JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 3, 509–518 (1990)

ROLE OF EXCIPLEX AND ION PAIR IN THE PHOTOSENSITIZED OXYGENATION OF 1,4-DIPHENYL-1,3-BUTADIENE

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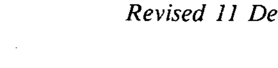
9,10-Dicyanoanthracene (DCA) sensitized the photooxygenation of 1,4-diphenyl-1,3-butadiene(1a) and its 4,4′-dimethoxy derivative (1b) to afford the corresponding endoperoxides 2 and the other oxidized products such as aldehydes and epoxides. The mechanism of the DCA-sensitized photooxygenation of 1 was diversified by solvent polarity. In non-polar solvents the reaction involves an exciplex intermediate, which leads to formation of triplet DCA (^{3}DCA*) with an efficiency of 0·64 in the case of 1a. The resulting ^{3}DCA* acts as a sensitizer for the generation of singlet oxygen (^{1}O$_2$) and thus ^{1}O$_2$ reaction occurs exclusively to give 2. On the other hand, single electron-transfer quenching of ^{1}DCA* by 1 is feasible in polar acetonitrile and a primary ion pair can be formed. Competing with fast back electron-transfer deactivation, the primary ion pair produces free ions in limited yield to furnish electron transfer oxygenation. In the case of the DCA–1a system, free ions were produced with an efficiency of *ca* 4%. Thus, in acetonitrile, electron-transfer oxygenation partly took place to give the other oxidized products, whereas the ^{1}O$_2$ pathway was still valid and responsible for the formation of 2. The effect of solvent polarity was apparently less pronounced in the case of 1b because the reactivity of 1b toward ^{1}O$_2$ is about five times higher than tht of 1a. For such ^{1}O$_2$-reactive substrates, the electron-transfer pathway would become dominant only when the substrate concentration is impractically high.

INTRODUCTION

Electron-deficient aromatic compounds such as cyanoaromatics are capable of photosensitizing the oxygenation of olefins[1,2] and various substrates[3] which are not necessarily reactive to singlet oxygen (^{1}O$_2$). Arylolefins and polyalkylolefins are relatively good electron donors and their radical cations can be generated electroechemically[4] or by photoinduced electron transfer reactions in polar solvents.[5] Indeed, unique oxygenation reactions of olefin radical cations have been reported.[4,6] An electron-transfer mechanism was once assigned to try to explain universally the characteristic feature of the reactions. Recent developments in this area, however, have revealed that singlet oxygen can be involved and may participate in the photosensitized reaction especially when substrates used are reactive to ^{1}O$_2$. Foote and co-workers[7] investigated 9,10-dicyanoanthracene (DCA)-sensitized photooxidations and demonstrated that excited triplet 9,10-dicyanoanthracene (^{3}DCA*) can be formed through quenching of excited singlet DCA (^{1}DCA*) by molecular oxygen or olefins and then ^{3}DCA* sensitizes the formation of ^{1}O$_2$. Thus, the photooxygenation reactions sensitized by cyanoaromatics potentially occur via a ^{1}O$_2$ pathway and an electron-transfer pathway competitively.

In some cases, a ^{1}O$_2$ pathway and an electron-transfer pathway can be distinguished by observing the corresponding products. Mattes and Farid[8] found that electron-transfer processes completely alter the regiochemistry of the photoinduced oxidation of 1,1-dimethylindene. Akasaka and Ando[9] reported an elegant example in which a sterically hindered methylenecyclopropane was utilized as a diagnostic tool to distinguish a ^{1}O$_2$ pathway from an electron-transfer pathway.

We sought a simple system which would show diverse reactivity in electron-transfer photooxygenation. It is known that 1,3-dienes react with ^{1}O$_2$ to give endoperoxides.[10] The reaction is one of the typical ^{1}O$_2$ reactions and can be classified as a Diels–Alder type[4 + 2] cycloaddition reaction.



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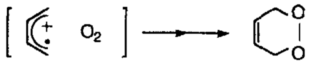
0894–3230/90/080509–10$05.00

Received 23 October 1989
Revised 11 December 1989

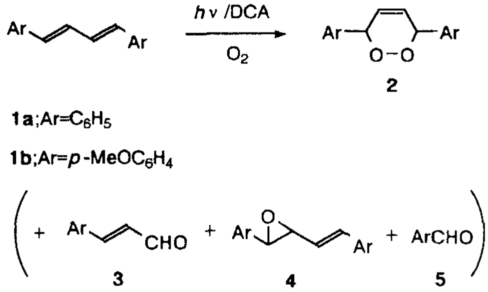
Relevance to this is the oxygenation of 1,3-dienes by catalysis with radical ion salts[11] and by electrochemical oxidation,[12] in which the radical cations of 1,3-dienes play an important role to give similar endoperoxides.



Intriguingly, Cao and co-workers[13] reported that electron-transfer oxidation of 1,4-diphenyl-1,3-butadiene was markedly different, whereas a $^1O_2$ reaction gave the endoperoxide. Accordingly, 1,4-diphenyl-1,3-butadiene seems to be a suitable substrate to define the scope of electron-transfer reactions[14] in conjunction with the oxygenation reaction. In this study, we focused on the fluorescence quenching process to investigate the role of exciplex and radical ions in the photosensitized oxygenation of 1,4-diphenylbuta-1,3-diene.

RESULTS

The photooxygenations were carried out in several solvents with DCA as an electron-acceptor sensitizer and the results were compared with those of the reactions with tetraphenylporphyrin (TTP) or Rose Bengal (RB) as typical $^1O_2$ sensitizers (Table 1).



