Singlet Oxygen Production from Singlet and Triplet States of 9,10-Dicyanoanthracene

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Abstract: The mechanism and quantum yield of singlet oxygen ($^1O_2$) production by 9,10-dicyanoanthracene (DCA) has been investigated in benzene and acetonitrile; $^1O_2$ is produced from both the singlet and triplet states of DCA. Intersystem crossing enhanced by 2,5-dimethyliodobenzene (DMIB) provided a direct route to ^3DCA and allowed determination of the individual contributions of ^3DCA and ^1DCA to $^1O_2$ production. Enhanced intersystem crossing can make the triplet pathway a major route under some conditions and can result in high quantum yields of $^1O_2$.

Introduction

The oxygenation of organic compounds photosensitized by dicyanoanthracene (DCA) has been extensively studied and has been shown to go by two competing mechanisms, a "Type I" electron-transfer process and a "Type II" process via singlet oxygen ($^1O_2$).[1,2] The Type I process is exemplified by the photooxygenation of trans-stilbene (TS) in CH_3CN.[3,4] In this process, singlet excited ^1DCA undergoes electron transfer from TS to form a radical cation ($TS^{•+}$) and a radical anion ($DCA^{•-}$). The subsequent reaction of $^3O_2$ with these radical ions gives benzaldehyde and other oxidation products.

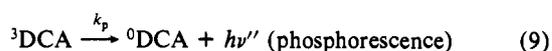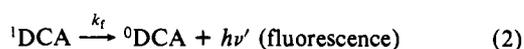$$^1DCA + TS \rightarrow DCA^{•-} + TS^{•+} \xrightarrow{^3O_2} TSO_2 + DCA$$
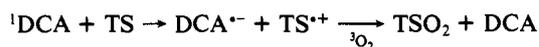
The Type II process via $^1O_2$ is exemplified by the DCA-sensitized photooxygenation of 1,2-dimethylcyclohexene, a typical olefinic $^1O_2$ substrate.[5] In this mechanism, excited DCA is quenched by oxygen with energy transfer to form $^1O_2$, which then oxidizes 1,2-dimethylcyclohexene to give a characteristic product distribution. Rose bengal sensitized oxidation gives a very similar product distribution, and this fact and additional kinetic evidence confirmed an $^1O_2$ pathway for this substrate. Radical autoxidation gives a distinctly different product distribution. Several other alkenes gave product distributions which provided a similar "fingerprint" for $^1O_2$ in the DCA-sensitized oxygenation.[5–8]

Several possible reactions of excited DCA are shown in Scheme I. Although product distribution studies and detection of 1268-nm luminescence provided evidence for $^1O_2$ production,[9] the intersystem crossing yield for DCA reported by Manring et al.[10] was only 1.7% in CH_3CN, indicating that direct formation of triplet DCA (reaction 3) is not a major pathway for the formation of $^1O_2$ by DCA. The route to $^1O_2$ could involve direct energy transfer to $^3O_2$ from ^1DCA, either with (reaction 4) or without (reaction 7) the production of ^3DCA. An alternative is $^3O_2$ enhancement of the intersystem crossing of ^1DCA to form ^3DCA (reaction 5), which then transfers energy to oxygen (reaction 10). The first

mechanism has an overall maximum quantum efficiency for $^1O_2$ formation of 2.0 since both reactions 4 and 10 give $^1O_2$. The second and third mechanisms have maximum overall quantum efficiencies of 1.0.

