Determination of the Room Temperature Intersystem Crossing Quantum Yield of Quinoline in Alcoholic Solvents

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Summary: The room temperature intersystem crossing quantum yields, ϕ_t of quinoline in three most commonly used alcoholic solvents have been measured by the method of photosensitized peroxidation of 1,3-diphenylisobenzofuran. The proposed reaction mechanism stipulates that triplet quinoline molecules generated from their excited singlet state transfer their excitation energy to oxygen molecules present in the reaction solution. The subsequently formed excited singlet state molecular oxygen, O_2 ($^1\Delta_g$) will then peroxidize the 1,3-diphenylisobenzofuran substrate. Rate equations derived on the basis of this mechanism are used to plot experimental data and calculate results. ϕ_t values of 0.24 ± 0.04, 0.18 ± 0.04 and 0.23 ± 0.04 have been obtained for methanol, ethanol and isopropanol, respectively.

Introduction

In view of the very important role played by the excited triplet state in photophysical and photochemical processes associated with many organic and inorganic substances, the determination of the quantum yields of intersystem crossing, ISC, i.e., triplet formation efficiencies, ϕ_t has been receiving increasing attention since around the middle of the sixties. This attention was, however, mostly directed towards aromatic hydrocarbons. Heterocyclic molecules have received much less attention.

The aim of this work is to evaluate ϕ_t for quinoline at room temperature in three most commonly used alcoholic solvents: methanol, ethanol and isopropanol. It is hoped that the work will be followed up to include some aprotic solvents as well.

Few reports on the value of ϕ_t for this heterocyclic molecule have been published. A value of 0.16 in ethanol and 0.32 in dry benzene at 29°C were reported by Lamola and Hammond [1]. Hadley [2] reported a value of 0.50 ± 0.10 in rigid alcoholic glass at 77°K. Lai and Lim [3] reported that both fluorescence and triplet yields of quinoline and isoquinoline decreased with increase of temperature. Survey of recent literature did not reveal anything new regarding the value of ϕ_t for quinoline although some relevant photo studies on this molecule have been published [4-6].

The significance of quinoline which motivated this work stems from several properties that make it a particularly useful triplet sensitizer in photosensitized reactions. These desirable properties are:

Its longest wavelength absorption band peaks at about 313 nm which makes it particularly suitable for work with the 313 nm mercury line.

Its longest wavelength absorption band is sharp and strong ensuring very little or practically no absorption of radiation by the substrate as well as minimal interference in the absorption and/or emission properties of the substrate.

Its triplet energy is high enough (E_T = 21600 cm^{-1} or 463 nm (2) which results in almost diffusion controlled energy transfer to many substrates.

Several methods have been employed for the evaluation of ϕ_t in solution at room temperature. These methods include flash absorption spectroscopy which was employed by Bowers and Porter [7] and flash absorption coupled with fluorescence efficiency measurements employed by Medinger and Wilkinson [8]. Parker and Joyce [9] measured ϕ_t of compounds through their sensitization of the P-type delayed fluorescence of perylene whereas Sandros [10] used sensitized biacetyl phosphorescence to measure the triplet yield of a number of aromatic sensitizers. Lamola and Hammond [11] determined ϕ_t for compounds through their sensitization of reactions involving the triplet state of a substrate. Stevens *et al.*, [12] used the auto-peroxidation reaction with singlet molecular oxygen, $O_2(^1\Delta_g)$ to determine the ISC quantum yield of several organic compounds.

The method adopted in this work for the determination of the room temperature ϕ_t for quinoline is essentially an adaptation of the last method. The $O_2(^1\Delta_g)$ which peroxidizes the 1,3-diphenylisobenzofuran substrate is generated by the quenching of quinoline triplets. The choice of 1,3-diphenylisobenzofuran as a substrate is based on its strong reactivity with singlet molecular oxygen, $O_2(^1\Delta_g)$ and on the ease of following this reaction [13].

