

SINGLET-OXYGEN REACTIONS IN CYANOAROMATIC-SENSITIZED PHOTO-OXIDATIONS

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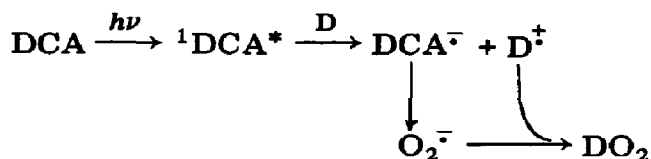
Summary

Cyanoaromatic-sensitized photo-oxidations of substrates (α -pinene, β -pinene, 3,4-dihydro-2H-pyran, 1,4-diphenyl-1,3-butadiene, limonene and cyclohexadiene) which react readily with singlet oxygen were studied. It was proved that a singlet-oxygen reaction takes place in each of the above photo-oxidations. The solvent polarity and solvent viscosity have the same influence on both the quantum yields of photo-oxidations and the fluorescence quenching rate constants. All the experiments support the suggestion that electron transfer occurs between the sensitizer excited singlet state and the substrate. The singlet oxygen formed then acts as a reactive intermediate in the subsequent process through back electron transfer. In carbon tetrachloride, the products of all the above substrates are the same as in the dye-sensitized photo-oxidations and singlet oxygen may be generated through intersystem crossing which leads to the triplet-excited reaction.

1. Introduction

Cyanoaromatic-sensitized photo-oxidations have received much attention during the last decade. Electron-deficient sensitizers, such as 9,10-dicyanoanthracene (DCA) and 9-cyanoanthracene (CNA), sensitize the photo-oxidation of certain substrates (D, donor) which cannot undergo photo-oxygenation with singlet oxygen but may react readily with oxygen via an electron transfer pathway [1, 2]. Radical-ion intermediates, DCA^- , CNA^- and D^+ , have been characterized by transient absorption spectroscopy, chemically-induced dynamic nuclear polarization (CIDNP) and electron spin resonance (ESR) spectroscopy on irradiation of solutions of DCA or CNA and various quenchers in deoxygenated acetonitrile [3, 4]. Thus the mechanism of the reaction (see Scheme 1) has been further verified by direct observation.

Recently, it has become apparent that singlet-oxygen reactions can be involved in both DCA- and CNA-sensitized photo-oxidations [2, 5, 6]. The T-T spectra of the sensitizers' triplet states [7] and singlet-oxygen



Scheme 1.

luminescence at 1270 nm [5] have also been already detected. The related reactions and their mechanisms are still interesting problems which need further investigation.

Our own interest, however, has been centred around possible singlet-oxygen reactions involved in electron transfer photo-oxidations. Cyanoaromatic-sensitized photo-oxidations of substrates (α -pinene, β -pinene, 3,4-dihydro-2*H*-pyran, 1,4-diphenyl-1,3-butadiene, limonene and cyclohexadiene) which react readily with singlet oxygen were studied and we found that the solvent as well as the substrate play an important role in determining the way in which the reaction takes place.

2. Experimental details

2.1. Apparatus

${}^1\text{H}$ nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-360 NMR spectrometer (in carbon tetrachloride or in CDCl_3). IR spectra were determined on a Perkin-Elmer 577 IR spectrometer. UV spectra were recorded on a Hitachi model 340 spectrophotometer. Mass spectra were taken on a Finnigan model 4021c gas chromatography-mass spectrometry instrument (GC-MS). Fluorescence spectra were determined on a Perkin-Elmer Ls-5 or Hitachi MPF-4 fluorescence spectrophotometer and lifetimes were determined using a single-photon counting technique on the Ortec 9200 system model SP-7X nanosecond fluorescence spectrophotometer (Applied Photophysics).

Analyses using high-performance liquid chromatography (HPLC) were carried out on a Waters model 480 instrument interfaced with a Waters model 730 data module. A C-18 reverse-phase column eluted with 80% methanol in water was used for HPLC, and gas-liquid chromatography (GLC) analyses were carried out on a Shanghai Fenxiyiqichang model 100 gas chromatograph.

2.2. Materials

The following materials were used: α -pinene (Shanghai Shijizongchang), β -pinene (Carl Roth OHG), 1,4-diazabicyclo[2.2.2]octane (DABCO) (Aldrich), methylene blue (MB) (Aldrich), 2,6-di-*t*-butyl-*p*-cresol (DTBC) (Beijing Huagongchang), rose bengal (RB) (Shanghai Biuoben Meuxingchang), DCA (Eastman Kodak), CNA (Aldrich), 2,3-dimethyl-2-butene (Fluka) and *trans,trans*-1,4-diphenyl-1,3-butadiene (Merck). Limonene (Fugian Zangzou

xiangliuochang) was redistilled before use, and deuterated acetonitrile (Beijing Huagongchang), deuterated benzene (Aldrich) and tetraphenylporphyrin (TPP) were synthesized and purified according to the literature.