Scheme I

$$^1DCA \xrightarrow{k_{ic}^1} {}^0DCA \tag{1}$$

$$^1DCA \xrightarrow{k_f} {}^0DCA + h\nu' \text{ (fluorescence)} \tag{2}$$

$$^1DCA \xrightarrow{k_{isc}} {}^3DCA \tag{3}$$

$$^1DCA + {}^3O_2 \xrightarrow{k_{eo}^1} {}^3DCA + {}^1O_2 \tag{4}$$

$$^1DCA + {}^3O_2 \xrightarrow{k_{ico}} {}^3DCA + {}^3O_2 \tag{5}$$

$$^1DCA + {}^3O_2 \xrightarrow{k_{qo}^1} {}^0DCA + {}^3O_2 \tag{6}$$

$$^1DCA + {}^3O_2 \xrightarrow{k_{sf}^1} {}^0DCA + {}^1O_2 \tag{7}$$

$$^3DCA \xrightarrow{k_{ic}^3} {}^0DCA \tag{8}$$

$$^3DCA \xrightarrow{k_p} {}^0DCA + h\nu'' \text{ (phosphorescence)} \tag{9}$$

$$^3DCA + {}^3O_2 \xrightarrow{k_{eo}^3} {}^0DCA + {}^1O_2 \tag{10}$$

$$^3DCA + {}^3O_2 \xrightarrow{k_{qo}^3} {}^0DCA + {}^3O_2 \tag{11}$$

Energy transfer from both singlet and triplet DCA to $^3O_2$ is energetically allowed. The DCA triplet energy is 41.8 kcal/mol,[11] which is high enough to allow exothermic transfer to $^3O_2$ to give $^1O_2$ ($^1\Delta_g$, 23 kcal/mol). Since the DCA singlet energy is 66 kcal/mol,[11] there is a 24.2 kcal/mol singlet–triplet energy gap, which is also large enough to excite $^3O_2$ to $^1O_2$.[11] Dobrowolski, Ogilby, and Foote[9] measured the $^1O_2$ quantum yield ($\Phi_{^1O_2}$) in both C_6H_6 and CH_3CN by comparison of the 1268-nm luminescence of $^1O_2$ produced by DCA and diacenaphtho[1,2-b:1',2'-b]thiophene. The $\Phi_{^1O_2}$ of diacenaphtho[1,2-b:1',2'-b]thiophene was determined by actinometry with 2-methyl-2-pentene. They found $\Phi_{^1O_2}$ for DCA to be 2.0 in CH_3CN and 1.56 in C_6H_6, extrapolated to infinite oxygen concentration.

However, the $^1O_2$ emission signals in this work were extremely noisy, and extrapolation led to a very large error in the quantum yield. Acridine has recently been introduced as a standard; its singlet oxygen yield has been determined by luminescence[12,13] and

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Table I. Results of Plot of $\Phi\bar{\imath}_{O_2}^1$ vs $[^3O_2]^{-1}$ for DCA (Figure 1)

solvent	$\Phi\bar{\imath}_{O_2}^\infty$	corr coeff
C_6H_6	1.56 ± 0.10	1.000
CH_3CN	1.46 ± 0.10	0.999

thermal lensing,[13] and its triplet yield is also well-documented.[14] Using acridine as a standard, we have redetermined the value of $^1O_2$ production from DCA in both acetonitrile and in benzene with an improved detector. We also prepared ^{3}DCA directly, using enhanced intersystem crossing with 2,5-dimethyliodobenzene and determined the yield of $^1O_2$ by this path.