2

1a;Ar=C_6H_5

1b;Ar=p-$MeOC_6H_4$

3 **4** **5**

Reactivity of 1a and 1b toward singlet oxygen

When TPP or RB was used as a sensitizer, exclusive formation of endoperoxide **2** was observed. In order to assess the reactivity of **1a** toward $^1O_2$, Stern–Volmer analysis was examined. As shown in Figure 1, plots of reciprocal relative quantum yield vs reciprocal concentration of **1a** for the TPP- and RB-sensitized reactions gave straight lines, consistent with the prediction from a general scheme for photosensitized $^1O_2$ reactions (Scheme 1). Thus, the TPP- and RB-sensitized photooxygenation of **1a** could be analysed as a typical case of a $^1O_2$ reaction. According to Scheme 1, the quantum yield (Φ) for the formation of **2** is as follows:

$$\Phi = \Phi(^1O_2) \times \frac{k_r[\mathbf{1}]}{k_d + k_r[\mathbf{1}]} \qquad (1)$$

If the relative quantum yield is used,

$$(\Phi_{rel})^{-1} \propto (1 + \beta[\mathbf{1}]^{-1}) \qquad (2)$$

where β is the so-called 'acceptor half-value concentration'[15a] and is equal to k_d/k_r ratio.

$$\beta = \frac{k_d}{k_r} \qquad (3)$$

The β values for the photosensitized oxygenations in carbon tetrachloride and acetonitrile were obtained as 0·0069 and 0·056 M from the slope/intercept ratios of the TPP- and RB-sensitized oxygenations, respectively (Figure 1a and b). Since these values are equal to the k_d/k_r ratios, $^1O_2$ lifetimes[15a] of $\tau = k_d^{-1} = 700 \times 10^{-6}$ and 30×10^{-6} s in carbon tetrachloride and acetonitrile, respectively, permit us to calculate the rate constants to be $k_r(CCl_4) = 2 \cdot 1 \times 10^5$ $l\,mol^{-1}\,s^{-1}$ and $k_r(CH_3CN) = 6 \cdot 0 \times 10^5$ $l\,mol^{-1}\,s^{-1}$. The rate constant for **1b** was estimated to be $k_r(CCl_4) = 1 \cdot 1 \times 10^6$ $l\,mol^{-1}\,s^{-1}$ by comparing the relative rates of photooxygenation.

DCA-sensitized photooxygenation of 1

DCA-sensitized oxygenation also gave the endoperoxide **2** as a sole product in non-polar solvents such as carbon tetrachloride or benzene. In acetonitrile or methylene chloride, however, DCA gave a decreased amount of **2** with concomitant formation of other oxidized products **3**, **4** and **5**. Another interesting feature of the reactoin is that the formation of the endoperoxide was selectively quenched by the addition of 1,4-diazabicyclo[2.2.2]octane, which is known to be an excellent $^1O_2$ quencher ($k = 3 \times 10^7$ $l\,mol^{-1}\,s^{-1}$).[15b] The results in Table 1 indicate that the DCA-sensitized oxygenations in non-polar solvents occur exclusively by a $^1O_2$ pathway and that an electron-transfer pathway can compete with a $^1O_2$ pathway in polar solvents such as acetonitrile, where electron-transfer quenching of $^1DCA^*$ by **1** can be significant.

Quantum yields for the DCA-sensitized photooxygenation were measured in carbon tetrachloride and acetonitrile. The quantum yield is dependent on the concentration of **1a**, and it increased with increasing concentration of **1a**. The Stern–Volmer plots are shown in Figure 2. In carbon tetrachloride the plot gave a straight line ($r = 0 \cdot 9999$) with an intercept of 1·56 and a slope of $1 \cdot 49 \times 10^{-2}$ M. The intercept value indicates that the limiting quantum yield is as high as 0·64. In contrast, the Stern–Volmer plot in acetonitrile did not give a straight line. Apparently, the observed curve seems to be a consequence of at least two competitive pathways for the oxygenation.

DCA fluorescence quenching study

Because of its high fluorescence quantum yield

Table 1. Photosenitized oxygenation of 1,4-diaryl-1,3-butadiene(**1**)[a]

Dine	Solvent	Sensitizer	Irradiation time/h	Product yield/%			Recovery/%
				2	**3**	**4**	
1a	CH_3CN	DCA	2	22	21	7	9
1a[b]	CH_3CN	DCA	2	0	14	9	36
1b[c,d]	CH_3CN	DCA	2	80	3	3	5
1a	CH_2Cl_2	DCA	2	15	4	12	51
1a	C_6H_6	DCA	2	6	0	0	94
1a	CCl_4	DCA	1	83	0	0	17
1b[c,d]	CCl_4	DCA	4	80	0	0	11
1a	CH_3CN	RB	2	94	0	0	0
1b[c,d]	CH_3CN	RB	2	95	0	0	0
1a[e,f]	CH_2Cl_2	MB[g]	4	86	0	0	0
1a	CCl_4	TPP	0·5	100	0	0	0
1b[c,d]	CCl_4	TPP	0·5	100	0	0	0

[a] Unless indicated otherwise, 5 ml of solution containing $5{\cdot}0 \times 10^{-2}$ mmol of diene and $1{\cdot}0 \times 10^{-4}$ M of sensitizer was irradiated by using a 2-kW xenon lamp at 15 °C and analysed by HPLC.

[b] In the presence of $1{\cdot}3 \times 10^{-3}$ M of 1,4-diazabicyclo[2.2.2]octane.

[c] A suspension was irradiated owing to the limited solubility of **1b**.

[d] Yields by NMR.

[e] 1·00 mmol was used.

[f] Isolated yields.

[g] Methylene Blue.

$$\text{sens} \xrightarrow[I]{h\nu} \xrightarrow{\text{isc}} {}^3\text{sens}^*$$

$${}^3\text{sens}^* \xrightarrow{k_0} \text{sens}$$

$${}^3\text{sens}^* + {}^3O_2 \xrightarrow{k_q} \text{sens} + {}^1O_2$$

$${}^1O_2 \xrightarrow{k_d} {}^3O_2$$

$$\mathbf{1} + {}^1O_2 \xrightarrow{k_r} \mathbf{2}$$

Scheme 1

($\Phi_f > 0{\cdot}9$), and very low intersystem crossing quantum yield ($\Phi_{isc} = 0{\cdot}003$ in acetonitrile),[16] light absorption and radiative decay are the major photophysical processes which DCA undergoes. DCA fluorescence was efficiently quenched by **1a** ($E_p^{ox} = +1{\cdot}24$ V vs SCE) and **1b** ($E_p^{ox} = +0{\cdot}93$ V vs SCE), and the quenching rate constants (k_q) can be obtained experimentally by using the Stern–Volmer equation and the fluorescence lifetime (τ) of DCA;[13,17a,18]