2.3. Fluorescence quenching

Fluorescence quenching experiments were carried out at room temperature and relative fluorescence intensities at an appropriate wavelength were measured using a voltmeter. Solutions of the fluorescer (1×10^{-5} M) and quencher were degassed by bubbling nitrogen through them for 4 min. The excitation wavelength for DCA was 400 nm and that for CNA was 380 nm. The quenching results were analysed according to the Stern-Volmer equation and exciplex emission data were obtained by direct recording or by normalization. Singlet excited state lifetimes in various solvents were determined by single-photon counting at room temperature using least-squares iterative deconvolution methods in the data treatment. Solutions of 1×10^{-5} M DCA or CNA were deoxygenated by bubbling nitrogen through them for 10 min.

2.4. Irradiation procedures

All solutions for analytical photolyses were placed in Pyrex glass test tubes. The concentrations of substrates were about (1×10^{-2}) - (2×10^{-2}) M and the concentration of DCA or CNA was 1×10^{-4} M except when noted. The tubes were stoppered after oxygen was bubbled through the solutions for 4 - 5 min prior to irradiation at about 0 °C. During the photolysis, the tubes rotated around the light source on a merry-go-round. After irradiation, the products formed in some cases were reduced using triphenylphosphine and then quantitatively determined by GC or HPLC.

In preparative photolyses, tubes of 100 ml capacity were used. Oxygen was constantly bubbled through the solution during irradiation. The photolysates were concentrated on a rotary evaporator and the residues were separated by thin-layer chromatography (TLC) with benzene as eluent. The isolated products were analysed by IR, MS and ^1H NMR spectroscopy.

2.5. Photochemical instrumentation

The photolyses of singlet oxygen using dye sensitizers were carried out using a 500 W tungsten lamp in a water-cooled Pyrex glass immersion well.

The photolyses sensitized with DCA or CNA were carried out using a 450 W medium pressure Hanovia lamp in a water-cooled Pyrex glass immersion well with a uranium glass filter (cut-off wavelength shorter than 360 nm) or a Corning 3-73-3389 filter (cut-off wavelength shorter than 420 nm).

3. Results and discussion

3.1. Electron transfer fluorescence quenching and exciplexes of cyanoanthracenes

We have studied the quenching of DCA and CNA fluorescence by a series of compounds which are the usual substrates and quenchers for singlet-

TABLE 1

Fluorescence quenching rate constants with 9,10-dicyanoanthracene as sensitizer

Substrate	k_q ($\times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) in various solvents				
	CH_3CN^a	C_6H_6^b	CCl_4^c	$(\text{CH}_2)_6^d$	$n\text{-C}_6\text{H}_{14}^e$
1,4-Diphenyl-1,3-butadiene	2.6	2.0	1.6	2.3	4.3
DABCO	1.86	1.49	0.86	1.09	2.54
2,5-Dimethylfuran	1.30	0.89	0.82	0.86	2.40
DTBC	1.10	0.72	0.65	0.78	1.64
3,4-Dihydro-2H-pyran	1.24	0.68	0.20		0.12
2,3-Dimethyl-2-butene	1.10	0.32	0.10		0.44
α -Pinene	1.13	0.046	0.0046	0.0045	0.006
β -Pinene	0.67	0.0057	0.004	0.0036	0.005
2,3-Dimethyl-1,3-butadiene	0.18	0.016	0.022		0.038

^aThe dielectric constant $\epsilon = 37.50$; $\eta = 0.345$ cP.^b $\epsilon = 2.28$; $\eta = 0.652$ cP.^c $\epsilon = 2.24$; $\eta = 1.04$ cP.^d $\epsilon = 2.02$; $\eta = 1.02$ cP.^e $\epsilon = 1.89$; $\eta = 0.294$ cP.

TABLE 2

Fluorescence quenching rate constants with 9-cyanoanthracene as sensitizer

Substrate	k_q ($\times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) in various solvents ^a				
	CH_3CN	C_6H_6	CCl_4	$(\text{CH}_2)_6$	$n\text{-C}_6\text{H}_{14}$
1,4-Diphenyl-1,3-butadiene	1.47	0.88	1.7	0.93	2.4
DABCO	1.43	1.20	0.92	0.53	2.30
2,5-Dimethylfuran	0.81	0.11	0.11	0.16	0.13
DTBC	0.63	0.18	0.66	0.42	0.99
3,4-Dihydro-2H-pyran	0.14	0.002	0.0022		
2,3-Dimethyl-2-butene	0.084	0.001	0.0017		0.0015
α -Pinene	0.0023	0.0008	0.0014		0.0006
β -Pinene	0.12	0.0057	0.0044		0.0082
2,3-Dimethyl-1,3-butadiene	0.01	0.0082	0.0071		0.0015