Experimental Section

$^1O_2$ **Quantum Yields.** The apparatus was a modification of the one previously described.[15] DCA was excited at 355 nm using the third harmonic of a Quanta-Ray DCR-2 Nd:YAG laser. The laser pulse was filtered to remove any fundamental from the laser using a 355-nm pass/1060-nm reflecting mirror (Newport Corp.), followed with a KG-3 (Schott Glass) infrared absorbing filter. The 355-nm pulse was also filtered with a 355-nm pass/532-nm reflecting mirror. The near-infrared emission from $^1O_2$ was monitored at right angles to the laser beam and filtered with an RG-850 cutoff filter (Schott Glass) and a silicon 1100-nm cutoff filter (Infrared Optics). The detector was a 2-mm germanium diode (Opto-Electronics), with a preamplifier (OP-37, Analog Devices) operating in a transimpedance mode with a 500-KΩ feedback resistor, followed with a Comlinear CLC E220 amplifier. The signal from the detector was fed to a transient digitizer (Analogic Data 6000) where it was signal-averaged (a maximum of 16 shots) and then transferred to a PDP-11/73 for analysis. The lifetimes were determined using the Guggenheim method, and the infinity values were calculated using the Kedzey–Swinborne method.[16] Quantum yields were determined by extrapolation of emission intensities to zero time as defined by the trigger pulse from a photodiode (MRD510), which monitored laser scatter from the Pellin-Brocca prism of the PHS (Prism harmonic separator) of the laser. The intensities at time zero were corrected to 100% absorption from an absorbance of 0.8 and compared to the $^1O_2$ quantum yield of acridine under air. All absorbances were measured on a Beckman 25 spectrophotometer. Various oxygen concentrations were achieved by purging the solvent with air, pure oxygen, or a 59.8:40.2 oxygen/nitrogen mixture.

Fluorescence Quenching. Fluorescence quenching experiments were performed on a SPEX Fluorolog 2 fluorimeter, exciting DCA (2.61 × 10^{-7} M) at 390 nm and monitoring the 434-nm fluorescence of DCA in benzene.

DCA Triplet Yield. The transient absorption spectrometer was as previously described,[17] with the following modifications. The detector was an RCA IP-28 photomultiplier tube (PMT) wired in a high-current configuration. The output of the PMT was monitored across a variable-load resistor (50 Ω–100 KΩ), which could be adjusted for gain, followed by an LH0032 operational amplifier (National Semiconductor) followed by a LH0033 buffer amplifier (National Semiconductor). A bucking circuit, which applied a positive voltage in series with the output voltage across the load resistor, was used to obtain the full 6.4-V range of the digitizer. The monochromator was a 0.25 m f/3.5 Jarrell-Ash Model 82-410 with 500-μm slits. Triplet–triplet absorption of DCA was monitored at 440 nm after deoxygenation by purging with argon for 15 min. The absolute quantum yield for ^{3}DCA production was determined from the extinction coefficients of ^{3}DCA (9000 cm^{-1} M^{-1})[11] and acridine (25 000 cm^{-1} M^{-1})[14] at 440 nm and the value of 0.84 for $\Phi_{3acridine}$, which is based upon $^1O_2$ production quantum yields using the thermal lensing technique and the reported S_Δ of 1.0.[13,18]

Materials. DCA (Aldrich Chemical Co.) was recrystallized from toluene. DMIB was used as received (Lancaster Synthesis). Acridine (Aldrich) was recrystallized from toluene. All solvents were spectrograde (Mallinkrodt) or Gold Label (Aldrich).
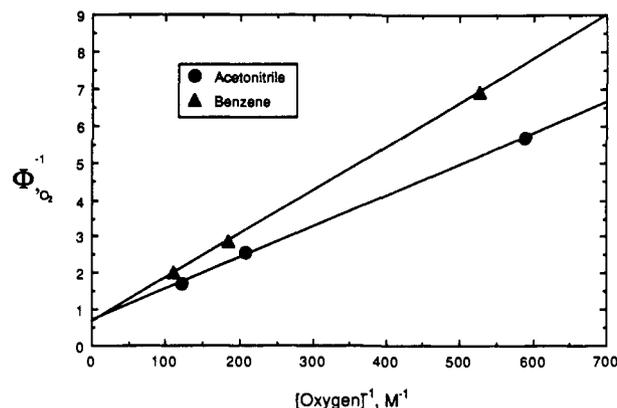
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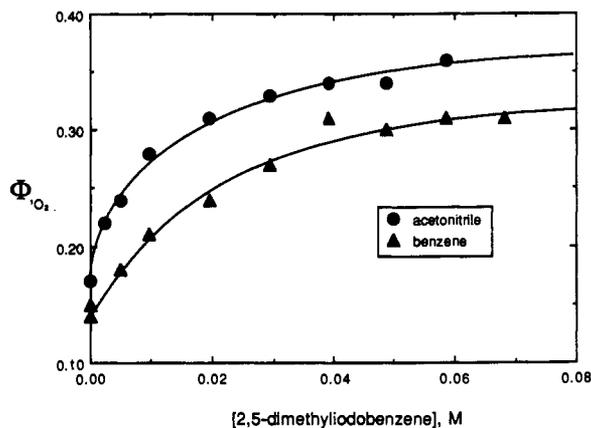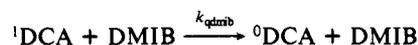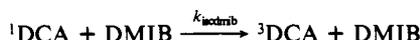
Figure 1. Plot of $\Phi\bar{\imath}_{O_2}^1$ vs $[^3O_2]^{-1}$ for DCA in C_6H_6 and CH_3CN. Φ_{1O_2} was determined by reference to acridine-sensitized $^1O_2$ emission. The absorbances of DCA (2.64 × 10^{-4} M) and acridine (1.02 × 10^{-4} M) were 0.7 at 355 nm.