Kinetic Analysis

The various photophysical and photochemical processes likely to be involved in this sensitized photoperoxidation reaction are given in scheme I below. In this kinetic scheme, Q represents quinoline, F represents 1,3-diphenylisobenzofuran, $^3O_2$ represents ground state molecular oxygen, $O_2(^3\Sigma_g)$, $^1O^*_2$ represents excited singlet state molecular oxygen, $O_2(^1\Delta_g)$, the asterisk denotes electronic excitation and the number on the top left indicates state multiplicity.

Scheme I

a.	$Q + h\upsilon \longrightarrow {}^1Q^*$	Excitation
b.	$^1Q^* \longrightarrow Q$	Internal conversion
c.	$^1Q^* \longrightarrow Q + h\upsilon$	Fluorescence
d.	$^1Q^* \longrightarrow {}^3Q^*$	Intersystem crossing
e.	$^1Q^* + {}^3O_2 \longrightarrow {}^3Q^* + {}^1O^*_2$	Singlet energy transfer
f.	$^1Q^* + {}^3O_2 \longrightarrow {}^3Q^* + {}^3O_2$	Induced intersystem crossing
g.	$^3Q^* \longrightarrow Q$	Triplet unimolecular relaxation
h.	$^3Q^* + {}^3O_2 \longrightarrow Q + {}^1O^*_2$	Triplet energy transfer
i.	$^1O^*_2 \longrightarrow {}^3O_2$	Unimolecular relaxation
j.	$^1O^*_2 + F \longrightarrow FO_2$	Peroxidation

This seemingly formidable kinetic scheme is some what simplified by experimental findings. Stevens and coworkers [12,14] have concluded that the spin-allowed energy transfer process (process (e)) is unimportant even for molecules with singlet-triplet splitting much greater than 7882 cm^{-1}, which is the energy required to excite ground state molecular oxygen to the $O_2(^1\Delta_g)$ state. Potashnik *et al.*, [15] have reached the same conclusion by laser kinetic spectroscopy and attributed that to the involvement of a higher triplet state, T_2. This explanation is applicable to the case of quinoline as it has been reported [2] that quinoline has two higher triplet states T_2 and T_3 both lower in energy than its first excited singlet state.

It has also been reported [14] that the triplet state unimolecular relaxation (process (g)) does not become competitive with oxygen quenching of that state (process (h)) except at very low oxygen concentrations. Since, in the present work, the dissolved oxygen concentration is greater than 10^{-3} M even for the smallest O_2/N_2 ratio used, it will not be unsafe to disregard process (g). The above kinetic scheme is thus reduced to the following excitation and subsequent deactivation processes depicted in scheme II below:

Scheme II

$$Q + h\upsilon \longrightarrow {}^1Q^*, I_a \text{ (absorption intensity)}$$

1.	$^1Q^*$	Q	$, k_1$
2.	$^1Q^*$	$Q + h\upsilon_f$	$, k_2$
3.	$^1Q^*$	$^3Q^*$	$, k_3$
4.	$^1Q^* + {}^3O_2$	$^3Q^* + {}^3O_2$	$, k_4$
5.	$^3Q^* + {}^3O_2$	$Q + {}^1O^*_2$	$, k_5$
6.	$^1O^*_2$	$^3O_2$	$, k_6$
7.	$^1O^*_2 + F$	FO_2	$, k_7$

The rate of formation of $^1O^*_2$ which is equal to the rate of formation of $^3Q^*$ is given by

$$\text{Rate of formation of } {}^1O^*_2 = \text{Rate of formation of } {}^3Q^*$$

$$= \frac{k_3 + k_4[^3O_2]}{k_1 + k_2 + k_3 + k_4[^3O_2]} \times I_a$$

Quinoline is a very weak fluorescer with ϕ_f of ca. 0.05 (16). As mentioned earlier, its ϕ_t is ca. 0.16. This means that for quinoline, $k_1 > k_3 > k_2$. Furthermore, Since process (4) is basically spin forbidden and since the maximum solubility of oxygen in alcohol at 1 atm oxygen pressure is ca. 10^{-2} M [17], the quantity $k_4[^3O_2]$ is expected to be much smaller than k_1 - not to mention the other two constants - and may be safely neglected in the denominator. Thus,

$$\text{Rate of formation of } {}^1O^*_2 = \frac{k_3 + k_4[^3O_2]}{k_1 + k_2 + k_3} \times I_a$$