^aThe dielectric constants and viscosities are given in the footnote to Table 1.

oxygen reactions. From the experimental data, all the quenching followed the well-known Stern-Volmer equation [8] and gave straight lines with intercepts of unity. From the slopes ($k_q\tau_s$) of these straight lines and the lifetimes of the sensitizer τ_s in nitrogen-saturated solvents for DCA and CNA, a large number of values of the quenching rate constant k_q for quenchers in individual solvents were obtained (see Table 1). For DCA in acetonitrile, benzene, carbon tetrachloride and *n*-hexane, τ_s is 15.3 ns (from ref. 9), 12.4 ns (from ref. 9), 11.61 ns and 13.03 ns respectively. For CNA in the same solvents, τ_s is 17.2 ns (from ref. 9), 12.53 ns, 12.98 ns and 13.81 ns

respectively. The τ_s values were measured by single-photon counting (see Section 2) except those which were taken from the literature [9].

In non-polar solvents (such as *n*-hexane, methylcyclohexane and carbon tetrachloride) exciplexes were formed. Solutions of DCA with each of the substrates 2,5-dimethylfuran, 3,4-dihydro-2*H*-pyran, 1,4-diphenyl-1,3-butadiene, α -pinene and β -pinene exhibited weak, structureless exciplex emission and the following maximum wavelengths of exciplex emission were obtained: DCA-2,5-dimethylfuran (in methylcyclohexane or carbon tetrachloride), 518 nm ($19\,305\text{ cm}^{-1}$); DCA-3,4-dihydro-2*H*-pyran (in carbon tetrachloride), 550 nm ($18\,182\text{ cm}^{-1}$); DCA-1,4-diphenyl-1,3-butadiene (in *n*-hexane), 570 nm ($17\,544\text{ cm}^{-1}$); DCA- α -pinene (in methylcyclohexane), 575 nm ($17\,391\text{ cm}^{-1}$); DCA- β -pinene (in methylcyclohexane), 569 nm ($17\,575\text{ cm}^{-1}$).

The free-energy change (ΔG) for DCA-D and that for CNA-D in acetonitrile were calculated by the Weller equation [10] (see Table 3). These values of ΔG were plotted against the experimental values of k_q . The points all fall on the theoretical line calculated by Rehm and Weller [10] for an electron transfer process and parallel to that reported by Eriksen and Foote [11] and Araki *et al.* [12] (see Fig. 1). This correlation strongly supports the electron transfer mechanism for the quenching of the fluorescence of DCA and CNA by the substrates listed in Tables 1 and 2.

Tables 1 and 2 reveal that the solvent polarity and solvent viscosity have a great influence on fluorescence quenching reactions. For weak electron donors (such as 2,3-dimethyl-2-butene, 3,4-dihydro-2*H*-pyran, α -pinene and β -pinene which have relatively high half-peak oxidation potentials) the main factor which influences the k_q values is the solvent polarity. Their k_q values are basically in the order of solvent polarity: acetonitrile > benzene > carbon tetrachloride > *n*-hexane, cyclohexane. The k_q values in acetonitrile are higher than those in *n*-hexane by two or three orders of magnitude. The

TABLE 3

The free-energy changes for 9,10-dicyanoanthracene-D and 9-cyanoanthracene-D in acetonitrile using the Weller equation

Substrate	k_q ($\times 10^{10}\text{ M}^{-1}\text{ s}^{-1}$)		$E_{1/2}^{\text{ox}}(\text{D}/\text{D}^+)$		ΔG (kcal mol $^{-1}$)	
	DCA	CNA	DCA	CNA	DCA	CNA
1,4-Diphenyl-1,3-butadiene	2.6	1.47	1.18	1.18	-18.22	-7.84
DABCO	1.86	1.43	0.63	0.63	-32.96	-20.52
2,5-Dimethylfuran	1.30	0.81	1.30	1.30	-17.53	-5.07
DTBC	1.10	0.63	1.17	1.17	-20.52	-8.07
3,4-Dihydro-2 <i>H</i> -pyran	1.24	0.14	1.48	1.48	-11.30	-0.92
α -Pinene	1.13	0.0023	1.63	1.63	-9.92	+2.54
β -Pinene	0.67	0.12	1.82	1.82	-5.53	+6.92
2,3-Dimethyl-1,3-butadiene	0.18	0.01	1.83	1.83	-5.30	+7.15