Results

The quantum yield for $^1O_2$ production with contributions from both ^{1}DCA and ^{3}DCA is shown in eq 1,

$$\Phi_{1O_2} = \frac{(k_{eto}^1 + k_{sf}^1)[^3O_2]}{k_{ox}^1[^3O_2] + \tau\bar{\imath}_{DCA}^1} + \frac{(k_{eto}^1 + k_{isco})[^3O_2] + k_{isc}}{k_{ox}^1[^3O_2] + \tau\bar{\imath}_{DCA}^1}S_\Delta \quad (1)$$

where lumped constants are defined as follows:

$$\tau\bar{\imath}_{DCA}^1 = k_{ic}^1 + k_f + k_{isc}$$

$$k_{ox}^1 = k_{qo}^1 + k_{sf}^1 + k_{eto}^1 + k_{isco}$$

$$k_{ox}^3 = k_{qo}^3 + k_{eto}^3$$

As defined by Gorman et al.,[12] S_Δ is as follows:

$$S_\Delta = \frac{k_{eto}^3}{k_{ox}^3}$$

Since the direct intersystem crossing yield for DCA is very small as shown by Manring, Gu, and Foote[10] (and confirmed below), $k_{isc} \ll k_{eto}^1[^3O_2]$, and eq 1 may then be rewritten in reciprocal form as follows:

$$\Phi\bar{\imath}_{O_2}^1 = \left(\frac{k_{ox}^1}{k_{eto}^1 + k_{sf}^1 + S_\Delta(k_{eto}^1 + k_{isco})}\right) + \left(\frac{\tau\bar{\imath}_{DCA}^1}{k_{eto}^1 + k_{sf}^1 + S_\Delta(k_{eto}^1 + k_{isco})}\right)\frac{1}{[^3O_2]} \quad (2)$$

The reciprocal of the intercept of a plot of eq 2 vs $[^3O_2]^{-1}$ is $\Phi_{O_2}^\infty$, the quantum yield of singlet oxygen at infinite oxygen concentration:

$$\Phi_{O_2}^\infty = \frac{k_{eto}^1 + k_{sf}^1}{k_{ox}^1} + \frac{S_\Delta(k_{eto}^1 + k_{isco})}{k_{ox}^1}$$

In the limiting case where reaction 4 predominates, $k_{eto}^1 = k_{ox}^1$ and $S_\Delta = 1$, $\Phi_{O_2}^\infty$ is 2.0. In the other limiting case, where reaction 5 dominates ($k_{eto}^1 + k_{sf}^1 \ll k_{isco}$), $^1O_2$ is produced only from ^{3}DCA formed by $^3O_2$-enhanced intersystem crossing of ^{1}DCA (k_{isco}). Under these conditions and where k_{isc} is small, eq 2 simplifies to eq 3.