$$= \phi_t I_a + k' I_a [^3O_2]$$

Where $\phi_t = \dfrac{k_3}{k_1 + k_2 + k_3}$ is the intersystem quantum

yield of quinoline crossing in the absence of dissolved oxygen; and the new constant,

$$k' = \frac{k_4}{k_1 + k_2 + k_3}$$

Rate of peroxidation reaction,

$$R_{perox.} = I_a \{\phi_t + k' [{}^3O_2]\} \left\{\frac{k_7[F]}{k_6 + k_7[F]}\right\}$$

$$(R_{perox.})^{-1} = \left\{\frac{1}{I_a \{\varphi_t + k'[{}^3O_2]\}}\right\} \left\{1 + \frac{k_6}{k_7[F]}\right\}$$

At any fixed dissolved oxygen concentration, the first parenthesis will be constant and therefore a plot of $(R_{perox.})^{-1}$ vs. $[F]^{-1}$ should give a straight line the y-intercept of which is equal to the first parenthesis. If the intercept–at any give dissolved oxygen concentration is denoted by T, then :

$$T = \frac{1}{I_a \{\phi_t + k' [{}^3O_2]\}}$$

$$T^{-1} = I_a \phi_t + I_a k' [{}^3O_2]$$

i.e., the value of T or T^{-1} is a function of dissolved oxygen concentration. A plot of T^{-1} vs. dissolved oxygen concentration, $[{}^3O_2]$ should give a straight line, the intercept of which is equal to $\phi_t I_a$.

Results and Discussion

Data Treatment

Photolysis data were plotted by a HP LaserJet printer attached to a Pentium Dell-100 personal computer. Figure 1 a&b are typical of such plots.

Absorbance readings were converted to concentration by use of the molar absorptivity of 1,3-diphenylisobenzofuran. A polynomial curve – fitting program was used to get the equations of the various curves. These equations were then differentiated and the photoperoxidation reaction rates, $R_{perox.}$ (slopes) and corrected concentrations of 1,3-diphenyliso-

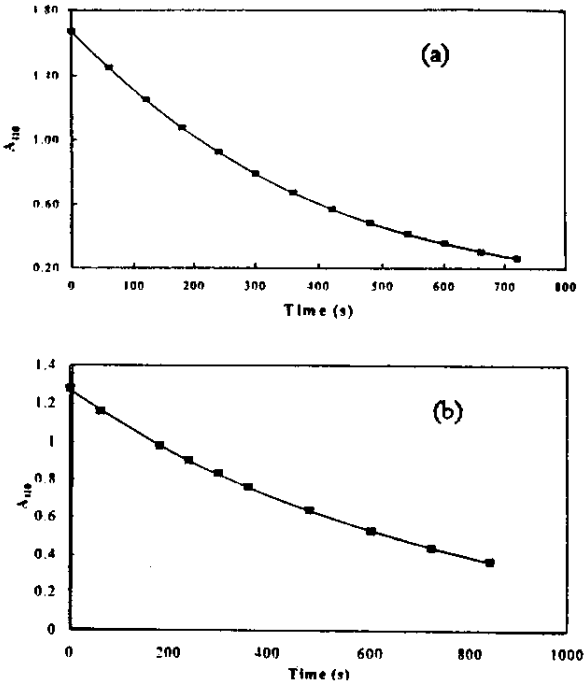

Fig. 1: Disappearance of 1,3-diphenylisobenzofuran during quinoline-sensitized photoperoxidation.
(a) in isopropanol, 10% O_2, I_a = 2.4 x 10^{-6} einst. $L^{-1}s^{-1}$.
(b) in methanol, 40% O_2, I_a = 9.1 x 10^{-7} einst. $L^{-1}s^{-1}$.

benzofuran, [F] at the various photolysis time intervals were read by the computer. Sample data obtained in this manner is shown in Table 1.

