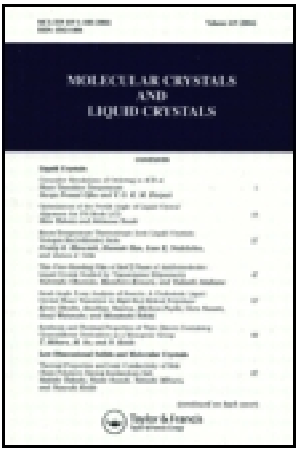

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ELECTRON-TRANSFER SENSITIZED CYCLOREVERSION OF RUBRENE ENDOPEROXIDE

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Abstract

Rubrene endoperoxide (RO_2) quenches the fluorescence of 9,10-dicyanoanthracene (DCNA) in benzonitrile and undergoes simultaneous cycloreversion with a limiting quantum yield of 0.07 ± 0.01 which increases by ~50% in the presence of an external magnetic field of 600 gauss. No quenching or cycloreversion is observed with either anthracene as sensitizer or benzene as solvent. Chloranil (triplet) sensitized cycloreversion of RO_2 has a limiting quantum yield of 0.62 ± 0.03.

It is proposed that cycloreversion involves the state $^3RO_2(\pi_{OO}^*, \sigma_{CO}^*)$ produced by geminate recombination of the triplet radical-ion pair, formed directly from the chloranil triplet state or by spin-rephasing of the singlet ion pair produced by RO_2 quenching of the DCNA fluorescent state.

Keywords: Photo-sensitized, cycloreversion, electron transfer, endoperoxide

INTRODUCTION

The (4+2) cycloreversion of the endoperoxides AO_2 of certain aromatic hydrocarbons A

$$AO_2 \longrightarrow A + O_2$$

has been accomplished thermally[1,2], by direct photolysis at wavelengths < 300 nm[3,4], by x-radiolysis[5] and by energy transfer from triplet sensitizers of sufficient energy[6,7]. We present evidence here for the electron-transfer sensitized cycloreversion of rubrene endoperoxide using singlet and triplet electron-accepting sensitizers previously reported to be effective in the electron-transfer sensitized (4+4) cycloreversion of dianthracene[8].

EXPERIMENTAL

9,10-dicyanoanthracene (DCNA) and p-chloranil from Aldrich were used as sensitizers for the cycloreversion of rubrene endoperoxide (RO_2) prepared photochemically from rubrene (Aldrich) using polymer-bound rose bengale (Dyetel) and purified as described previously[9]. Solvents benzene and benzonitrile from Aldrich were twice chromatographed on activated alumina prior to use; solutions were purged with solvent-saturated N_2 for 20 minutes prior to and during exposure in a 2 cm diameter cylindrical quartz cell, to 366 nm radiation isolated from a 100 watt d.c. mercury arc by appropriate filters. Aberchrome 540 (Aberchromics) was used as actinometer.

Quantum yields of cycloreversion were estimated from initial rates of rubrene formation monitored in absorption at 532 nm on a Perkin-Elmer spectrophotometer (Model 552); typically 1% cycloreversion was produced by a 60s exposure under the conditions described with no underlying absorption due to secondary (rearranged) products. Control experiments established the photochemical stability of both sensitizers during exposure. An SLM-Aminco spectrofluorometer (Model SPF 500C) was used to measure relative fluorescence quantum yields of DCNA as a function of RO_2 concentration and the fluorescence lifetime of the (unquenched) sensitizer was obtained by time-correlated single photon counting (Edinburgh Instruments System 199).

Two ceramic bar magnets (Edmund Scientific Model B40,818) were used to apply a magnetic field of 600 ± 100 gauss to the photolytic cell when required.

RESULTS AND DISCUSSION

Singlet Sensitization

The quenching of DCNA fluorescence by rubrene endoperoxide RO_2 in benzonitrile is accompanied by RO_2 cycloreversion with a quantum yield γ_c which increases with RO_2 concentration. This behaviour is quantitatively described by a relationship of the form

$$1/\gamma_c = 1 + k_2/k_3 + k_1/k_3[RO_2] = (1 + 1/K_{sv}[RO_2])/\gamma_c^{\infty} \qquad \text{I}$$

derived from the simple scheme (S=sensitizer):-

$$^1S^* \longrightarrow S + h\nu \qquad 1.$$

$$^1S^* + RO_2 \longrightarrow S + RO_2 \qquad 2.$$

$$^1S^* + RO_2 \longrightarrow S + R + O_2 \qquad 3.$$

where $\gamma_c^\infty = k_3/(k_2 + k_3) = 0.07 \pm 0.01$ and $K_{SV} = (k_2 + k_3)/k_1 = 90 \pm 7\ M^{-1}$ equal within the combined error limits to the Stern-Volmer constant obtained from fluorescence quenching data (Table 1). This indicates sensitizer singlet state initiation of the cycloreversion sequence; triplet state initiation is considered to play an insignificant role since this would not give the required RO_2 concentration dependence of γ_c and the fluorescence quantum yield of DCNA in benzonitrile, relative to its reported value[10] of 0.87 in cyclohexane, was found to be 0.95 ± 0.06.