$$\Phi\bar{\imath}_{O_2}^1 = \frac{k_{ox}^1}{k_{eto}^1 S_\Delta} + \frac{\tau\bar{\imath}_{DCA}^1}{S_\Delta k_{eto}^1[^3O_2]} \quad (3)$$

The reciprocal of the intercept of the plot of this equation (infinite oxygen concentration) is as follows:

$$\Phi_{O_2}^\infty = \frac{k_{eto}^1 S_\Delta}{k_{ox}^1} \quad (4)$$

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Figure 2. $^1O_2$ quantum yield ($\Phi_{^1O_2}$) versus 2,5-dimethyliodobenzene concentration in CH_3CN and C_6H_6 under air. [DCA] in acetonitrile was 1.0×10^{-4} M and in benzene was 2.56×10^{-4} M.

In the limiting case where $k_{eto}{}^1 = k_{ox}{}^1$ and $S_\Delta = 1$, $\Phi^\infty_{^1O_2}$ for this mechanism is 1.0. If $\Phi^\infty_{^1O_2}$ is greater than 1, the first mechanism is active and both singlet and triplet DCA contribute to $^1O_2$ production. If it is less than or equal to 1, either mechanism or a combination could apply. The plot of $\Phi^{-1}_{^1O_2}$ vs $[^3O_2]^{-1}$ is shown in Figure 1 for both C_6H_6 and CH_3CN, and the results are summarized in Table I.

$^1O_2$ **Produced from ^3DCA.** If S_Δ from ^3DCA were known, the relative contributions to $^1O_2$ production of both ^1DCA and ^3DCA could be determined. It was shown by Manring et al.[10] that 2,5-dimethyliodobenzene (DMIB) enhances the intersystem crossing of DCA and allows the direct production of ^3DCA. We used this technique to measure S_Δ for DCA by measuring $\Phi_{^1O_2}$ as a function of DMIB concentration. Scheme II outlines mechanisms for ^3DCA production. In this scheme, $k_{iscdmib}$ is the

Scheme II

$$^1DCA + DMIB \xrightarrow{k_{iscdmib}} {}^3DCA + DMIB$$

$$^1DCA + DMIB \xrightarrow{k_{qdmib}} {}^0DCA + DMIB$$

rate constant of enhanced intersystem crossing and k_{qdmib} is the rate of quenching without triplet production. From Schemes I and II, the quantum yield for $^1O_2$ production is as follows:

$$\Phi_{^1O_2} = \frac{k_{eto}{}^1[^3O_2]}{k_{ox}{}^1[^3O_2] + k_q[DMIB] + \tau^{-1}_{^1DCA}} + \frac{(k_{eto}{}^1 + k_{isco})[^3O_2] + k_{isc} + k_{iscdmib}[DMIB]}{k_{ox}{}^1[^3O_2] + k_q[DMIB] + \tau^{-1}_{^1DCA}} S_\Delta \quad (5)$$

where $k_q = k_{iscdmib} + k_{qdmib}$. Figure 2 is a plot of $\Phi_{^1O_2}$ versus DMIB concentration and shows that DMIB strongly enhances the production of $^1O_2$ as a result of the increased ^3DCA yield from the enhanced intersystem crossing.