$$\frac{I_0}{I} = 1 + k_q\tau[\mathbf{1}] \tag{4}$$

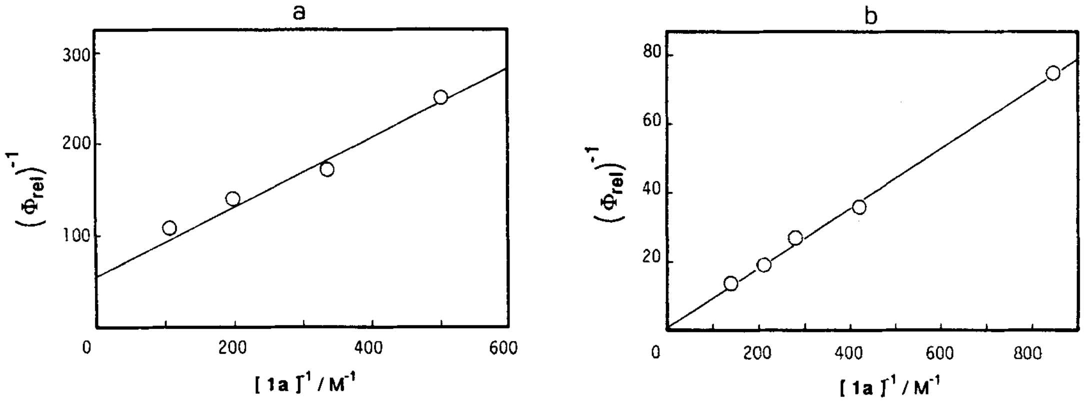


Figure 1. Stern–Volmer plots for the photosensitized oxygenation of **1a**: (a) in carbon tetrachloride with tetraphenylporphyrin as a sensitizer and (b) in acetonitrile with Rose Bengal as a sensitizer. (a) Intercept 55 and slope 0·378 M (r = 0·992); (b) intercept 1.53 and slope 0·0858 M ($r = 0{\cdot}999$)

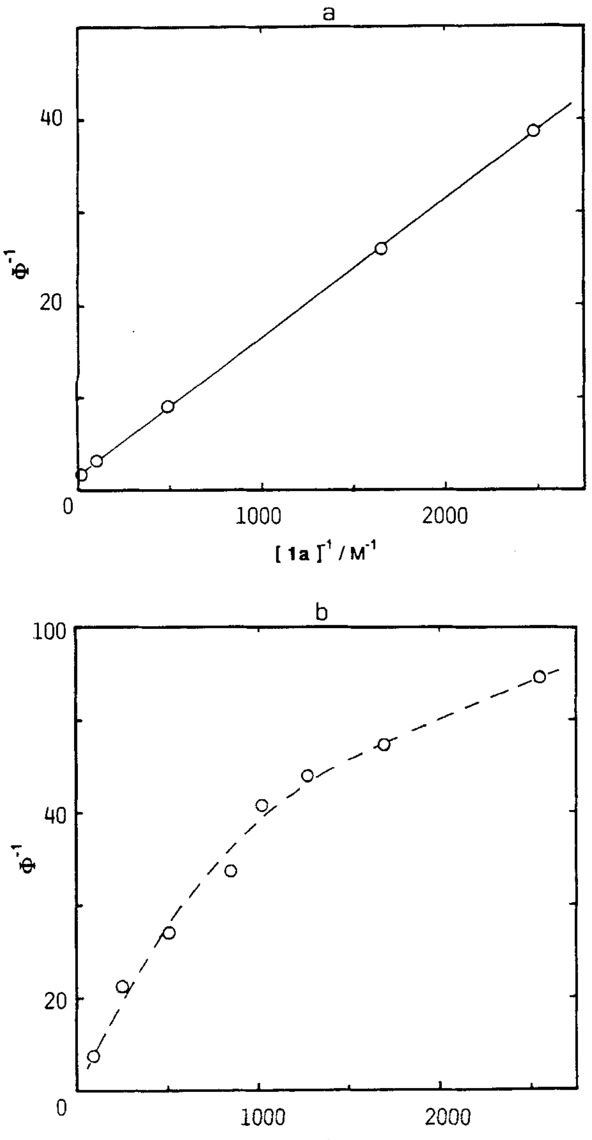


Figure 2. Stern–Volmer plots for the DCA-sensitized photooxygenation of **1a**; (a) in carbon tetrachloride and (b) in acetonitrile. (a) Intercept 1.56 and slope $1{\cdot}49\times10^{-2}$ M ($r = 0{\cdot}999$)

Table 2. Rate constants for DCA fluorescence quenching in several solvents

Quencher	Solvent	τ^a/ns	$k_q\tau$/l mol^{-1}	k_q/l mol^{-1} s^{-1}
1a	CH_3CN	$13{\cdot}4^b$	321	$2{\cdot}4\times10^{10}$
1a	CH_2Cl_2	$11{\cdot}7^b$	268	$2{\cdot}3\times10^{10}$
1a	C_6H_6	$11{\cdot}2^b$	195	$1{\cdot}7\times10^{10}$
1a	CCl_4	$10{\cdot}9^b$	122	$1{\cdot}1\times10^{10}$
1b	CH_3CN	$13{\cdot}4^b$	342	$2{\cdot}6\times10^{10}$
1b	CH_2Cl_2	$11{\cdot}7^b$	329	$2{\cdot}8\times10^{10}$
O_2	CH_3CN	$15{\cdot}3^c$	99	$6{\cdot}5\times10^{9}$
O_2	C_6H_6	$12{\cdot}4^c$	52	$4{\cdot}2\times10^{9}$
O_2	CCl_4	$11{\cdot}6^c$	32	$2{\cdot}8\times10^{9}$

[a] Lifetime of ^{1}DCA*.
[b] In aerated solutions.
[c] In degassed solution, taken from Refs 13, 17a and 18.

where I_0 and I_q are the fluorescence intensity of DCA in the absence and presence of a quencher, respectively. Molecular oxygen also quenches ^{1}DCA* and the quenching rate constants were obtained similarly. The values are given in Table 2.

