THE PHOTOCHEMISTRY OF ISATIN

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Summary

Isatin does not show fluorescence or phosphorescence under any conditions. After excitation it undergoes rapid intersystem crossing to the triplet state (τ = 340 ns in deaerated benzene). This triplet state is capable of hydrogen abstraction, yielding a product analogous to pinacol, isatide. In the absence of a hydrogen-atom donor, isatoic acid anhydride is formed as the main product.

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1. Introduction

The starting point of our investigation was to answer the question whether isatin shows fluorescence and/or phosphorescence under certain conditions. We observed a weak emission in a number of experiments, and this was strongest in a deaerated methanol solution, but the reproducibility was very unsatisfactory and there was no good accord between the fluorescence excitation spectrum and the absorption spectrum. In the course of our studies we have shown that this emission was due to decomposition products formed in a photochemical reaction.

In this paper we report on the photochemistry of isatin in different solvents, and include some nanosecond laser flash spectroscopic results for a transient species of isatin.

2. Experimental details

2.1. Materials

Isatin was recrystallized several times with water. *N*-Acetylisatin was synthesized according to ref. 1, and *N*-methylisatin was prepared according to ref. 2 and recrystallized with benzene. For comparison, isatide, isatoic acid anhydride (1-*H*-benz[3,1]oxazine-2,4-dione), *N,N'*-diacetylisatide and *N*-acetylisatic acid were synthesized according to refs. 3, 4, 5 and 6 respectively.

The identity and the purity of these compounds were established by elemental analysis, melting point determination, IR spectroscopy, mass spectrometry, proton nuclear magnetic resonance spectroscopy (^{1}H NMR), ^{13}C NMR and thin-layer chromatography.

2.2. Techniques

UV–visible absorption spectra were recorded on an M40 spectro-photometer (Carl Zeiss Jena, G.D.R.).

Fluorescence and fluorescence excitation spectra of solutions with optical densities below 0.05 were measured with an FICA MKII (France) self-correcting spectrofluorometer. Fluorescence quantum yields were obtained using quinine bisulphate in 1.0 M H_2SO_4 ($\phi_F = 0.55$) as the standard. Deaerated solutions were prepared by bubbling oxygen-free nitrogen through the solutions for 15 - 30 min, and then the samples were either stoppered or sealed. A stabilized high pressure mercury lamp (HBO 200) with appropriate filters or a high intensity monochromator was used for irradiation. Quantum yield determinations were made spectrophotometri-cally using a chemical actinometer system as described in ref. 7. For the determination of the chemical yield, 50 ml of a saturated isatin solution was deaerated, sealed and irradiated until it had completely decomposed. The precipitate was then separated and both the precipitate and the solution were analysed.

Fluorescence lifetime measurements were obtained using a sampling technique (N_2 laser apparatus; LIF 200, ZWG, G.D.R.). For the nanosecond laser flash photolysis a set-up was used as described in ref. 8 (excitation by the second harmonic of a Q-switched ruby laser; $\lambda = 347.2$ nm; pulse width, 15 ns or less; pulse energy, about 60 mW s).

3. Results and discussion

3.1. UV–visible absorption spectra and photochemical reactions

The UV–visible absorption spectra of isatin and N-acetylisatin are shown in Fig. 1. The effect of the solvent on the position of the longest-wavelength absorption band is given in Table 1. The bathochromic shift of the position of the longest-wavelength absorption band of isatin which results on increasing the polarity of the solvent indicates that the $n\pi^*$ transition has some charge transfer character (the nitrogen atom being the electron donor and the β-carbonyl group the acceptor). (For quantum chemical calculations concerning the nature of the longest-wavelength transition of isatin see ref. 9.) Reducing the donor ability of the nitrogen atom as in N-acetylisatin results in the "normal" behaviour of an $n\pi^*$ transition.