Defining the following parameters,

$$F = k_{ox}{}^1[^3O_2] + k_q[DMIB] + \tau^{-1}_{^1DCA} \quad (6)$$

$$C = k_{eto}{}^1[^3O_2] + S_\Delta((k_{eto}{}^1 + k_{isco})[^3O_2] + k_{isc})$$

eq 5 can be rewritten as follows:

$$\Phi_{^1O_2} \times F = C + S_\Delta k_{iscdmib}[DMIB] \quad (7)$$

F, the rate of decay of ^1DCA in the presence of the quenchers $^3O_2$ and DMIB, can be calculated, since the rate constants of ^1DCA fluorescence quenching by DMIB (k_q) and ^1DCA fluorescence quenching by $^3O_2$ (k_{ox}) and the ^1DCA fluorescence lifetime ($\tau_{^1DCA}$) are known from the literature,[19] and k_q for DMIB in C_6H_6 is measured by standard Stern–Volmer techniques (Figure

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Table II. Rate Constants for ^1DCA Fluorescence Quenching by DMIB (k_q) and $^3O_2(k_{ox}{}^1)$, and $\tau_{^1DCA}$ in CH_3CN and C_6H_6

solvent	k_q, s^{-1}	$k_{ox}{}^1$, s^{-1} [b]	$\tau_{^1DCA}$, ns[c]
C_6H_6	2.82×10^9	5.0×10^9	12.4
CH_3CN	8.76×10^9 [a]	6.8×10^9	15.2

[a] Reference 10. [b] Ogilby, personal communication. [c] Reference 19.

Table III. Parameters from plot of $\Phi_{^1O_2} \times F$ vs [DMIB] (Figure 4)

solvent	$S_\Delta k_{iscdmib}$, s^{-1}	C,[a] s^{-1}	corr coeff
C_6H_6	$(1.12 \pm 0.01) \times 10^9$	$(1.38 \pm 0.05) \times 10^7$	0.997
CH_3CN	$(3.37 \pm 0.3) \times 10^9$	$(1.22 \pm 0.1) \times 10^7$	0.998

[a] $C = k_{eto}{}^1[^3O_2] + S_\Delta((k_{eto}{}^1 + k_{isco})[^3O_2] + k_{isc})$.
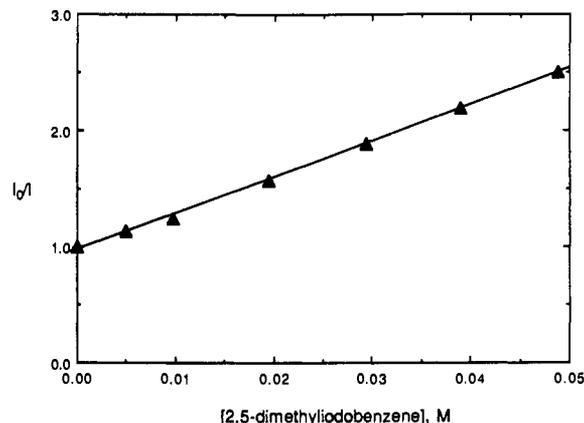

Figure 3. Stern–Volmer plot of quenching DCA (2.61×10^{-7} M) fluorescence by 2,5-dimethyliodobenzene (DMIB) in air-saturated C_6H_6. DCA was excited at 390 nm with fluorescence monitored at 434 nm.
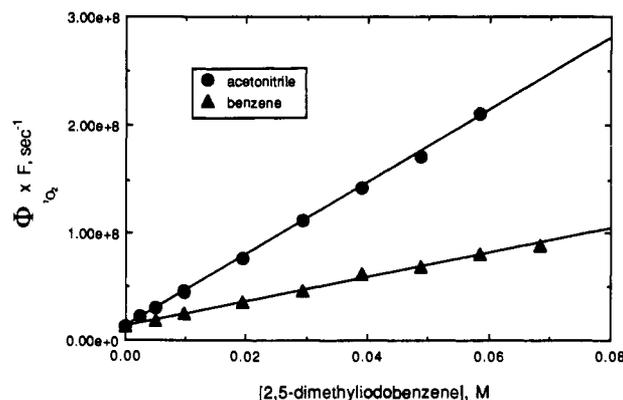

Figure 4. $^1O_2$ quantum yield ($\Phi_{^1O_2}$) $\times F$ vs 2,5-dimethyliodobenzene (DMIB) in air-saturated CH_3CN and C_6H_6. [DCA] in CH_3CN was 1.0×10^{-4} M and in C_6H_6 was 2.56×10^{-4} M.