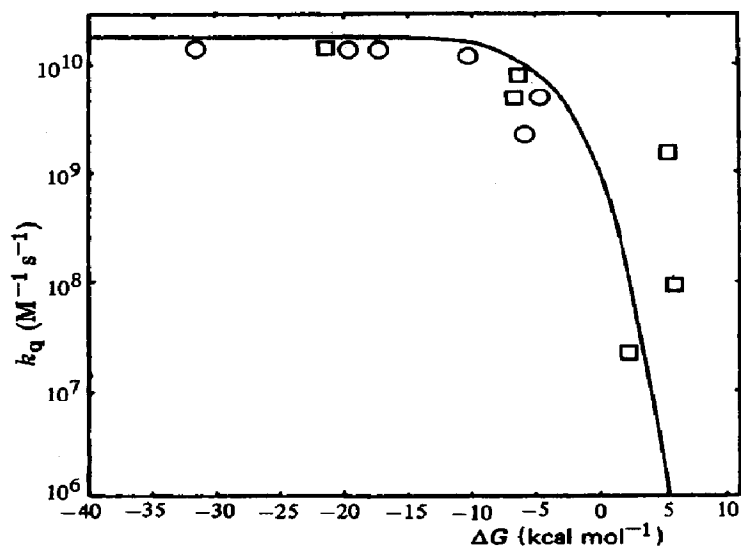


Fig. 1. Plot of k_q vs. ΔG : \square , CNA; \circ , DCA. (The solid line was calculated by Rehm and Weller.)

k_q values of strong electron donors (such as 1,4-diphenyl-1,3-butadiene, DABCO, 2,5-dimethylfuran and 2,6-di-*t*-butyl-*p*-cresol which have relatively low half-peak oxidation potentials) in various solvents are all of the order of magnitude of the diffusion-controlled rate constants ($10^9 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). Under these circumstances the k_q values obviously depend on the reverse order of the viscosity: *n*-hexane > acetonitrile > benzene > cyclohexane > carbon tetrachloride. *n*-Hexane has the lowest polarity and viscosity among these solvents. Therefore the k_q values in *n*-hexane for the weak electron donors are the smallest but for strong electron donors they are the largest. The magnitude of the k_q values in *n*-hexane clearly shows the solvent effect.

3.2. Cyanoaromatic-sensitized photo-oxidations

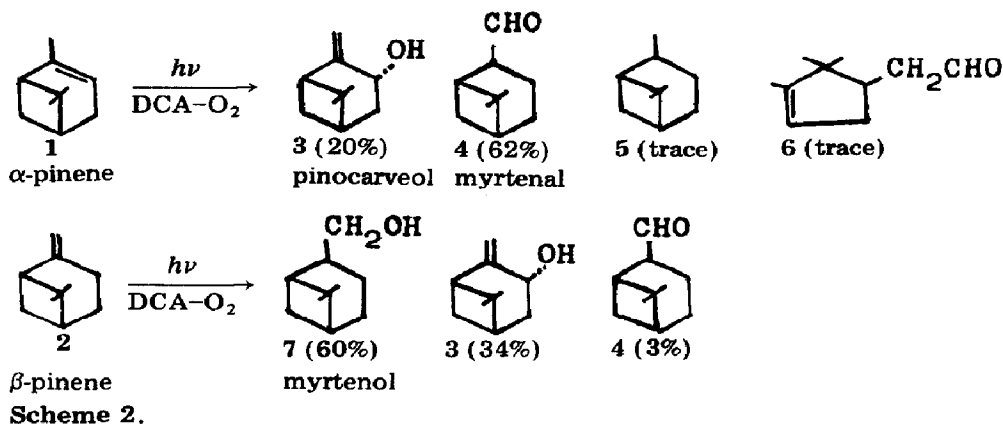
3.2.1. Photo-oxidation of α - and β -pinene

Irradiation (above 360 nm) of an oxygen-saturated solution of α -pinene or β -pinene [13] with DCA in acetonitrile followed by reduction gave the products shown in Scheme 2.

GLC was used to monitor the reaction process and the rates of conversions were calculated from the consumption of substrates. The products were separated by column chromatography and identified by their IR spectra, GLC behavior, GC-MS spectra and by comparison with authentic samples. The products formed in these reactions are the ene product, pino-carveol 3 from α -pinene and myrtenol 7 from β -pinene, and the non-ene products or the electron transfer photo-oxidation products.

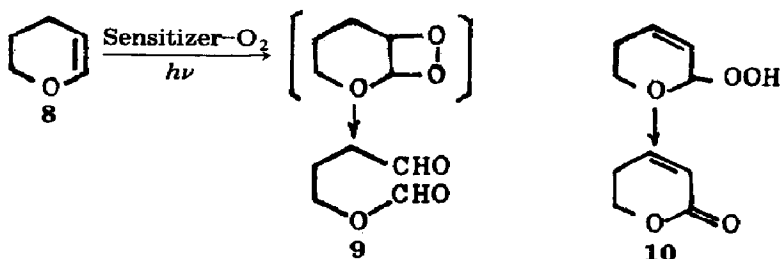
3.2.2. Photo-oxidation of 3,4-dihydro-2H-pyran

The DCA- and CNA-sensitized photo-oxidations of 3,4-dihydro-2H-pyran [14] in various solvents (acetonitrile, dichloromethane, benzene,



carbon tetrachloride and *n*-hexane) were investigated and compared with the photo-oxidations using the dye sensitizers MB and TPP [15]. Irradiation of an oxygen-saturated solution of 3,4-dihydro-2*H*-pyran with DCA, CNA or dye sensitizer gave the products and product distribution shown in Scheme 3 and Table 4. The products were separated and identified by GLC and compared with authentic samples.