The photochemical reaction can be followed by monitoring the absorption spectrum in a dilute solution (at higher concentrations the solution becomes turbid owing to the formation of a precipitate). An example is given in Fig. 2. The quantum yield of this reaction is strongly dependent on
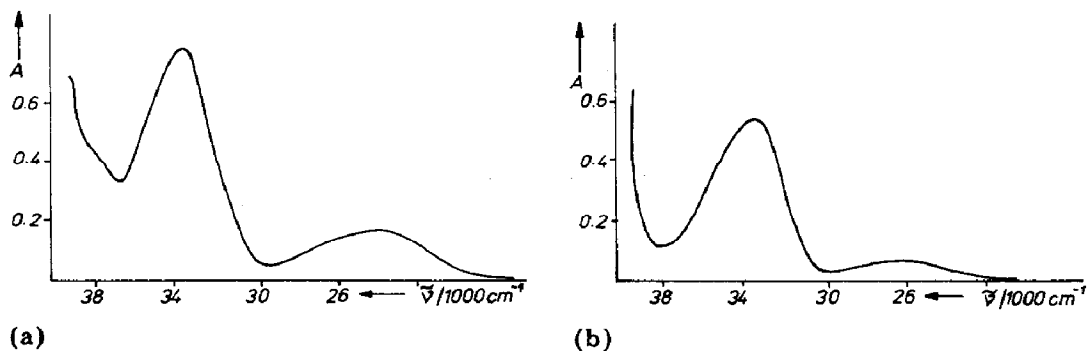
Fig. 1. Absorption spectra of (a) isatin in methanol and (b) N-acetylisatin in ethanol.

TABLE 1

Effect of solvent on the longest-wavelength absorption maximum $\tilde{\nu}_A$ of isatin and N-acetylisatin

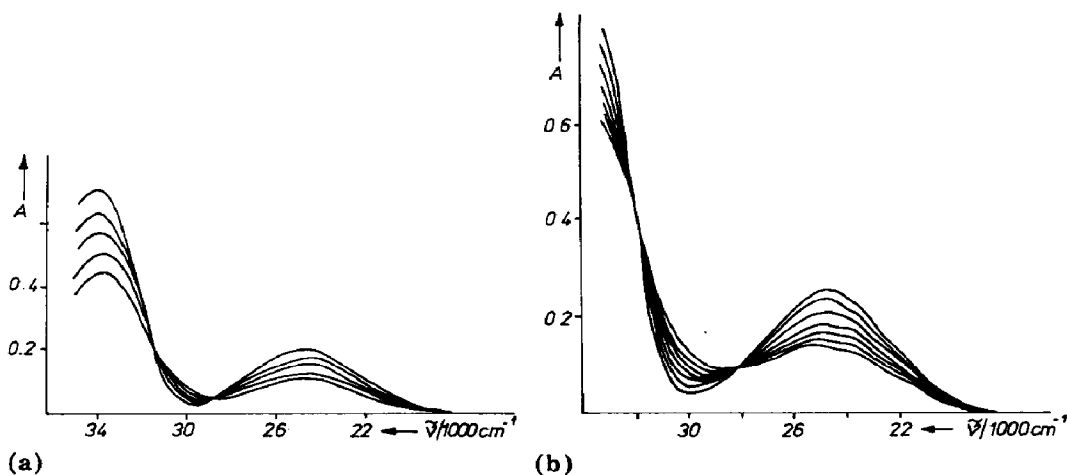| Solvent	$\tilde{\nu}_A$ (cm^{-1})	
	Isatin	*N-Acetylisatin*
Cyclohexane	25300	26670
Benzene	24810	—
Toluene	24810	26370
Chloroform	24100	—
Dimethyl sulphoxide	23920	27030
Dimethylformamide	23920	—
Acetonitrile	24100	—
Ethanol	23810	28800

Fig. 2. Photochemical decomposition of isatin (a) in argon-purged cumene (λ_{irr} = 405 nm); (b) in argon-purged benzene (λ_{irr} = 405 nm).

TABLE 2

Effect of oxygen on the photochemical quantum yield ϕ_R of the decomposition of isatin

Oxygen concentration	Photochemical quantum yield ϕ_R		
	Xylene	Cumene	Benzene
Argon purged	0.035	0.060	0.018
Air saturated	0.015	0.002	0.003
Oxygen saturated	0.006	—	—

the oxygen concentration and the solvent (Table 2). It is highest in toluene, xylene and cumene; practically no photochemical reaction occurs in methanol, ethanol or isopropanol.