3). The values of these constants are listed in Table II along with the values of $\tau_{^1DCA}$.

With the rate constants from Table II, F was calculated for each data point. A plot of eq 7 for both C_6H_6 and CH_3CN is shown in Figure 4. The calculated slopes and intercepts of the plots allow calculation of the parameters in Table III.

^3DCA **Yields from DMIB Determination of $k_{iscdmib}$.** In order to determine the yield of $^1O_2$ from ^3DCA, it was necessary to determine the absolute yield of ^3DCA produced by DMIB quenching of ^1DCA. This was accomplished by measuring the transient absorbance of ^3DCA at 440 nm. From the absorbance and the extinction coefficient,[14] the concentration of triplet can be calculated. This was compared to the absorbance of acridine triplet[14] (whose quantum yield is 0.84)[13] under identical conditions. The singlet oxygen and triplet quantum yields are related as follows:

$$\Phi_{^1O_2} = S_\Delta \Phi_{triplet}$$

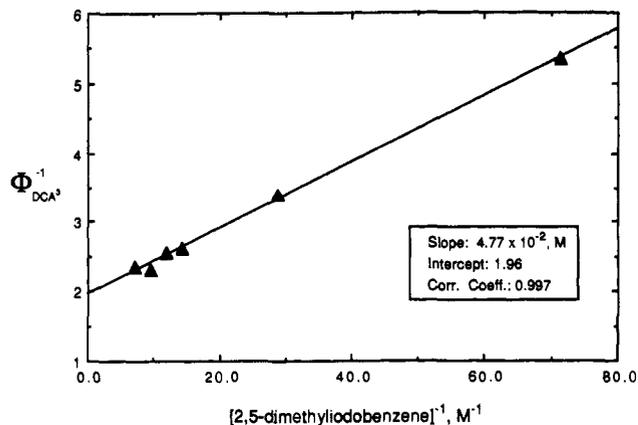where S_Δ is defined as above[12] and $\Phi_{triplet}$ is the quantum yield

Figure 5. Plot of $\Phi^1{}_{3DCA}$ vs $[DMIB]^{-1}$ in C_6H_6. Deoxygenated DCA (1.2 × 10⁻⁴ M) was excited at 355 nm.

of triplet formation. For acridine, S_Δ is 1.0.[12,13] From Schemes I and II, the quantum yield for ^{3}DCA production in the absence of $^3O_2$ is the following:

$$\Phi_{3DCA} = \frac{k_{isc} + k_{iscdmib}[DMIB]}{k_q[DMIB] + \tau^{-1}_{DCA}} \qquad (8)$$

Inverting eq 8 yields:

$$\Phi^{-1}_{3DCA} = \frac{k_q}{k_{iscdmib}} + \frac{\tau^{-1}_{DCA}}{k_{iscdmib}[DMIB]} \qquad (9)$$

A plot of the data according to eq 9 is shown in Figure 5. The value of $k_{iscdmib}$ can be calculated using values from either the slope ($k_q/k_{iscdmib}$) or the intercept ($\tau^{-1}_{DCA}/k_{iscdmib}$) of eq 9, since both k_q and τ_{DCA} are known (Table II). The value obtained from the intercept is 1.49 × 10⁹ M⁻¹ s⁻¹, whereas that obtained from the slope is 1.69 × 10⁹ M⁻¹ s⁻¹, in good agreement.

