Photophysical Study of a Series of Cyanines

Part III. The direct photooxidation reaction [1]

Shukri Lepaja
Quendra a Arsimit të Mesë, të Orientuar 38240 Podujevë, Yougoslavie
Henry Strub
Laboratoire de Synthèse et de Photochimie Organiques, L. A. CNRS No. 135, Ecole Nationale Supérieure de Chimie, 68093 Mulhouse Cedex, France
Daniel-Joseph Lougnot
Laboratoire de Photochimie Générale, ERA CNRS No. 386, Ecole Nationale Supérieure de Chimie, 68093 Mulhouse Cedex, France

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The main degradative pathway of tricarbocyanine dyes in aerated solutions is demonstrated to be a photooxidation; using sensitization techniques and specific quenchers, this reaction is established to proceed via singlet oxygen *for a part*, and the site at which this species attacks the polymethinic skeleton is unambiguously determined. The major photoproduct is identified as being 1,3,3-trimethyl-2-indolinone.

Direct Photooxidation of Tricarbocyanine Dyes

Introduction

During the past decade, cyanine dyes which were known hitherto as spectral sensitizers in silver halide photography, have found a new commercial application: this class of dyes, and expecially polycarbocyanines, have been extensively used as laser dyes [2]. However, two points attract the attention of chemists who were entrusted with improving the performances of this type of lasers:

(i) the conversion yields are actually very low and never exceed a few percents; this problem has been demonstrated to be connected to transient species which are generated in the active medium by the pumping light and which absorb photons and act as dead-loss pathways [3]; their mastery is difficult to reach and requires a thorough knowledge of the photophysical behaviour of the dyes;

(ii) the second point refers to chemical and photochemical stability, a property which governs the longevity of the dye used as an active medium and determines its ability to work in the repetitive mode. A number of paths by which cyanine dyes in general may become degradated have been outlined [4].

Photooxidation has been established to play the major part in the degradation mechansim of cyanine, carbocyanine and dicarbocyanine dyes [5]. Tricarbocyanine photodegradation is in process of thorough elucidation [6]. In that case, oxygen and light are also the essential agents of the degradation of these long chain polymethine cyanines.

The present paper is concerned with the documentation of this reaction and with the unambiguous determination of the oxidation site.

Experimental Part

The dyes used herein were prepared and purified by standard synthetic procedures [7]. All dye samples appeared to be pure by thin layer chromatography (one spot). The sensitizers – Rose Bengal and Thionine-Eastman certified grade – were recrystallized first from water, then from ethanol.

Quantitative photolyses were performed on an optical bench employing the following appropriately connected elements: (1) a 250 W Osram xenon lamp, (2) a mount for 2′ × 2′ optical filters, (3) a 4 in. Pyrex collimating lens, (4) a masked sample holder for 1 cm × 1 cm optical cells. Chemical actinometry up to 460 nm was effected with ferrioxalate according to the technique described by Parker [8]. Beyond 460 nm and especially in the near infrared part of the spectrum, the lamp was calibrated at the wavelengths used in the present work with an

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Reprint requests to Dr. D. J. Lougnot, Laboratoire de Photochimie Générale, Èquipe de Recherche Associèe au CNRS 3, rue Alfred Werner, 68093 Mulhouse Cedex, (France).

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adequate set of interferencial narrow band filters and a red photomultiplier RCA XP 1005. The response curve of the photomultiplier being calibrated at 410 nm and 460 nm by chemical actinometry as a preliminary, the absolute intensities emitted in the red and near infrared became readily available through simple proportion.

Degradation involving quantum yield measurements were generally carried out to less than 10% conversion in order to allow colorimetrical determinations of dye consumption. Photosensitized degradations under laser excitation were done by irradiation in a 1 × 1 cm spectrophotometric cell through a calibrated mask. A telescope was employed to spread the laser optimally over the entire sample. The laser was a Spectra Physics argon laser – model 171.19 – associated with a Scientech 360 power meter.