When the quenching experiments were carried out in carbon tetrachloride with **1a**, a broad and weak emission band appeared in the longer wavelength region than the DCA fluorescence itself. The excitation spectrum monitored at the band maximum (565 nm) was identical with the DCA absorption spectrum. A similar emission band at $\lambda_{max} = 585$ nm was observed in benzene. In methylene chloride or acetonitrile, however, no such emission could be detected. We assigned these emissions as being due to exciplex formation.[17]

Flash photolysis study

A microsecond flash photolysis study provided information on the transient species generated via the fluorescence quenching process. Flash photolysis of degassed carbon tetrachloride or benzene solution containing 5×10^{-3} M of **1a** and 5×10^{-5} M of DCA gave rise to a transient absorption as shown in Figure 3. The absorption intensity extrapolated to time zero was dependent on the concentration of **1a** and increased with increasing concentration of **1a**. The transient species was extremely sensitive to oxygen and no appreciable absorption was detected in oxygen-saturated or aerated solutions. We assigned this band as being due to the formation of ^{3}DCA* on the basis of its oxygen-sensitive nature. A similar spectrum was also observed when ^{3}DCA* was generated by using the triplet energy transfer technique with 9-cyanophenanthrene ($E_T = 58{\cdot}1$ kcal mol^{-1})[16] as a triplet donor.

We observed that the first-order decay rate of ^{3}DCA* was dependent on the concentration of **1a**. When the concentration of **1a** was higher, the observed decay rate was faster, indicative of possible energy-transfer quenching of ^{3}DCA* by **1a**. In the absence of **1a** a similar but much weaker absorption could be detected and its decay rate was of the order of 10^4 s^{-1}. A Stern–Volmer plot of the observed decay rate (k_{obs}) vs concentration of **1a** gave an intercept of $5{\cdot}0\times10^3$ s^{-1}

and a slope of $3{\cdot}0\times10^{6}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ (Figure 3, inset).

$$k_{obs}=k_{dt}+k_{qt}[\mathbf{1}] \quad (5)$$

These values correspond to the decay rate constant k_{dt},

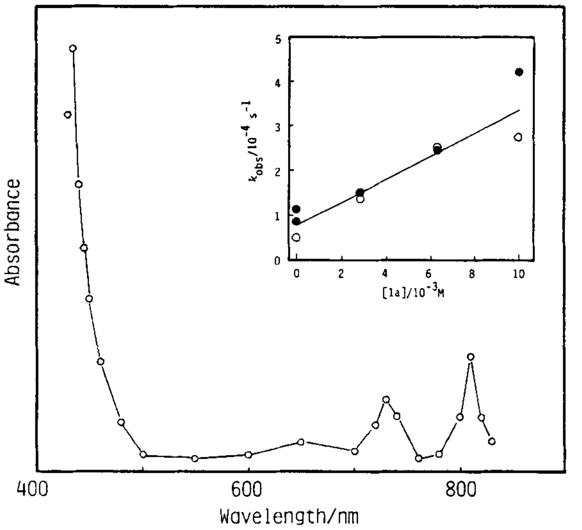


Figure 3. Transient absorption spectrum obtained 60 μs after flash photolysis of carbon tetrachloride solution containing 5×10^{-5} M of DCA and $5{\cdot}0\times10^{-3}$ M of **1a**. The inset shows plots of the observed transient decay rates (k_{obs}) vs concentration of **1a** monitored at (○) 435 nm and (●) 810 nm

of ^{3}DCA*, and the quenching rate constant k_{qt}, respectively. Thus, the lifetime of ^{3}DCA* in carbon tetrachloride was determined as $1/k_{dt}=2{\cdot}0\times10^{-4}$ s.

In degassed acetonitrile, entirely different transient absorption was observed. As shown in Figure 4, flash photolysis of the DCA–**1a** system gave an intense absorption at $\lambda_{max}=535$ nm. We assigned the absorption as being due to the formation of the radical cation of **1a** ($\mathbf{1a}^{+\cdot}$). Consistent with this assignment was the fact that the transient spectrum was completely replaced by the spectrum of diphenylamine radical cation ($\lambda_{max}=670$ nm) when diphenylamine was added, and that similar spectra were also observed when other acceptor sensitizers such as 2,6,9,10-tetracyanoanthracene or 2,9,10-tricyanoanthracene were used. Further, the observed spectrum compares well with the spectrum of $\mathbf{1a}^{+\cdot}$ generated by the radiolysis technique,[19] in which an absorption maximum appeared at 550 nm in a 2-chlorobutane matrix at 77 K. Similar absorption was also observed for $\mathbf{1b}^{+\cdot}$ ($\lambda_{max}=600$ nm). Absorption due to DCA$^{-\cdot}$ could barely be seen around 700 nm. When the system was aerated, the absorption due to DCA$^{-\cdot}$ disappeared because of secondary electron transfer from DCA$^{-\cdot}$ to O_2.[5a]

Kinetic analyses of the decay rates of $\mathbf{1a}^{+\cdot}$ and $\mathbf{1b}^{+\cdot}$ revealed that their decay process was greatly affected by molecular oxygen. In degassed acetonitrile, the decay profiles of $\mathbf{1a}^{+\cdot}$ and $\mathbf{1b}^{+\cdot}$ were second order with rate constants of $k=2{\cdot}3\times10^{10}$ and