Table-1: Quinoline–sensitized photoperoxidaion of 1,3-diphenylisobenzofuran in methanol, 40 % O_2, I_a = 9.1 x 10^{-7} einst. $L^{-1}s^{-1}$

Photolysis Time (sec.)	10^5 [F]	$10^8 R_{perox.}$	10^{-4} / [F]	$10^{-7} / R_{perox.}$
0	4.42	6.21	2.26	1.61
60	4.06	5.76	2.46	1.74
180	3.42	4.94	2.92	2.03
240	3.14	4.56	3.19	2.19
300	2.87	4.20	3.48	2.38
360	2.63	3.87	3.80	2.58
480	2.20	3.28	4.54	3.05
600	1.84	2.78	5.43	3.60
720	1.53	2.37	6.53	4.22
840	1.27	2.06	7.89	4.86

A sample plot of $(R_{perox.})^{-1}$ vs. $[F]^{-1}$ is shown in Fig. 2. The linearity of such plots was best when relatively high concentrations of 1,3-

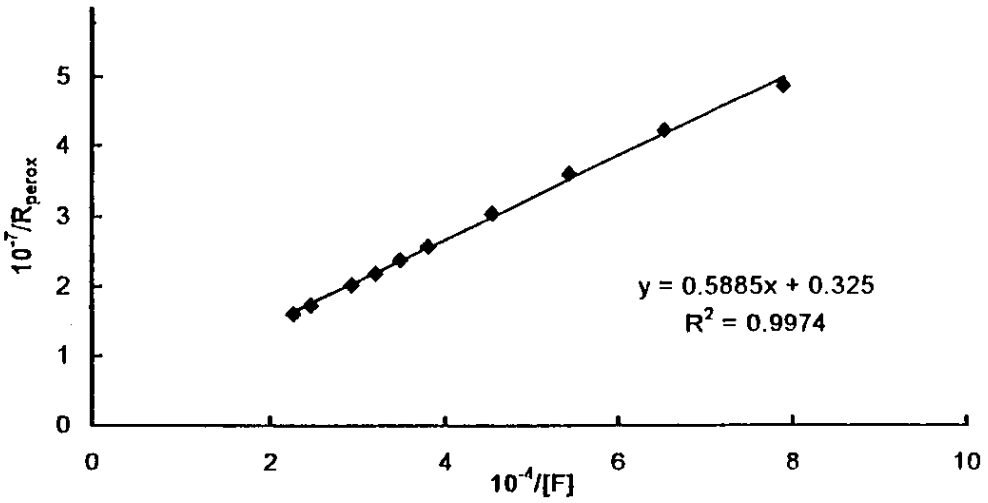

Fig. 2: Plot of reciprocal rate of the photo-peroxidation reaction vs. reciprocal concentration of 1,3-diphenylisobenzofuran in methanol, 40% O_2, $I_a = 9.1 \times 10^{-7}$ einst. $L^{-1}s^{-1}$.

diphenylisobenzofuran (ca. 6×10^{-5} M) were used. It may be appropriate to point out here that when quinoline was photolysed alone, it did not suffer any chemical change as was manifest from the constancy of its absorption peak at 313 nm.

For each of the three solvents, average values of reciprocal intercepts, T^{-1}, obtained from plots such as that shown in Fig. 2 are themselves plotted in Fig. 3 against volume percent of oxygen in the purging gas stream. Percent oxygen in the purging gas is used instead of the actual concentration of dissolved oxygen since the two quantities are proportional. According to the previously derived relation, the y-intercept of this linear plot is equal to $\phi_t I_a$.

The triplet yield of quinoline, ϕ_t at zero dissolved oxygen concentration is calculated for each solvent from the value of the intercept and the independently measured value of I_a. Table 2 summarizes the results obtained.

Table-2: Summary of results.

	Methanol	Ethanol	Isopropanol
Intercept	2.18×10^{-7}	1.63×10^{-7}	5.51×10^{-7}
I_a (einst.$L^{-1}s^{-1}$)	9.1×10^{-7}	9.1×10^{-7}	2.41×10^{-6}
ϕ_t	0.24 ± 0.04	0.18 ± 0.04	0.23 ± 0.04

The result obtained in this work for ϕ_t in ethanol is in good agreement with the previously reported value[1]. The values of ϕ_t in methanol and isopropanol are practically equal and ca. 30% higher than that in ethanol. This may be due to solvent properties and in particular possible solvent dependence of excited state quinoline lifetime.