The oxygen dependence of the photochemical reaction suggests that the triplet state of isatin may be involved. Further confirmation of this idea comes from the fact that *trans*-stilbene also quenches this reaction (Stern–Volmer constant $K_{SV} = 2900$ M^{-1}). Since solvents such as toluene, xylene and cumene are typical hydrogen-atom donors, the photochemical reaction of a carbonyl compound such as isatin could be expected to involve hydrogen-atom abstraction and a product related to pinacol may be expected. Analysis of the photoproduct indeed revealed that isatide (1) was formed as the main product (more than 90%). Thus, the following reaction scheme can be given:

Scheme 1.
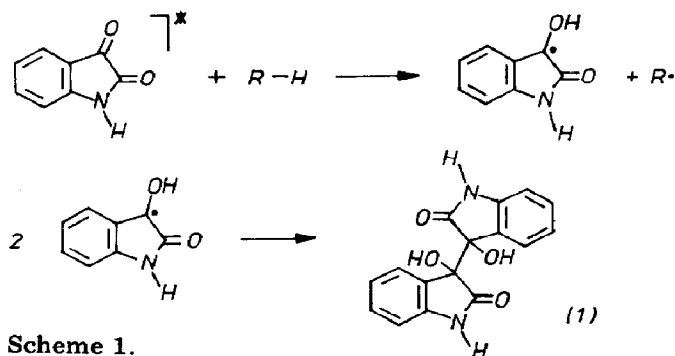
Quite a different photochemical reaction was observed in benzene. Since benzene is a very poor hydrogen-atom donor, it was not surprising that no isatide could be detected. Nevertheless, photodecomposition of isatin also occurs in benzene, although with a lower yield (Table 2). The product analysis yielded isatoic acid anhydride (1-*H*-benz[3,1]oxazine-2,4-dione) (2). It is quite astonishing that this product should be formed because chemically it can only be formed from isatin by the action of a strong oxidant (*e.g.* chromic acid). In our case, it is formed photochemically in the absence of oxygen. A possible mechanism could be the reaction of an excited isatin molecule with a ground state molecule:
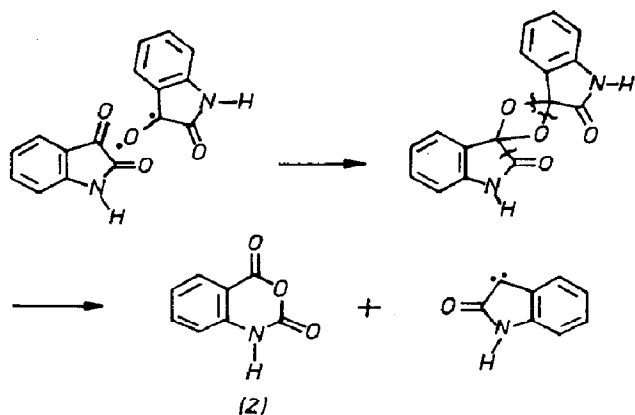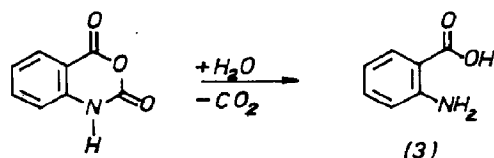
Scheme 2.

There was some support for this suggestion from the finding that the quantum yield for the decomposition of isatin and that for the product formation increased with increasing isatin concentration (Table 3). However, a kinetic analysis gave no satisfactory results.

TABLE 3

Effect of isatin concentration on the photochemical quantum yield

| Isatin concentration (×10⁻⁴ M)	Photochemical quantum yield ϕ_R
7.2	0.018
5.0	0.016
3.3	0.015
1.4	0.013

From the determination of the chemical yield it can be concluded that the traces of oxygen still remaining could not account for the total amount of isatoic acid anhydride formed in the photochemical reaction. Therefore, the involvement of oxygen can be excluded. However, owing to the formation of somewhat polymeric byproducts and the sensitivity of these products to the atmosphere, an exact determination of the chemical yield was not possible. We also tried to utilize the fluorescence of isatoic acid anhydride to monitor the photochemical reaction. In this way we found that once formed the isatoic acid anhydride reacts further to give anthranilic acid (3) (which is a strongly fluorescent species), possibly hinting at the involvement of water:

Scheme 3.