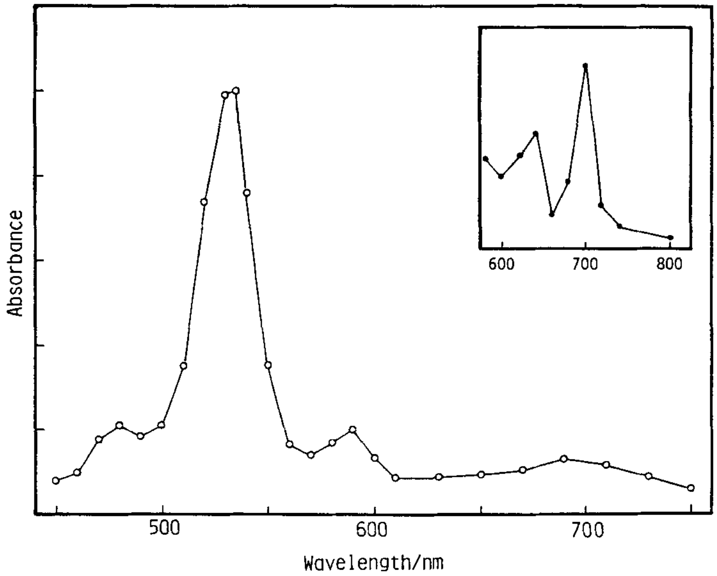
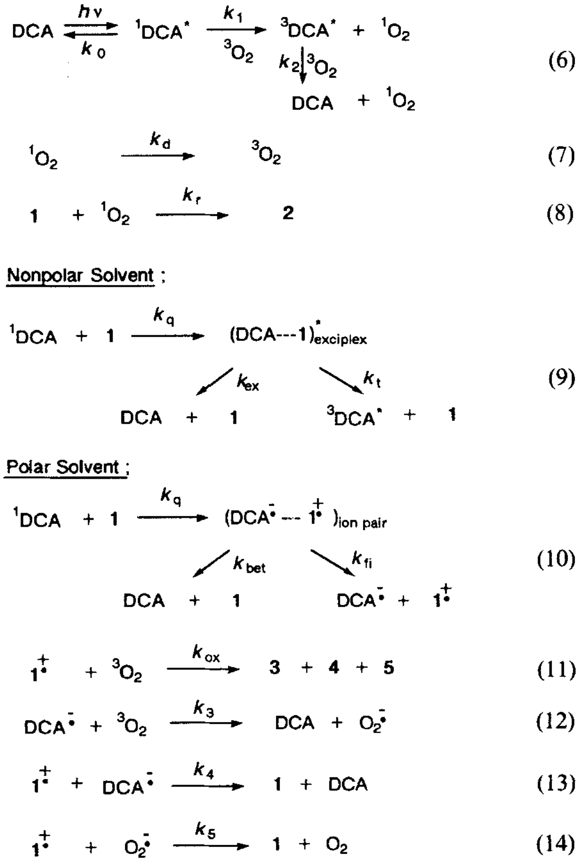


Figure 4. Transient absorption spectrum obtained 60 μs after flash photolysis of acetonitrile solution containing 5×10^{-5} M of DCA and $5{\cdot}0\times10^{-3}$ M of **1a**. The inset is the absorption spectrum of DCA$^{-\cdot}$ obtained from similar flash photolysis of DCA–dimethylaniline in acetonitrile

$2{\cdot}0\times10^{10}\,\mathrm{l\,mol^{-1}\,s^{-1}}$, respectively, [$\varepsilon(\mathbf{1a})=6{\cdot}8\times10^4$ and $\varepsilon(\mathbf{1b})=10{\cdot}6\times10^4\,\mathrm{l\,mol^{-1}\,cm^{-1}}$][20] whereas oxygen saturation led to the observation of pseudo-first-order decay with the rate constants of $k=3{\cdot}6\times10^4$ and $7{\cdot}8\times10^3\,\mathrm{s^{-1}}$ for $\mathbf{1a}^{+\cdot}$ and $\mathbf{1b}^{+\cdot}$, respectively. These results indicate that both $\mathbf{1a}^{+\cdot}$ and $\mathbf{1b}^{+\cdot}$ are very reactive to molecular oxygen.

DISCUSSION

The results of the DCA-sensitized photooxygenation of **1** indicate that $^1O_2$ is involved in the reaction and leads exclusively to the formation of **2**. Carbon tetrachloride is a particularly useful solvent for such a $^1O_2$ reaction process, not only because its polarity is low (dielectric constant is 2·24 at 20 °C)[21] but also because lifetime of $^1O_2$ is much longer (700 μs)[15a] than in other solvents. Electron-transfer oxygenation occurs competitively in a polar solvent such as acetonitrile to afford **3**, **4** and **5**. The observed diverse reactivity, particularly in the case of **1a**, is adequately described as a consequence of the solvent-dependent nature of the DCA fluorescence quenching process. Consistent with the results, we propose a mechanism as shown in Scheme 2.



Scheme 2

$^1O_2$ can be produced via DCA fluorescence quenching by molecular oxygen regardless of solvent polarity, but to a limited extent [reaction (6), k_1 and k_2].[7] Although Cao *et al.*[13] pointed out the possibility of an external heavy atom effect of carbon tetrachloride on the intersystem crossing of $^1\mathrm{DCA}^*$ to give $^3\mathrm{DCA}^*$, it is not likely as we did not observe any enhanced T–T absorption of $^3\mathrm{DCA}^*$ in carbon tetrachloride compared with that in benzene. We also confirmed that even carbon tetrabromide exhibits very little heavy atom effect ($\leqslant 1\%$).[16]

Therefore, when the solvent polarity is low, an exciplex intermediate must play a key role for the generation of $^3\mathrm{DCA}^*$ [reaction (9)]. Considering the long lifetime of $2{\cdot}0\times10^{-4}$ s that we determined, $^3\mathrm{DCA}^*$ can be quenched completely by molecular oxygen to produce $^1O_2$. In polar acetonitrile, while the $^1O_2$ process remains, single electron-transfer quenching is feasible [reaction (10)]. Competing with back electron transfer (k_{bet}), the primary ion pair dissociates (k_{fi}) to give free ions. The observed pseudo-first-order decay of $\mathbf{1}^{+\cdot}$ in oxygen-saturated acetonitrile indicates that $\mathbf{1}^{+\cdot}$ can be trapped by molecular oxygen more efficiently than otherwise fatal charge recombination with $\mathrm{DCA}^{-\cdot}$ and/or $O_2^{-\cdot}$. In the case of **1b**, the electron-transfer oxidation occurs less pronouncedly because the reactivity of **1b** toward $^1O_2$ is five times higher than that of **1a**. Although it is conceivable that the electron-transfer pathway for the oxidation of **1b** would become dominant when its concentration is very high, it is impossible to address this point experimentally owing to the limited solubility of **1b** in acetonitrile. Accordingly, the following photokinetic treatment is mainly based on the results with **1a**, while aiming at the general understanding of electron-transfer photoreactions in conjunction with the oxygenation reaction.

The mechanism in non-polar solvents, as shown in Scheme 2, explains well the observed Stern–Volmer plots in Figure 2a. According to the exciplex mechanism in Scheme 2, the quantum yield for the formation of **2** is expressed as

$$\Phi=\Phi(^1O_2)\times\frac{[\mathbf{1}]}{[\mathbf{1}]+\beta}\tag{15}$$

where $\Phi(^1O_2)$ represents the quantum yield for $^1O_2$ formation:

$$\Phi(^1O_2)=\Phi(^3\mathrm{DCA}^*)=\frac{2k_1[O_2]+f_tk_q[\mathbf{1}]}{k_0+k_1[O_2]+k_q[\mathbf{1}]}\tag{16}$$

where f_t is the efficiency of $^3\mathrm{DCA}^*$ generation from the exciplex intermediate:

$$f_t=\frac{k_t}{k_{\mathrm{ex}}+k_t}\tag{17}$$

When the concentration of **1a** is high enough, equation (16) predicts that the maximum $\Phi(^1O_2)$ value is nearly equal to f_t and hence the maximum $\Phi = f_t$ according to equation (15). The experimental value of 0·64 (Figure 2a) for the limiting quantum yield is, indeed, a good indication that $f_t = 0{\cdot}64$.