Quantitative analysis for dye degradation were performed on a Cary model 15 spectrophotometer. The concentrations were deduced from optical densities measured at the absorption maximum (740 nm for HITC and 800 nm for IR 140). IR spectra were recorded with a Perkin-Elmer apparatus, model 580 B. ^{1}H NMR spectra at 80 MHz were obtained with a Brucker W.P. 80 D.S. spectrometer. The spectra are Fourier transform of 500 free induction decays obtained under the following conditons: 45 ° pulse angle, 8 K data points, 1875 Hz spectrum width, and a pulse delay of 2 s. Photodegradation for NMR analyses were performed by full blast irradiation in 5 nm NMR tubes of acetone-d_6-solutions containing ca. 2×10^{-3} M dye through a cutoff filter which prevents spurious UV irradiation.

All solutions were prepared and handled under adequate safelight conditions. Deaeration was accomplished by bubbling through the solutions a aolvent saturated N_2 flow at 1 l/min.

Results

1. The dyes

The polymethines investigated herein are both tricarbocyanines: the model compound – hexamethylindotricarbocyanine iodide (HITC) – is one of the most commonly used dyes capable of producing laser effect in the near infrared; this dye is reputed to have a good stability in alcohols and DMSO [9]. The second dye labeled as IR 140 by Eastman Kodak is also a polymethine with, as a major difference, a polymethinic chain rigidized by bridging the central carbons together. This series of IR dyes and IR 140 in particular, have actually been designed with the aim of increasing the fluorescence quantum yield of polycarbocyanine: in fact, this process which is known to compete with internal conversion was expected to be indirectly favoured with decreasing the flexibility of the polymethine chain [10]. Formulae are given in Figure 1.

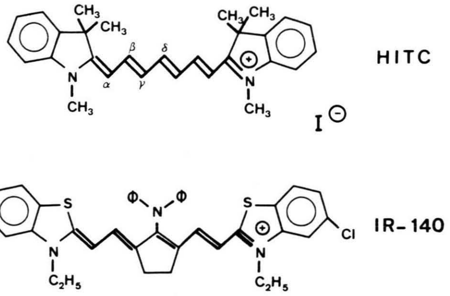


Fig. 1. Developed formulae of HITC and IR 140.

2. The role of oxygen

Figure 2 demonstrates the determinant part played by oxygen in the photolysis of IR 140 taken as an example. The results referring to HITC are quite simular, except the overall degradation rate which is significantly slower. The curve marked N_2 corresponds to a dye solution deaerated by N_2 bubbling only. As could be expected, this procedure is not thorough enough to reduce the residual oxygen concentration far below the dye concentration (ca.

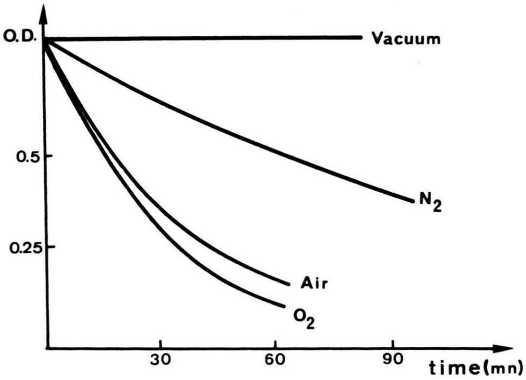


Fig. 2. Influence of dissolved oxygen upon the degradation rate of IR 140 in DMSO. Each sample was photolyzed through a cut-off filter transmitting λ > 520 nm.

Table 1. Photolysis quantum yields of the dyes in aerated solution; $\lambda_{excit} = 695$ nm and initial OD = 0.80.

$\Phi \times 10^4$	MeOH	Acetone	DMSO	Chloroform
HITC	0.5	1.5	2.7	8
IR 140	6	19	39	37

10^{-5} M), whence the requirement of high vacuum techniques in this deaeration. The degradation quantum yields are reported in Table 1.