Thus, the mechanism given above remains rather speculative and a more detailed investigation, perhaps under conditions where oxygen and water are rigorously excluded, might be necessary to evaluate the true mechanism of the reaction.

The results obtained with *N*-acetylisatin may be of interest. For this compound in deaerated xylene a decomposition quantum yield of 0.25 was found, which is about six times greater than that for isatin. However, the product formed is neither the corresponding *N,N'*-diacetylisatide nor *N*-acetylisatoic acid anhydride, but is *N*-acetylisatic acid (4):

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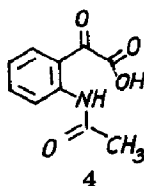
This compound is obviously formed by photohydrolysis, again indicating that water may play a crucial role. In addition, this result underlines the role of the nitrogen atom as an electron donor. The more this role is restricted the higher is the photochemical reactivity of the carbonyl group. This is further supported by the observation that *N*-methylisatin (methyl substitution increases the ability of the nitrogen atom as an electron donor) is photochemically completely inactive. By following the same line of reasoning one can also understand the absence of a photoreaction in alcohol solution, because this solvent, as indicated indirectly by the bathochromic shift, favours a charge transfer.

3.2. Nanosecond laser flash photolysis

A saturated solution of isatin in benzene ($c = 5.3 \times 10^{-4}$ M) was flashed by the second harmonic of a ruby laser ($\lambda = 347.2$ nm). A transient spectrum was obtained with a maximum at 420 nm. The decay time τ of this transient in an argon-purged solution amounted to 340 ns. In an air-saturated solution a value of $\tau = 165$ ns was obtained. With an oxygen concentration of 1.9×10^{-3} M a quenching rate constant $k_q = 1.7 \times 10^9$ M^{-1} s^{-1} is obtained, which is quite a reasonable value for triplet quenching by oxygen. The addition of *trans*-stilbene ($c = 9.4 \times 10^{-4}$ M) to an argon-purged benzene solution led to the lifetime being shortened to 80 ns, which yields the quenching constant $k_q = 1 \times 10^{10}$ M^{-1} s^{-1}, corresponding to a diffusion-controlled quenching reaction and strongly indicating that the transient species can be assigned to the triplet state of isatin.

Keeping in mind that the photoreactions are also quenched by oxygen and stilbene and that no fluorescence could be observed, it can be concluded that all the photoreactions are performed via the triplet state, which is reached by a very fast intersystem crossing process.

3.3. Fluorescence

Returning to our starting point, the original aim of our studies was to find out whether isatin shows any fluorescence or phosphorescence. There-

fore the emission behaviour of isatin was studied in a variety of solvents. In all cases a weak emission in the range 370 - 390 nm could be observed. However, a comparison with the fluorescence of the isolated photoproducts revealed that these photoproducts were the origin of this emission. This finding could be further supported by the observation that when a solution of isatin is prepared in the dark, and the fluorescence monochromator is set at the expected fluorescence wavelength to avoid the sample being exposed too long to the excitation light, it does not show any emission ($\phi_F < 10^{-4}$). After several minutes the fluorescence began to build up, and this clearly indicates that the fluorescence originates from photodecomposition products. Also, at the temperature of liquid nitrogen (in both ethanol and toluene), no emission could be observed as soon as the formation of decomposition products was prevented.

Absorption and fluorescence data for isatoic acid anhydride and anthranilic acid are given in Table 4.

TABLE 4

Absorption and fluorescence data of the decomposition products, isatoic acid anhydride and anthranilic acid (λ_A, longest-wavelength absorption maximum; ϵ, absorption coefficient at λ_A; λ_F, fluorescence maximum; ϕ_F, fluorescence quantum yield; τ_F, fluorescence lifetime)

Solvent	λ_A (nm)	ϵ ($M^{-1}\,cm^{-1}$)	λ_F (nm)	ϕ_F	τ_F (ns)
Isatoic acid anhydride					
Benzene	313	—	365	0.08	—
Ethanol	316	3600	375	—	—
1,2-Dichloroethane	313	3600	365	0.06	1.5
Anthranilic acid					
Benzene	338	—	390	0.35	6.6
Ethanol	335	—	405	0.52	10.5
1,2-Dichloroethane	347	4800	418	0.30	6.6

Acknowledgments

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