Rewriting equation (15) gives

$$(\Phi')^{-1} = \left(\frac{\Phi}{\Phi(^1O_2)}\right)^{-1} = 1 + \beta[\mathbf{1}]^{-1} \tag{18}$$

Since $\Phi(^1O_2)$ can be calculated with $f_t = 0{\cdot}64$ and with k_q and k_1 values from DCA fluorescence quenching experiments, Φ' can be calculated based on the quantum yield data of Figure 2a. The results are replotted as shown in Figure 5. The plot is linear with a slope of 0·0085 M and an intercept of 0·99 ($r = 0{\cdot}999$). In accord with the prediction from equation (18), the slope of 0·0085 M is in good agreement with the β value of 0·0069 M obtained from TPP-sensitized photooxygenation of **1a** in carbon tetrachloride.

Alternatively, the quantum yields can be calculated according to equation (15) [and (16)] by using experimental value of $\beta = 0{\cdot}0069$ M and the quenching rate constants. For example, Figure 6 shows the simulated Stern–Volmer plots with different f_t values. The calculated plots are more or less linear when f_t is larger than 0·4, whereas smaller f_t values significantly bend the lines upward with increasing concentration of **1a**. The calculated plot with $f_t = 0{\cdot}64$ gave a straight line with a slope of $1{\cdot}30 \times 10^{-2}$ M, consistent with the experimentally obtained slope of $1{\cdot}49 \times 10^{-2}$M in Figure 2a.

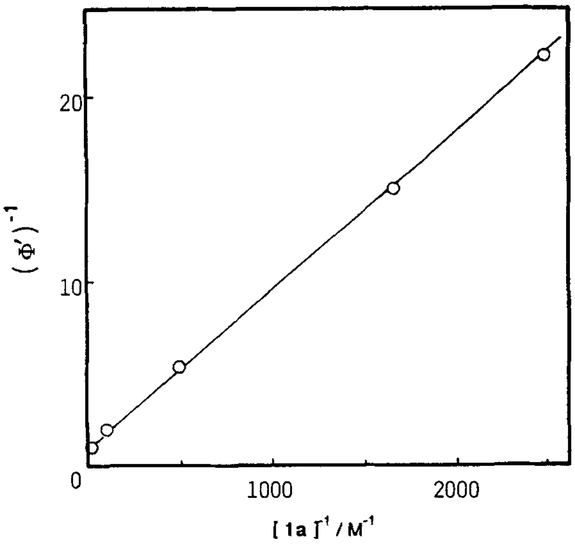


Figure 5. Plots of $(\Phi')^{-1}$ vs reciprocal concentration of **1a**. The data sets in Figure 2a were used for replotting according to equation (18)

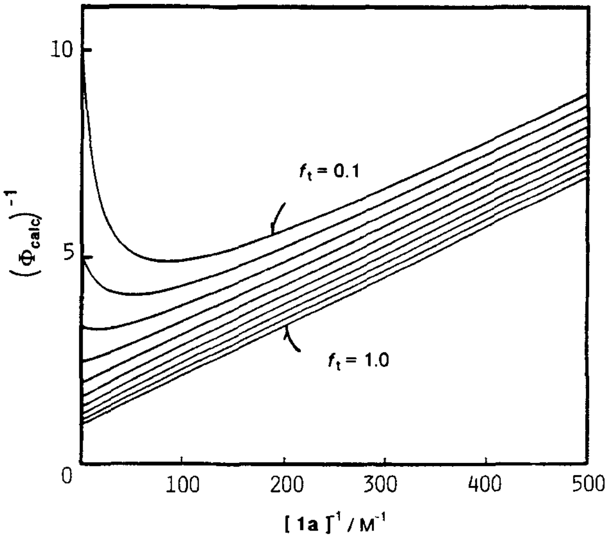


Figure 6. Simulated Stern–Volmer plots with different f_t values in 0·1 increments according to equations (15) and (16). $\beta = 0{\cdot}0069$ M was used for calculation

Therefore, it is most likely that the exciplex intermediate ultimately produces $^3DCA^*$ with an intersystem crossing efficiency as high as 0·64. f_t is an important factor in the DCA-sensitized photooxygenation, and the quantum yield is crucially dependent on f_t.

The radical ion process as evidenced by the direct observation of the transient absorption of $\mathbf{1}^{+\cdot}$ is feasible in polar solvents such as acetonitrile. Although the $^1O_2$ mechanism competes, the electron-transfer mechanism becomes significant when the concentration of **1a** is high. Hence, the quantum yield can be expressed as the sum of a $^1O_2$ process and an electron-transfer process;

$$\begin{aligned}\Phi &= \Phi(^1O_2 \text{ process}) + \Phi(\mathbf{1}^{+\cdot} \text{ process}) \\ &= \left[\Phi(^1O_2) \times \frac{[\mathbf{1}]}{[\mathbf{1}] + \beta}\right] + (f_{fi}\Phi_{ip})\end{aligned} \tag{19}$$

where Φ_{ip} is the quantum yield for ion-pair formation via electron-transfer quenching of DCA fluorescence and f_{fi} is the efficiency of free ion formation:

$$\Phi_{ip} = \frac{k_q[\mathbf{1}]}{k_0 + k_1[O_2] + k_q[\mathbf{1}]} \tag{20}$$

$$f_{fi} = \frac{k_{fi}}{k_{bet} + k_{fi}} \tag{21}$$

$$\Phi(^1O_2) = \frac{2k_1[O_2]}{k_0 + k_1[O_2] + k_q[\mathbf{1}]} = \Phi_{ip} \times \frac{2k_1[O_2]}{k_q[\mathbf{1}]} \tag{22}$$