For the photo-oxidation of 3,4-dihydro-2*H*-pyran sensitized by the cyanoanthracenes (DCA and CNA) in the above solvents except *n*-hexane, the products and product distribution as well as the solvent effect are the same as those in the reaction of singlet oxygen. Under both conditions, product 9 is formed preferentially in polar solvents and product 10 in non-



Scheme 3.

TABLE 4

The photo-oxidation products and product distribution of 3,4-dihydro-2*H*-pyran

Sensitizer	Ratio of products 9:10 (see Scheme 3) in various solvents				
	CH ₃ CN	CH ₂ Cl ₂	C ₆ H ₆	CCl ₄	<i>n</i> -C ₆ H ₁₄
MB or TPP	87:13	74:26	9:91	10:90	15:85
DCA	89:11	78:22	10:90	9:91	No reaction
CNA	89:11	79:21	9:91	11:89	No reaction

polar solvents. Therefore we may assume that the cyanoaromatic-sensitized photo-oxidation proceeds in the same way as singlet-oxygen oxidation.

The lifetime of singlet oxygen in deuterium solvents is much longer than that in the corresponding undeuterated solvents [16]. If singlet oxygen is an intermediate, the solvent isotope effect should reveal it. The cyanoaromatic-sensitized photo-oxidation of 3,4-dihydro-2*H*-pyran was studied in CD₃CN, CH₃CN, C₆D₆ and C₆H₆ respectively. Table 5 shows that for the cyanoaromatic-sensitized photo-oxidation of 3,4-dihydro-2*H*-pyran the reaction rate in CD₃CN is 3.75 - 3.79 times greater than that in CH₃CN, and in C₆D₆ it is 7.50 - 7.79 times higher than that in C₆H₆. These results prove further that the cyanoaromatic-sensitized photo-oxidation of 3,4-dihydro-2*H*-pyran proceeds through singlet oxygen.

TABLE 5

Solvent isotope effect on the cyanoaromatic-sensitized photo-oxidation of 3,4-dihydro-2*H*-pyran

<i>Solvent</i>	<i>Sensitizer</i>	$\Phi_p(D)/\Phi_p(H)$
CD ₃ CN-CH ₃ CN	DCA	3.75
C ₆ D ₆ -C ₆ H ₆	DCA	7.79
CD ₃ CN-CH ₃ CN	CNA	3.79
C ₆ D ₆ -C ₆ H ₆	CNA	7.50

3.2.3. Photo-oxidation of 1,4-diphenyl-1,3-butadiene

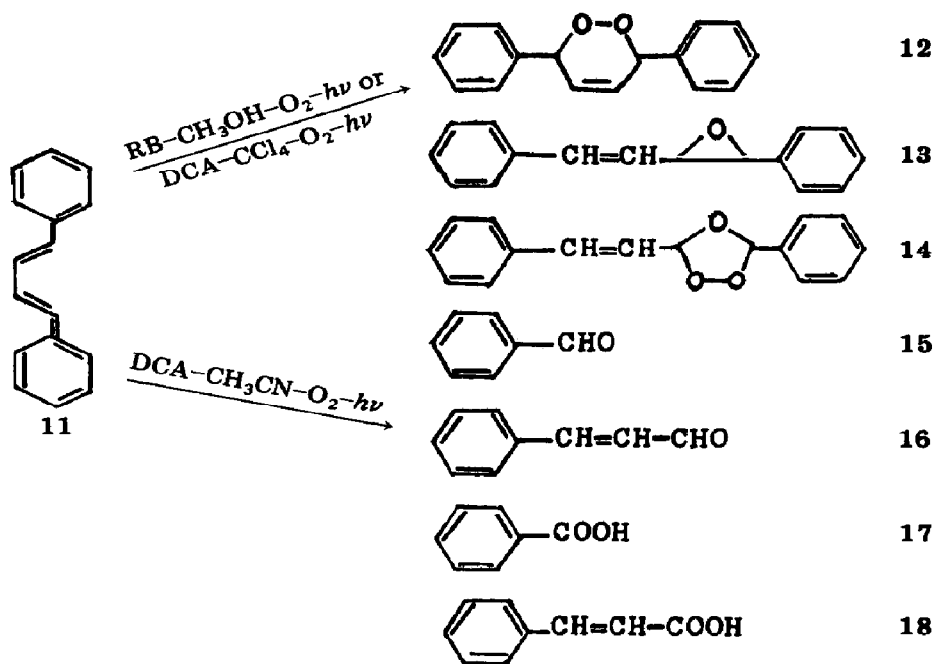
For 1,4-diphenyl-1,3-butadiene [17], the cyanoaromatic-sensitized photo-oxidation is greatly different from the dye-sensitized photo-oxygenation. The product of singlet-oxygen oxidation is its 1,4-adduct [18], but in the cyanoaromatic-sensitized photo-oxidation the main products are the corresponding epoxide 13, ozonide 14, aldehydes 15 and 16 and acids 17 and 18.