3. *The oxidation mechanism*

The photolysis of these dyes is henceforth considered as a photooxidation, a conclusion which is in agreement with previous statement concerning polymethine with shorter polymethine chains. However, the question araises as to whether this degradation proceeds via a cage reaction involving the dye and oxygen or whether it is merely a diffusion controlled autosensitized photooxidation via singlet oxygen. The following procedure has been called for to determine the relative extent of these two processes. In a first step, specific quenchers of singlet oxygen have been gradually incorporated in a dye solution; the results obtained with diazabicyclooctane as a quencher, are reported in Fig. 3 which shows that, even at huge concentrations, DABCO is not able to fully inhibit the dye photolysis. This conclusion is also arrived at with HITC in any solvent, except that the extent of the residual degradation is more or less important.

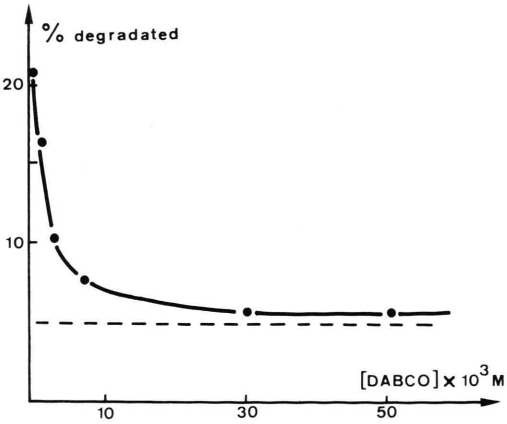


Fig. 3. Influence of DABCO concentration upon the degradation of IR 140 in CH_3CN. Each sample was photolyzed during 10 mn through a cutt-off filter transmitting $\lambda > 520$ nm.

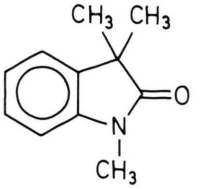
It must therefore be concluded that the two oxidative reactions mentioned above proceed concurrently in aerated solutions of HITC and IR 140.

An important point to be emphasized concerns the reaction products. Actually, when comparing the spectra or the TL chromatograms of the photoproducts, generated by direct irradiation, and the ones obtained by classic photosensitization (monochromatic excitation of a triplet sensitiser such as thionine by the 514 line of an argon laser), it becomes evident that the two pathways qualitatively result in the same set of photoproducts. The detailed mechanistic investigation of these two reactions is under way and will form the subject of a forthcoming paper [6]. Anyhow, owing to that conclusion, the problem of the identification of the oxidation site becomes easier to approach. In fact, the close likeness between the photoproducts generated by the two reaction pathways (at least with regard to the major elements) allows the photolysis mechanism to be reduced to a global reaction affecting one site and resulting in a set of products as far at least as the chemical aspect of the photolysis is considered.

4. *The IR spectra*

This work being devoted to the identification of the oxidation site and to the determination of the agents of the photodegradation, infrared spectroscopy was used, only as an analytical tool. In that context, the IR spectra of HITC and IR 140 were recorded at different stages of photolysis.

In the case of HITC, the major change appears in the region corresponding to carbonyl vibrations. In particular, an intense band is observed at 1711 cm^{-1}, a wavenumber where 1,3,3-trimethyl-2-indoline (**1**) also exhibits a characteristic absorption [11]. Though less plain, the case of IR 140 is quite similar, with a carbonyl absorbing at 1700–1720 cm^{-1}.



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5. *The NMR spectra*

This study was undertaken in acetone which appeared to be the best solvent in terms of (i):

Table 2. ^{1}H-NMR data relative to HITC, its photoproduct and authentic indolinone **1** obtained in d_6-acetone.

Product	Chem. Shift [ppm]	Multi- plicity	Assignment	
HITC	1.72	S	12 H	Geminated CH_3
	3.69	S	6 H	CH_3 on nitrogen
	6.39	D	2 H	$H\alpha$
	6.59	T	2 H	$H\gamma$
	7.1–7.6	–	8 H	Aromatics
	7.87	T	1 H	$H\delta$
	8.04	DD	2 H	$H\beta$
1	1.28	S	6 H	Geminated CH_3
	3.16	S	3 H	CH_3 on nitrogen
	6.87–7.35	–	4 H	Aromatics
Photo- product	1.28	S		Geminated CH_3
	3.16	S		CH_3 on nitrogen
	3.30	S		?
	6.5–8.3	–		Aromatics

solubility; a concentration of 1 mg in 1 ml is easily reached; (ii) photolysis duration; the time required to degradate a large part of the dye and to induce significant changes in its spectrum is in the order or a few hours; (iii) degradation mechansim; though faster than in solvents of current use in laser technology, the degradation behaves identically herein [12]; and (iv) spectrum identification; the spectra of starting material, photolysis products, solvent and residual water slightly overlap but the disentanglement is rather easy.