Since we did not observe exciplex formation or ^{3}DCA* formation in the present case in acetonitrile, it is reasonable to eliminate the possibility of ^{3}DCA* formation from the primary ion pair (occasionally, however, electron-transfer quenching may result in the formation of a triplet state,[8,14f,20] though this was not the case). Equation (19) can be rewritten by defining $\Phi'' = \Phi/\Phi_{ip}$:

$$\Phi'' = \frac{\Phi}{\Phi_{ip}} = \frac{2k_l[O_2]/k_q}{[1]+\beta} + f_{fi} \tag{23}$$

Φ'' is then simplified by substituting the experimental values of $k_q = 2{\cdot}4 \times 10^{10}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ and $k_l = 6{\cdot}5 \times 10^9\,\mathrm{l\,mol^{-1}\,s^{-1}}$ and an oxygen concentration of $8{\cdot}1 \times 10^{-3}$ M at saturation.[22] Under the conditions where $[\mathbf{1a}] \ll 0{\cdot}056\ \mathrm{M} = \beta$, Φ'' is estimated to be constant:

$$\Phi'' = \frac{0{\cdot}0044}{[1]+\beta} + f_{fi} \approx 0{\cdot}079 + f_{fi} \tag{24}$$

Φ'' can be calculated based on the measured Φ and calculated Φ_{ip}, and the resulting plot of Φ'' against [**1a**] is shown in Figure 7. Consistent with the evaluation with equation (24), the calculated Φ'' values are more or less constant and lie in the range 0·1–0·2 when $3{\cdot}92 \times 10^{-4}\ \mathrm{M} < [\mathbf{1a}] < 3{\cdot}92 \times 10^{-3}\ \mathrm{M}$, giving an average Φ'' value of 0·12. This leads to an estimate of f_{fi} of *ca* 0·04. Indeed, $f_i = 0{\cdot}04$ is in reasonable agreement with the value of 0·11 that we determined independently using emission absorption spectroscopy.[20]

Hence, the efficiency of the electron-transfer induced oxygenation is determined by the efficiency of free ion formation. Although electron-transfer quenching of ^{1}DCA* by **1a** occurs at a diffusion-controlled rate to generate a primary ion pair, the competing back electron-transfer process seriously lowers f_{fi} in spite of the relatively fast ionic dissociation rate of $k_{fi} = 5 \times 10^8\ \mathrm{s^{-1}}$.[23] If we assume $k_{fi} = 5 \times 10^8\ \mathrm{s^{-1}}$ for the DCA–**1a** system, k_{bet} is estimated to be as high as $9{\cdot}5 \times 10^9\ \mathrm{s^{-1}}$ according to equation (21) with $f_i = 0{\cdot}04$. As such, the electron-transfer oxidation takes some part in the DCA-sensitized photooxygenations, whereas the $^1O_2$ pathway can still be valid if $k_r \approx 10^6\,\mathrm{l\,mol^{-1}\,s^{-1}}$ or higher (in other words, $\beta \approx 0{\cdot}033$ M or smaller) and the substrate concentration is around or smaller than the β value. The electron-transfer oxidation process would become pronouncedly dominant only when the substrate concentration is impractically high, e.g. 10 M.

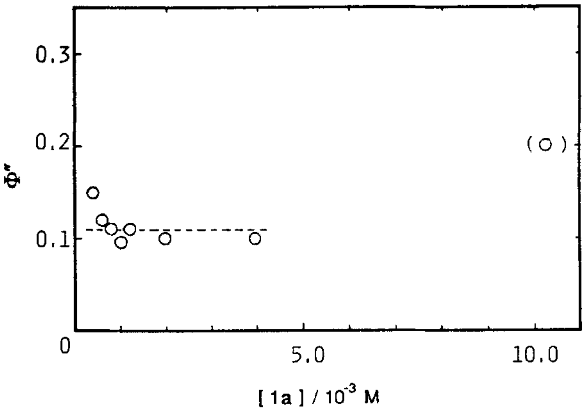


Figure 7. Plots of Φ'' vs concentration of **1a**. The data sets in Figure 2b were used for replotting according to equation (23). The broken line represents the average Φ'' of 0.12

CONCLUSION

The study of the DCA-sensitized photooxygenation of **1** showed that the mechanism of the reaction can be diversified by solvent polarity. In non-polar solvents the reaction involves an exciplex intermediate, which leads to the formation of ^{3}DCA* with an efficiency of 0·64 in carbon tetrachloride in the case of **1a**. The resulting ^{3}DCA* acts as a sensitizer for the generation of $^1O_2$. On the other hand, electron-transfer quenching of ^{1}DCA* by **1** is feasible in polar acetonitrile and a primary ion pair can be formed. However, the radical ion oxidation process is limited by fast back electron-transfer deactivation of the primary ion pair, despite the diffusion-controlled rate of the electron-transfer quenching of ^{1}DCA* by **1**. Hence the $^1O_2$ pathway can be still valid even in acetonitrile if k_r of the substrate is larger than *ca* $10^6\,\mathrm{l\,mol^{-1}\,s^{-1}}$ and the concentration of the substrate is not much higher than its β value.

An important feature of the electron-transfer photooxygenation is that k_{bet} is a crucial factor and depends on the thermodynamics of the back electron-transfer process.[24,25] Recently, Farid and co-workers[23b,c] provided convincing experimental verification of the Marcus theory[24] by using laser flash photolysis for the determination of quantum yields for free-ion formation via electron-transfer fluorescence quenching. We expect that the determination of f_{fi} with a series of donor–acceptor pairs would lead to additional verification of the Marcus theory in the photionduced electron-transfer process.

EXPERIMENTAL

Materials. Compound **1a** was purchased from Aldrich and was purified by silica gel column chromatography followed by recrystallization from methylcyclohexane; **1b** was synthesized from 4-methoxybenzaldehyde, succinic acid and lead(II) oxide according to the literature.[26a] TPP, RB and MB were supplied by Wako. DCA was synthesized from 9,10-dibromoanthracene and copper(I) cyanide in dry quinoline according to the reported method.[26b] Commercially available spectroscopic-grade solvents were distilled from calcium hydride.