The products obtained by irradiation (above 420 nm) of an oxygen-saturated solution of 1,4-diphenyl-1,3-butadiene with DCA in acetonitrile are shown in Scheme 4. The products were separated by chromatography (TLC, GLC and HPLC) and identified by spectroscopy (IR, UV, NMR and GC-MS) and elemental analysis. The IR spectra, NMR spectra, GLC and HPLC behavior and GC-MS spectra of products 13, 14, 15, 16, 17 and 18 are all the same as those of their authentic samples.

3.3. Solvent effect

3.3.1. The effect of solvent polarity and solvent viscosity

Taking α -pinene, β -pinene, 3,4-dihydro-2*H*-pyran and 1,4-diphenyl-1,3-butadiene as substrates, and acetonitrile, dichloromethane, benzene, cyclohexane and *n*-hexane as solvents, DCA-sensitized photo-oxidations were carried out. The polarity of the solvent has a great influence on the electron-transfer-sensitized photo-oxidation. On studying the fluorescence quenching



Scheme 4.

of the above substrates and their photo-oxidation in various solvents, we found that the more polar the solvent, the larger the quenching rate constant k_q and the greater the efficiency of oxidation and *vice versa*. Table 6 reveals that the relative quantum yields of all the above reactions increase with the solvent polarity: in the polar solvent acetonitrile, the reaction rate is always much greater than that in benzene. In a non-polar solvent, cyclohexane or *n*-hexane, no products were detected and all the substrate was recovered in the photo-oxidation of α -pinene, β -pinene, 3,4-dihydro-2*H*-pyran and 1,4-diphenyl-1,3-butadiene. It is clear that the above reactions proceed predominantly by way of electron transfer. Neither α -pinene nor β -pinene undergoes photo-oxidation if $k_q < 10^7 \text{ M}^{-1} \text{ s}^{-1}$. For β -pinene, there is almost no reaction even in benzene. For 3,4-dihydro-2*H*-pyran, the relative quantum yields are also basically in the order of solvent polarity without exception.

Taking acetone ($\eta = 0.304 \text{ cP}$) as solvent, the relative quantum yield of 1,4-diphenyl-1,3-butadiene ($\Phi_R = 1.1$) is greater than that in acetonitrile; but for the pinenes, the relative quantum yields (for α -pinene, $\Phi_R = 3.4$; for β -pinene, $\Phi_R = 0.25$) are much smaller than those in acetonitrile. For the strong electron donor, 1,4-diphenyl-1,3-butadiene, the relative quantum yields of the photo-oxidation, which show the same trend as its k_q values, depend on the solvent viscosity. Its Φ_R values in the various solvents are in the same order as the solvent viscosity: acetone > acetonitrile > dichloromethane > benzene > cyclohexane. For the weak electron donors, the pinenes, the relative quantum yields of the photo-oxidation also show a

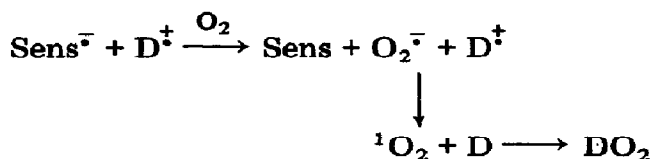
TABLE 6

Solvent polarity effect in cyanoaromatic-sensitized photo-oxidations

<i>Solvent</i>	ϵ	k_q ($\times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$)	Φ_R	$^1\text{O}_2$ (%)
<i>α-Pinene</i>				
CH ₃ CN	37.50	1.13	1	20
CH ₂ Cl ₂	8.93	0.66	0.7	33
C ₆ H ₆	2.28	0.046	0.34	82
(CH ₂) ₆	2.02	0.0045	0	0
<i>n</i> -C ₆ H ₁₄	1.88	0.005	0	0
<i>β-Pinene</i>				
CH ₃ CN	37.50	0.67	1	60
CH ₂ Cl ₂	8.93	0.147	0.35	62
C ₆ H ₆	2.28	0.0057	0.03	84
(CH ₂) ₆	2.02	0.0036	0	0
<i>n</i> -C ₆ H ₁₄	1.88	0.0046	0	0
<i>3,4-Dihydro-2H-pyran</i>				
CH ₃ CN	37.50	1.24	1	100
CH ₂ Cl ₂	8.93	—	0.62	100
C ₆ H ₆	2.28	0.68	0.12	100
(CH ₂) ₆	2.02	—	0	0
<i>n</i> -C ₆ H ₁₄	1.88	0.12	0	0
<i>1,4-Diphenyl-1,3-butadiene</i>				
CH ₃ CN	37.50	2.6	1	7
CH ₂ Cl ₂	8.93	—	0.47	28
C ₆ H ₆	2.28	2.0	0.11	85
(CH ₂) ₆	2.02	2.3	0	0
<i>n</i> -C ₆ H ₁₄	1.88	4.3	0	0