Discussion

The value of $\Phi^\infty_{1O_2}$ (at infinite $^3O_2$ concentration) for DCA is clearly greater than 1 (Table I) in both C_6H_6 and CH_3CN, confirming that the major pathway for production of $^1O_2$ is energy transfer from ^{1}DCA. Although the value in benzene agrees with that reported by Dobrowolski, Ogilby, and Foote,[9] the value of 1.46 in CH_3CN is somewhat smaller than the 2.0 they obtained. The present results have much lower error limits since the signal-to-noise ratio of our instrument was several orders of magnitude better than that of the previous apparatus. The value of Φ_{1O_2} determined for DNT by Dobrowolski, Ogilby, and Foote[9] was found to be too high. Recalibrated using the acridine standard, it is 0.46 ± 0.03 in benzene and 0.39 ± 0.02 in CH_3CN, compared to values of 0.98 and 0.62, respectively.

Since the rate constant of intersystem crossing enhancement ($k_{iscdmib}$) is known, S_Δ for ^{3}DCA can be calculated from the values

in Table III to be 0.70 ± 0.20 in benzene (error in extinction coefficient of ^{3}DCA absorption reported by Darmanyan[11]). The expression for Φ_{1O_2} can be written:

$$\Phi_{1O_2} = \Phi_{singlet} + \Phi_{triplet}S_\Delta \qquad (10)$$

where $\Phi_{singlet}$ (the yield of $^1O_2$ by direct quenching of ^{1}DCA) and $\Phi_{triplet}$ (the yield of ^{3}DCA via all routes) are given by eqs 11 and 12, respectively.

$$\Phi_{singlet} = \frac{(k_{eto}{}^1 + k_{sf}{}^1)[{}^3O_2]}{k_{ox}{}^1[{}^3O_2] + \tau^{-1}_{DCA}} \qquad (11)$$

$$\Phi_{triplet} = \frac{(k_{eto}{}^1 + k_{isco})[{}^3O_2]}{k_{ox}{}^1[{}^3O_2] + \tau^{-1}_{DCA}} \qquad (12)$$

Since S_Δ in benzene is 0.7, the maximum value of singlet O_2 quantum yield possible would be 1.7. Since Φ_{1O_2} at infinite O_2 is 1.56, it is clear that any contributions from $k_{sf}{}^1$ and k_{isco} must be very small, although they cannot be determined exactly. Thus, by far the predominant route to singlet oxygen comes from the double energy-transfer pathway in benzene. If the other pathways are actually zero, the quantum yield of singlet oxygen production from quenching ^{1}DCA is 0.86. Although S_Δ in CH_3CN is not known, the value of $S_\Delta k_{iscdmib}$ (3.37 × 10⁹:1.12 × 10⁹), obtained from eq 7 for both CH_3CN and C_6H_6, is 3.0, the same as the value of k_q (the total rate of ^{1}DCA quenching by DMIB) for the two solvents, suggesting that S_Δ is the same in the two solvents. Using this assumption, the quantum yield of singlet oxygen production from quenching ^{1}DCA in CH_3CN is 0.76.

From the intercept of eq 9, the efficiency of ^{3}DCA production by DMIB enhancement is 50%. This value implies that the value Manring, Gu, and Foote[10] determined for the natural intersystem crossing yield is too high by a factor of 2 since they assumed that DMIB quenches ^{1}DCA to yield ^{3}DCA with 100% efficiency. The quantum yield of natural intersystem crossing in DCA is therefore reduced from 1.7% to 0.85%. This low value, along with the low extinction coefficient (9000 cm⁻¹ M⁻¹),[11] explains why we could not detect ^{3}DCA absorption in the absence of intersystem crossing enhancers.

These results indicate that $^3O_2$ quenching of ^{1}DCA is essentially the only route to the production of $^1O_2$ by DCA and that quenchers of ^{1}DCA should decrease $^1O_2$ production unless they produce ^{3}DCA. This conclusion is tested for the *trans*-stilbene/DCA system in the accompanying paper.[20]

(20) Kanner, R. C.; Foote, C. S. *J. Am. Chem. Soc.*, following paper in this issue.