Instrumentation. NMR spectra were recorded on a Varian EM-390 90 MHz NMR spectrometer. A Shimadzu IR-435 spectrometer was used for IR measurements. Electronic spectra were measured on a Hitachi 340 spectrophotometer. Fluorescence quenching experiments were carried out on a Hitachi MPF-4 fluorescence spectrometer. Melting points were measured on a Yamato MP-21 melting point apparatus and were uncorrected. Cyclic voltammetric measurements were done in acetonitrile solution with 0·1 M tetraethylammonium perchlorate as supporting electrolyte and a saturated calomel electrode (SCE) as the reference electrode by using a Yanagimoto P-1000 voltammetric analyser equipped with a function generator. High-performance liquid chromatographic (HPLC) analyses were performed with a Waters HPLC system. The flash photolysis apparatus has been described previously.[27]

Preparative photooxygenation of 1,4-diphenyl-1,3-butadiene (1a). In a Pyrex test-tube, **1a** (207 mg, 1·00 mmol) and 1 mg of TPP were dissolved in 50 ml of methylene chloride. While being oxygenated with a stream of oxygen, the solution was irradiated with a 2-kW xenon lamp ($\lambda > 450$ nm, Toshiba Y-48 glass filter) for 3 h. After removal of the solvent *in vacuo*, the residue was chromatographed on a short silica gel column. Elution with a 1 : 1 mixture of hexane and methylene chloride afforded 208 mg (0·87 mmol, 86%) of **2a**. Recrystallization from ethanol gave analytically pure **2a** as colourless needles, m.p. 80–81 °C (lit.,[28] 81–82 °C). ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5·60 (2H, s), 6·28 (2H, s), 7·2–7·6 (10H, m). Mass spectrometry (80 °C, 25 eV): *m/z* 238 (M^+, 10%), 220 ($M^+ - H_2O$, 100%), 206 ($M^+ - O_2$, 28%), 191 (15%), 180 (11%), 133 (36%), 131 (15%), 115 (40%), 105 (93%). Elemental analysis: calculated for $C_{16}H_{14}O_2$, C 80·65, H 5.92; found, C 80·39, H 6·0%.

Preparative photooxygenation of 1,4-bis(4-methoxyphenyl)-1,3-butadiene (1b). Compound **1b** (99 mg, 0.37 mmol), 1 mg of methylene blue and 50 ml of methylene chloride were placed in a Pyrex test-tube and irradiated as described above. After removal of the solvent *in vacuo*, the residue was subjected to preparative TLC and developed with a 1 : 1 mixture of hexane and methylene chloride. A band with $R_F = 0{\cdot}5$ afforded 64 mg (0·21 mmol, 58%) of **2b** as a slightly yellow solid. Recrystallization from ethanol afforded analytically pure **2b** as colourless needles, m.p. 80–82 °C. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 3.78 (6H, s), 5·54 (2H, s), 6.24 (2H, s), 6·87 (4H, AA′XX′, 9.0 Hz), 7·31 (4H, AA′XX′, 9·0 Hz). Mass spectrometry (80 °C, 13·4 eV): *m/z* 298 (M^+, 4%), 280 ($M^+ - H_2O$, 100%). Elemental analysis calculated for $C_{18}H_{18}O_4$, C 72·47, H 6·08; found, C 72·46, H 6·17%.

Determination of β values. Volumes of 3 ml of solutions containing $2{\cdot}0 \times 10^{-4}$ M of sensitizer (TPP in carbon tetrachloride or RB in acetonitrile) and a certain amount of **1a** were prepared and saturated with oxygen with a stream of dry oxygen prior to photolyses. The photolyses were carried out to *ca* 5% conversion. In the case of the TPP-sensitized reaction, a 150-W xenon lamp equipped with a monochromator was used to irradiate at 515 nm with a 10-nm band width. A 300-W xenon lamp with a Tashiba Y-43 glass filter ($\lambda > 410$ nm) was used for RB-sensitized reactions. After the photolyses, the solutions were diluted appropriately and the decrease in the absorbance of **1a** ($\lambda_{max} = 335$ nm) was determined spectrophotometrically. Relative quantum yields were calculated according to the following equation:

$$\Phi_{rel} = \frac{(\text{relative concentration of } \mathbf{1a})[\text{conversion } (\%) \text{ of } \mathbf{1a}]}{\text{irradiation time (min)}}$$

Steady-state photooxygenation of 1a and 1b. This was examined under various conditions as summarized in Table 1. The photolyses were carried out with a 2-kW xenon lamp at 15 °C with a Toshiba Y-43 glass filter ($\lambda > 410$ nm) for DCA-sensitized reactions, or a Toshiba Y-48 glass filter ($\lambda > 450$ nm) for TPP- and RB-sensitized reactions. The resulting reaction mixtures were analysed by HPLC with *trans*-stilbene as an internal standard or by ^{1}H NMR with toluene as an internal standard.

DCA fluorescence quenching. Sample solutions containing $5{\cdot}0 \times 10^{-5}$ M of DCA and a given amount of **1** were prepared and the fluorescence spectra were recorded at 20 °C. The relative fluorescence intensities at the emission maxima were measured and analysed according to equation (4). When oxygen was used as a quencher, the relative fluorescence intensities of argon-saturated sample solutions were compared with those of aerated and oxygen-saturated sample solutions. Stern–Volmer analyses were based on the oxygen concentration at saturation[22] and the partial pressure of oxygen. The results are shown in Table 2. Cao *et al.*[13] reported k_q values of $2{\cdot}6 \times 10^{10}$ and $2{\cdot}0 \times 10^{10}$ l mol^{-1} s^{-1} for the DCA fluorescence quenching by **1a** in acetonitrile and benzene, respectively.

Quantum yields for the DCA-sensitized oxygenation of 1a. Quantum yields for the DCA-sensitized photooxygenation of **1a** in carbon tetrachloride and acetonitrile were determined by using the ferrioxalate actinometer system.[29] The photolysis apparatus consisted of a 150-W xenon lamp and a grating monochromator. A 3-ml volume of solution containing DCA (3×10^{-4} M in carbon tetrachloride, 2×10^{-4} M in acetonitrile) and a certain amount of **1a** was placed in a 10-mm cuvette and saturated with oxygen. The sample solution was irradiated at 420 nm with a 10-nm band width for a certain period to effect *ca* 10% conversion. After the photolyses, the solutions were diluted appropriately and the decrease in the absorbance of **1a** ($\lambda_{max} = 335$ nm) was determined spectrophotometrically.

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