similar trend to their k_q values, the main factor which influences Φ_R being the solvent polarity. Their Φ_R values are in the same order as the solvent polarity: acetonitrile > dichloromethane > benzene > cyclohexane and *n*-hexane.

Table 6 also shows that the percentage of singlet-oxygen products increases with decreasing solvent polarity. The stability of a radical-ion pair is lower in less polar solvents and singlet-oxygen formation seems to occur through back electron transfer, *i.e.* through the second-order homogeneous recombination process of radical ions separated completely [19, 20]:

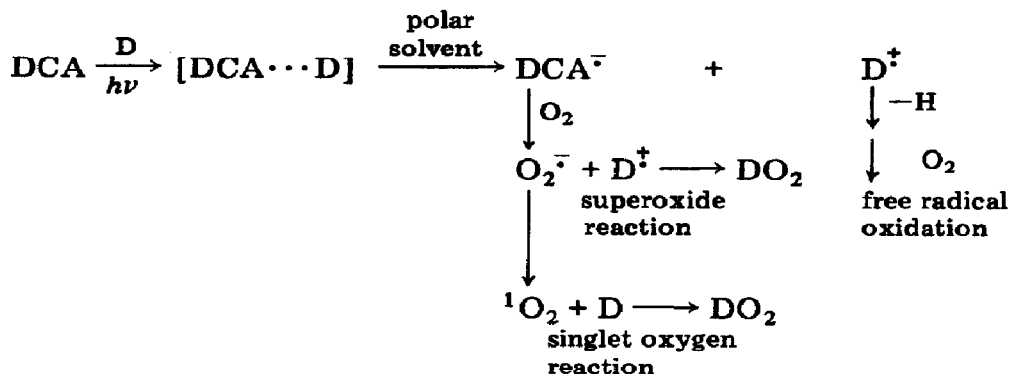


Scheme 5.

In the non-polar solvents, *n*-hexane and cyclohexane, a radical-ion pair could hardly be formed and separated completely, therefore no reaction was detected for α - and β -pinene, 3,4-dihydro-2*H*-pyran and 1,4-diphenyl-1,3-butadiene.

Using polystyrene-RB [13] as the sensitizer, the yields of the ene product of the photo-oxidation of α -pinene, whether in *n*-hexane or in acetonitrile, are all the same. It is quite clear that the formation of the ene product is not appreciably affected by the solvent polarity. On the basis of these data, it seems that our system behaves differently from that of Steichen and Foote [2] and Foote [6] where singlet-oxygen production was directly from the singlet cyanoaromatic.

All the experiments support the suggestion that electron transfer occurs from the substrate to the sensitizer excited singlet state and the singlet oxygen is then formed as a reactive intermediate in the subsequent process by way of back electron transfer from the superoxide to the radical cation of the substrate (see Scheme 6):



Scheme 6.

For 3,4-dihydro-2*H*-pyran, all the products are formed through the singlet-oxygen reaction. For 1,4-diphenyl-1,3-butadiene (and for the pinenes) after electron transfer, two distinct pathways, the superoxide reaction [20 - 24] or free-radical oxidation [20, 25, 26] and the singlet-oxygen reaction occur in competition.

3.3.2. The effect of carbon tetrachloride

Only when the solvent is changed to carbon tetrachloride, is the DCA-sensitized photo-oxidation of a variety of olefins absolutely different.

Although the polarity of carbon tetrachloride is similar to that of *n*-hexane and cyclohexane, in which no DCA-sensitized reaction can be detected, the reactions proceed rapidly in carbon tetrachloride. The relative quantum yields for product formation in the DCA-sensitized photo-oxidations of α - and β -pinene, 3,4-dihydro-2*H*-pyran and 1,4-diphenyl-1,3-butadiene in carbon tetrachloride are 4.39, 6.29, 4.54 and 3.11 times greater respectively than those in acetonitrile.