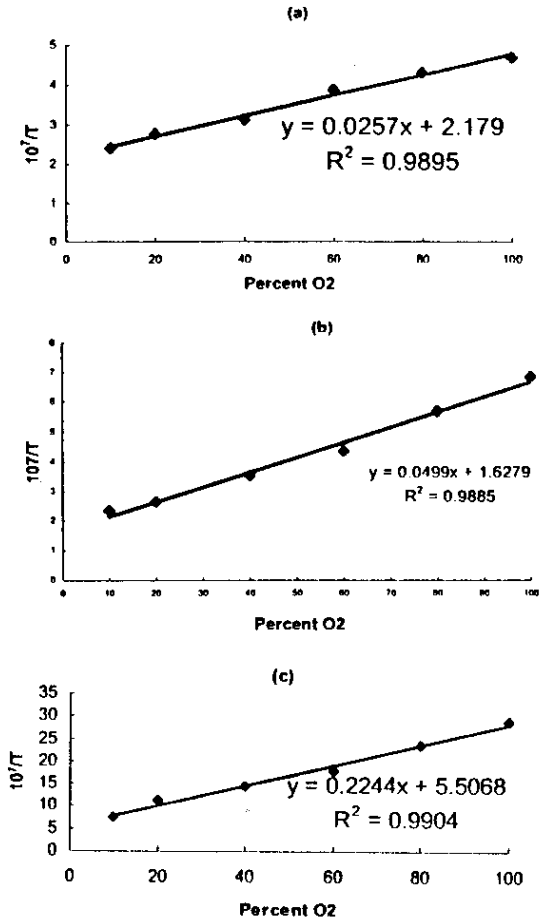

Fig. 3: Plot of reciprocal intercepts (from Fig. 2) vs. percent oxygen in the purging gas stream (a) in methanol (b) in ethanol (c) in isopropanol

An important remark regarding the method adopted in this work for the determination of ϕ_t is that there is a significant spread in the calculated values of T & T^{-1} and this spread is reflected in the estimated standard deviation of the result.

Experimental

Materials

Quinoline (Across chemicals) was purified by column chromatography on alumina. 1,3-diphenyl-isobenzofuran (Aldrich) was doubly recrystallized from methanol 1,10-phenanthroline (Fluka, > 99%), ferric cholide (BDH), potassium oxalate (BDH) and sodium acetate (PSPARK) were used without further purification. Methanol (Fluka, HPLC grade), ethanol (Gainland, A.R.) and isopropanol (Koch-Light) were fractionally distilled.

Methods

The photolysing light (313 nm) was isolated from a 100 w super pressure mercury lamp (WOTAN, HBO, 100 w) by means of a mono-chromator type F3.4 from Applied Photophysics. Photolysis was carried out in a 1-cm fused silica fluorescence cuvette placed in a cell holder fitted at the exit slit of the monochromator. The photolyte solution (3.0 mL), which was prepared from stock solutions, contained 5.1 x 10^{-4}M quinoline and ca. 6 x 10^{-5} M 1,3-diphenylisobenzofuran. The quinoline concentration was enough for almost total absorption of the photolysing light. This photolyte solution was continuously magnetically stirred by a small magnetic bar. Dissolved oxygen concentration in the photolyte solution was varied by purging for 15 minutes with different O_2/N_2 gas ratios using a Matheson model 7401 J flow meter. Volume percent of oxygen in the purging gas stream was varied from 10% up to 100% in the different runs. The gas mixture was first bubbled through two pre– saturating columns filled with the appropriate solvent and was kept bubbling slowly just under the surface of the photolyte solution throughout the photolysis time in order to maintain the constancy of dissolved oxygen concentration. Light intensity measurements were performed by standard ferrioxalate actinometry [18].

The rate of the sensitized photoperoxidation reaction of 1,3-diphenylisobenzofuran was easily followed by following the disappearance of its absorption band at 410 nm using either a Unicam UV/VIS 2–100 spectrophotometer or a Varian UV/VIS/NIR Cary 2390 spectrophotometer.

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