Together with the fluorescence lifetime $\tau = 1/k_1$ for DCNA in this solvent the Stern-Volmer constant K_{SV} (Table 1) provides the quenching rate constant

$$k_q = k_2 + k_3 = K_{SV}/\tau = 7 \pm 0.6 \times 10^9\ M^{-1}s^{-1}$$

equal to the diffusion-limited value estimated for a solvent with the viscosity (1.24 x 10_{-2} poise) of benzonitrile at 25°C. However the limiting cycloreversion quantum yield γ_c^∞ signifies that only 7% of efficient quenching encounters leads to cycloreversion of RO_2.

The data tabulated are consistent with an electron transfer quenching mechanism insofar as this is observed (together with cycloreversion) only for those systems in which formation of the geminate radical-ion pair as the primary quenching product is exoergic ($\Delta G_{rip} < O$). If the physical quenching process 2 is completed by geminate charge neutralization of this (singlet) ion pair in the sequence:-

$$^1S^* + RO_2 \longrightarrow {}^1(S^-...RO_2^+) \longrightarrow S + RO_2 \qquad (2)$$

cycloreversion may originate from either

a) the separated radical cation

$$^2RO_2^+ \longrightarrow {}^2R^+ + {}^{1,3}O_2 \qquad (3a)$$

followed by homogenous recombination of $^2R^+$ and $^2S^-$, or

b) the endoperoxide triplet state $^3RO_2^*(\pi_{OO^*}, \sigma_{CO}^*)$ which correlates with $R + O_2\ {}^3\Sigma_g^-$ and which may be produced by homogeneous recombination of separated radical-ions in the sequence

$$^1(S^- ... RO_2^+) \longrightarrow {}^2S^- + {}^2RO_2^+ \longrightarrow S + {}^3RO_2^* \qquad (3b)$$

or by geminate neutralization of the triplet radical-ion pair following spin-rephasing of the quenching product:-

$$^1(S^- ... RO_2^+) \longrightarrow {}^3(S^- ... RO_2^+) \longrightarrow S + {}^3RO_2^* \qquad (3c)$$

TABLE 1. Experimental parameters determined for the sensitized cycloreversion of rubrene endoperoxide

Sensitizer	τ(ns)	Solvent	$K_{SV}^b(M^{-1})$	γ_c^∞	ΔG_{rip}^c(eV)
DCNA	12.9	C_6H_5CN	80±7	0.07±0.01	-0.31
DMA[a]	16	C_6H_5CN	<7	<0.01	0.34
DCNA	12.4	C_6H_6	<7	<0.01	0.73
p-chloranil	—	C_6H_5CN	—	0.62±0.03	-1.1

[a] 9,10-dimethylanthracene

[b] Stern-Volmer constant for sensitizer fluorescence quenching by RO_2

[c] Free energy of geminate radical-ion pair formation estimated from Weller equation[18]

γ_c^∞ denotes limiting quantum-yield of RO_2 cycloreversion (see text).

Dissociation of the radical cation (process 3a) is not supported by the polarographic behaviour of RO_2 in benzonitrile (with 0.1 M tetraethylammonium perchlorate) since no rubrene could be detected in this solution after 12 minutes at an applied potential of 0.1 volt in excess of its oxidation potential (1.7 volts). The apparent stability of the cation RO_2^+ is consistent with its correlation with R + $O_2^+(^2\Pi_g)$ which is chemically forbidden in the Fukui sense. On the other hand, sequence 3b has been well-documented[11] for other systems whereas the spin-rephasing sequence 3c may account for an increase of 50% in the DCNA sensitized cycloreversion quantum yield observed in the presence of an external magnetic field of 600 gauss.

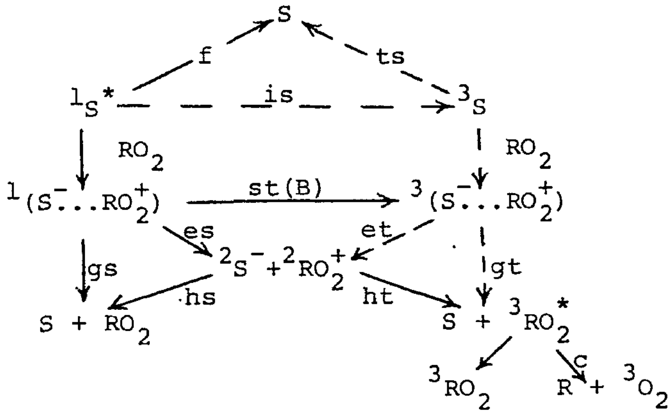
The proposed cycloreversion mechanism for DCNA sensitized cycloreversion of RO_2 is summarized by the solid arrows in Scheme 1. If homogeneous ion recombination (process 3b) is entirely responsible for the formation of $^{3}RO_2$. and subsequent cycloreversion at zero field strength the limiting quantum yield is given by (with $k_{ST} = 0$)

$$\gamma_c^{\infty} = \gamma_{es}\, k_{ht}/(k_{ht} + k_{hs}) \qquad \text{II}$$

where the cage escape efficiency is given by

$$\gamma_{es} = 4\gamma_c^{\infty}/3 \sim 0.1$$

if k_{hs}/k_{ht} has its spin statistical probability of 1/3, and $^{3}RO_2^{*}$ undergoes cycloreversion with unit efficiency.