The NMR spectrum of HITC was recorded in acetone-d_6; the assignments were made on the basis of a previously published NMR analysis of this type of long chain polymethine [13]. Table 2 summarizes the different characteristic resonance frequencies of HITC.

In the course of the photolysis, the lines assigned to starting material resonances decrease identically and three sharp singlets emerge at 1.28, 3.16 and 3.30 ppm and increase with the irradiation time. The intensities of these signals are proportional to 8, 4 and 1 respectively. Besides these lines the spectrum shows, after quite complete conversion a large mount which speads from 0.5 to 3.2 ppm, a region corresponding to hydrogens carried by sp^3 carbons.

The singlets at 1.28 and 3.16 ppm belong to the methyl groups of 1,3,3-trimethyl-2-indolinone the NMR frequencies of which are reported in Table 2. Upon comparison of the integrated intensity of these two peaks with that of the large mount in the sp^3 hydrogen region, and assuming that this mount only corresponds to methyl signals belonging to side products, the chemical yield is estimated to be at least 40% of **1**.

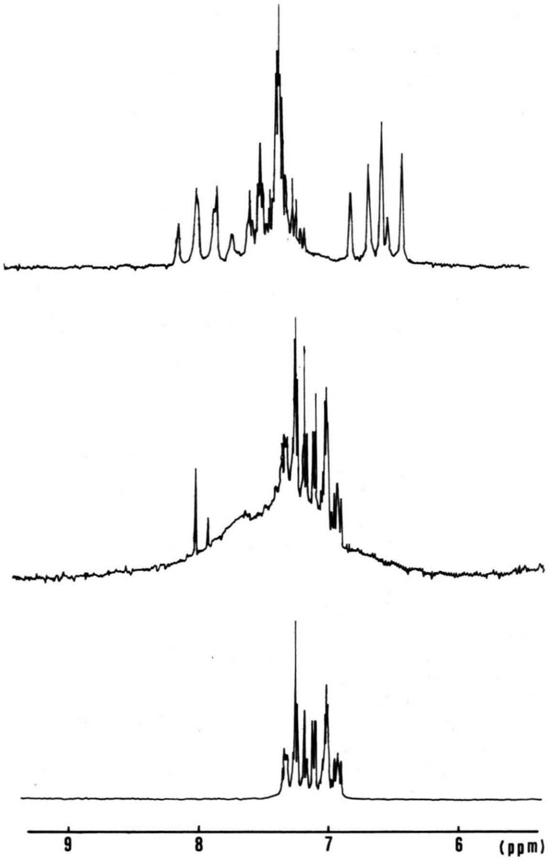

Fig. 4. ^{1}H-NMR spectra of the aromatic protons of HITC (*top*), photoproducts (*middle*) and authentic indolinone 1 (*bottom*) in d_6-acetone.

In the region corresponding to the aromatic protons one also observes another large band, out of which emerges a series of lines. These lines are unambiguously assigned to the four aromatic hydrogens of **1** by comparison with the spectrum of authentic material (Figure 4). It is worth noting that the integrated intensity ratio between the two components of this part of the spectrum leads also to a 40 percent chemical yield in favour of **1**.

Conclusion

Singlet oxygen was known to be able to induce degradation of most cyanines; this species is demonstrated herein to contribute to the photolysis of tricarbocyanines. However, ground state oxygen is also able to interact with a triplet excited dye molecule and to play a more or less important role in the overall reaction scheme which governs the photostability of these dyes.

By analogy with the results of previous studies devoted to shorter polymethines carrying the same type of end groups and owing to spectroscopical analysis, the site of the chain attack by singlet oxygen was determined. The major photoproduct is consistent with 1, 2 addition to the cyanine 2–8 bond followed by fragmentation to carbonyl compounds.

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