According to the three different types of reaction of singlet oxygen, we chose α -pinene, β -pinene and limonene as model compounds for the ene-type reaction, 3,4-dihydro-2*H*-pyran as a model compound for the 1,2-cycloaddition reaction and 1,3-cyclohexadiene and 1,4-diphenyl-1,3-butadiene for the 1,4-cycloaddition reaction, and we studied their DCA-sensitized photo-oxidations in carbon tetrachloride. The products of the reactions of these olefins with oxygen under the three sets of conditions are shown in Table 7. It is very interesting that for all these olefins the products are the same as those formed by dye-sensitized photo-oxygenation but different from those formed by DCA-sensitized photo-oxidation in acetonitrile. In addition, we also studied the DCA-sensitized photo-oxidation of tetraphenylethylene, *trans*-stilbene, toluene and 1,3,5-trimethylbenzene in carbon tetrachloride. With these substrates, which can undergo DCA-sensitized photo-oxidation in acetonitrile, no reactions occur in carbon tetrachloride, just as with singlet oxygen. All the above experimental results clearly reveal that in carbon tetrachloride the DCA-sensitized photo-oxidation occurs via a singlet-oxygen mechanism.

Quenching experiments with DABCO and DTBC are usually done to decide whether a reaction is going through a singlet-oxygen mechanism or a radical mechanism. This reaction is quenched readily by both DABCO and DTBC, but we would like to point out that they also quench DCA fluorescence significantly (Table 1). Therefore, these quenching experimental data can hardly be used to explain the mechanism of the reaction.

In order to explain the special case of the DCA-sensitized photo-oxidation in carbon tetrachloride, the charge transfer interaction of cyanoaromatic compounds with carbon tetrachloride was studied [28]. We consider that the singlet oxygen is generated from the exciplex of [DCA \cdots D] to the sensitizer triplet state through intersystem crossing strengthened by the heavy atom effect of carbon tetrachloride, but its generation from the excited charge transfer complex [DCA \cdots CCl₄] through intersystem crossing to the DCA triplet state also could not be neglected.

3.4. Kinetic treatment

If the proportionality constant K includes the fraction of the radical-ion pair (Sens $^{\cdot-}$ + D $^{\cdot+}$) which forms DO₂, the relative amount P of product formed is given by the following equation [1]:

$$P^{-1} = K \left(1 + \frac{k_f + k_d + k_{st} + k_0[O_2]}{k_D} \frac{1}{[D]} \right) \quad (1)$$

where $[D]$ is the concentration of substrates and the term $k_0[O_2]$ is obtained from the quenching of DCA fluorescence by O₂, and $k_f + k_d + k_{st} = \tau_s^{-1}$, which has been measured [11]. Thus a plot of P^{-1} vs. $[D]^{-1}$ allows the determination of k_D . Taking β -pinene as an example, k_D obtained from eqn. (1) in acetonitrile ($0.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) is very close to the k_q value ($0.67 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), which strongly suggests that fluorescence quenching is

TABLE 7

Photo-oxidations in different conditions

(1) MB- $h\nu$ -O ₂	94%					
(2) DCA- $h\nu$ -CH ₃ CN-O ₂	20%	62%		10%		5%
(3) DCA- $h\nu$ -CCl ₄ -O ₂	94%					
(1) MB- $h\nu$ -O ₂	95%					
(2) DCA- $h\nu$ -CH ₃ CN-O ₂	60%	34%				3%
(3) DCA- $h\nu$ -CCl ₄ -O ₂	93%					
(1) RB- $h\nu$ -O ₂	34%	10%	20%	5%	10%	20%
(2) DCA- $h\nu$ -CH ₃ CN-O ₂	27%	12%	19%	17%	10%	15%
(3) DCA- $h\nu$ -CCl ₄ -O ₂	34%	10%	20%	5%	10%	20%
(1) TPP- $h\nu$ -O ₂	90%	10%				
(2) DCA- $h\nu$ -CH ₃ CN-O ₂	11%	89%				
(3) DCA- $h\nu$ -CCl ₄ -O ₂	91%	9%				
(1) RB- $h\nu$ -O ₂	100%					
(2) DCA- $h\nu$ -CH ₃ CN-O ₂	—					
(3) DCA- $h\nu$ -CCl ₄ -O ₂	100%					
			C ₆ H ₅ CHO	C ₆ H ₅ CH=CHCHO	etc.	
(1) RB- $h\nu$ -O ₂	100%					
(2) DCA- $h\nu$ -CH ₃ CN-O ₂ (see ref. 27)						
(3) DCA- $h\nu$ -CCl ₄ -O ₂	100%					

also involved in the first step of product formation, as required by the proposed electron transfer mechanism.

4. Conclusion

All the experiments support the suggestion that cyanoaromatic-sensitized photo-oxidations of singlet oxygen reaction substrates proceed via electron transfer. In cyanoaromatic-sensitized photo-oxidations, singlet oxygen formation seems to occur through the recombination process of radical ions separated completely. In carbon tetrachloride, singlet oxygen may be generated from both the exciplex of [DCA \cdots D] and the excited charge transfer complex of [DCA \cdots CCl₄] through intersystem crossing which leads to the triplet-excited reaction.

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