Scheme 1. Proposed mechanism for singlet (solid arrows) and triplet (dashed arrows) electron acceptor sensitized cycloreversion of rubrene endoperoxide RO_2. Labels refer to geminate (g) and homogeneous (h) charge recombination in singlet (s) and triplet (t) configurations; e denotes cage escape, f-fluorescence emission, is-intersystem crossing and st(B) describes magnetic field dependent spin-rephasing of geminate ion-pair.

Triplet State Sensitization

The order of magnitude increase in γ_c^{∞} for RO_2 cycloreversion sensitized by the p-chloranil triplet state (Table 1), and the absence of an external magnetic field effect (at 600 gauss) for this system, supports the intermediary role of the triplet radical-ion pair which is the primary quenching product in this case. Of interest here is the finding that ~40% of these ion pairs do not undergo cycloreversion. If this were a consequence of cage escape followed by homogeneous recombination in the singlet channel

$$^3(S^-...RO_2^+) \longrightarrow {}^2S^- + {}^2RO_2^+ \longrightarrow S + RO_2$$

then

$$\gamma_c^{\infty} = 1 - \gamma_{et}k_{hs}/(k_{ha} + k_{ht}) = 0.62$$

or $\gamma_{et} = 4(1 - \gamma_c^{\infty}) = 1.5$

which is clearly unrealistic for the cage escape efficiency γ_{et} from the triplet geminate ion-pair. We suggest that cycloreversion from the $^3RO_2^*(\pi_{oo}^*\ \sigma_{co}^*)$ state competes with its internal conversion to the lower triplet state $^3RO_2(\pi_{oo}^*\ \sigma_{oo}^*)$ which is not a cycloreversion precursor in which case the cycloreversion from $^3RO_2^*(\pi_{oo}^*, \sigma_{co}^*)$ is given by $\gamma_T = \gamma_c^{\infty} = 0.62$. The proposed sequence of events initiated by RO_2 quenching of the chloranil triplet state is summarised by the dashed lines in Scheme 1.

CONCLUSIONS

The sensitized cycloreversion of RO_2 by DCNA singlet and chloranil triplet states is consistent with a reversible electron transfer mechanism which generates an excited endoperoxide triplet state $^3RO_2^*(\pi_{oo}^*, \sigma_{co}^*)$ cycloreversion precursor as summarized in Scheme I. Clearly this state must lie below the triplet state of chloranil at 260 kJ/mole[12] yet is inaccessible by energy transfer from the naphthalene triplet state at 255 kJ/mole since naphthalene does not sensitize cycloreversion in a non-polar solvent[6]. It is also noted that $^3RO_2^*(\pi_{oo}, \sigma_{co}^*)$ undergoes cycloreversion with an efficiency ≥ 0.62 whereas the triplet state of RO_2 sensitized by energy transfer from the benzene triplet state at 352 kJmole has an estimated cycloreversion efficiency of only 0.30.

It is tempting to speculate that triplet energy transfer from benzene in non-polar solvents produces a $^3RO_2(\pi_c, \pi_c^*)$ state of the endoperoxide, associated with the aromatic chromophore, which undergoes interchromophoric conversion to the state $^3RO_2^*(\pi_{oo}^*, \sigma_{co}^*)$ of the peroxy system. If, by analogy, direct excitation of the aromatic[1] $RO_2(\pi_c, \pi_c^*)$ state undergoes internal conversion to the corresponding singlet state of the peroxy chromophore $^1RO_2^*(\pi_{oo}^*, \sigma_{co}^*)$, which correlates with

$R + O_2{}^1\Delta_g$', providing the 'direct' cycloreversion sequence

$$RO_2 + h\upsilon \longrightarrow {}^1RO_2(\pi_c, \pi_c^*) \longrightarrow {}^1RO_2^*(\pi_{oo}^*, \sigma_{co}^*) \longrightarrow R + O_2{}^1\Delta_g$$

this would account for an observed rise time of the laser induced fluorescence of hydrocarbon R which exceeds[13] the estimated relaxation time of the excitation product ${}^1RO_2(\pi_c, \pi_c^*)$, and its viscosity independence[14]. This sequence is also consistent with the production of O_2 in its ${}^1\Delta_g$ state[15] in contrast to that involving a biradical ($-RO_2-$) intermediate[16,17]:-

$$RO_2 + h\upsilon \longrightarrow {}^1RO_2(\pi_c, \pi_c^*) \longrightarrow -RO_2- \longrightarrow R + {}^{1,3}O_2$$

which would be expected to produce the ${}^3\Sigma_g^-$ and ${}^1\Delta_g$ states of molecular oxygen in the spin-statistical ratio of 3:1.

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