showed that the enol form of acenaphthenone existed as a reaction intermediate which was formed in keto–enol tautomerization of $\text{ANO}^{+\cdot}$ (Scheme 2). This result provides a further insight into the ET mechanism of DCA with ANO and the unusual reactivity of ANO as an electron donor.

We are grateful for the financial support of this work by the National Science Foundation of China and in part by the Photochemistry Laboratory of the Institute of Photographic Chemistry.

References

1 W. H. Horspool, *Synthetic Organic Photochemistry*, Plenum Press, New York, 1984.
2 M. A. Fox and M. Chanon, *Photoinduced Electron Transfer*, Elsevier, 1988, Part C, 313.
3 P. K. Das, *Tetrahedron Lett.*, 1981, **14**, 1307.
4 R. Akaba, Y. Niimura, T. Fukushima, Y. Kawai, T. Tajima, T. Kuragami, A. Negishi, M. Kamata, H. Sakuragi and K. Tokumaru, *J. Am. Chem. Soc.*, 1992, **114**, 4460.
5 H. Bader and Y. H. Chiang, *Synthesis*, 1976, **4**, 249.
6 P. Gary Laroff and H. Fischer, *Helv. Chim. Acta.*, 1973, **56**, 2011.
7 K. Bowden and A. M. Last, *J. Chem. Soc., Perkin Trans.* 2, 1973, 1144.
8 C. S. Foote and J. Eriksen, *J. Phys. Chem.*, 1978, **82**, 2659.
9 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 2590.
10 J. Eriksen, C. S. Foote and T. L. Parker, *J. Am. Chem. Soc.*, 1977, **99**, 6455.
11 H. Masuhara and N. Mataga, *Acc. Chem. Res.*, 1981, **14**, 312.
12 Z. Q. Jiang, *Res. Chem. Intermed.*, 1990, **14**, 185.
13 H. D. Roth and Marcia L. M. Schilling, *J. Am. Chem. Soc.*, 1980, **102**, 4303.

Received, 20th September 1995; Com. 5/06215B