LASER PHOTOLYSIS OF INDOLE IN CYCLOHEXANE

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Summary

Indole in cyclohexane was studied by nanosecond laser photolysis. The fourth harmonic (265 nm, 30 ns FWHM) of a Q-switched Nd^{3+}-doped glass laser was used for excitation; transient absorption changes were measured by kinetic spectrophotometry. Transient absorption spectra appearing after excitation were attributed to the indole triplet state and to the indole radical, respectively. Extinction coefficients of the indole triplet were determined using triplet naphthalene as reference. From the decay kinetics, a triplet lifetime of 16 μs was obtained at low triplet concentrations. T—T annihilation was observed at higher triplet concentrations, with a rate constant of 7×10^9 s^{-1} M^{-1}. It was shown that the radical is formed in a one-photon process from the excited singlet state. A complementary study of 1-methylindole indicated that the radical is created by dissociation at the N—H bond. Extinction coefficients of the indole radical were also determined. A study of indole in methylcyclohexane as a function of temperature indicated that radiationless transition from the excited singlet state to the ground state is not significant.

Introduction

In a previous communication [1], we presented preliminary results on the primary photophysical and photochemical processes of indole in polar and non-polar solvents, obtained by nanosecond laser photolysis with excitation at 265 nm. Bent and Hayon [2], and Bryan *et al.* [3] used the same technique in studies of aqueous solutions of indole [2] and indole derivatives [2, 3], particularly tryptophan. Previous work by conventional flash photolysis [4, 5] had shown that a photoionization process is occurring in aqueous solution, in competition with fluorescence and intersystem crossing to the triplet state. In the laser studies, these processes could be studied in more detail owing to the higher time resolution available. The quantitative analysis

of the transient absorptions is complicated, however, because of the number of transient species involved (triplet indole, indole radical and radical cation, hydrated electron). To assist in this analysis, we have undertaken a complementary study of indole in cyclohexane. The photoionization reaction is absent in this solvent, and it was thus possible to study the indole triplet state without interference from the photoionization reaction products. The results obtained are discussed in the present article.

Experimental

A Q-switched Nd^{3+}-doped glass laser with frequency-quadrupling produced excitation light pulses at 265 nm with 30 ns pulse width at half-maximum. The laser light was directed into a 1 cm square spectrophotometry cell with polished windows, containing the sample. The transient light transmission changes in the sample were monitored in a crossed-beam configuration, using a xenon flash lamp (1 ms duration) as light source. The light intensity of the flash was constant within 2% over the maximum interval of measurement. After passing through the solution and through a monochromator, the measuring light was directed onto a photomultiplier tube whose signal was recorded as a function of time using one of the beams of a double-beam oscilloscope. The other beam received the integrated output from a photodiode viewing a small fraction of the laser light. The apparatus has been described briefly previously [6].

Indole (Merck) was purified by sublimation. 1-Methylindole (Fluka) and naphthalene (Aldrich, Golden Label) were used as received. Cyclohexane (Merck) and methylcyclohexane (Eastman) were of spectroscopic grade. The solutions were deaerated by 4 cycles of freeze–pump–thaw in a bulb sealed to the cell. They were saturated with argon between each degassing cycle and kept in argon atmosphere during the runs. The study was made at room temperature (23 °C) except where otherwise stated. In the low temperature runs, the sample cells were placed in a Dewar flask cooled by a flow of cold nitrogen gas. Absorption spectra were measured using a Cary 14 spectrophotometer.

Results and Discussion

Indole triplet spectrum

Laser pulse excitation at 265 nm of indole in deoxygenated cyclohexane produced a transient absorption with maxima at 350 and 430 nm [Fig. 1, curve (a)]. This absorption appeared with maximum intensity at the end of the pulse, and decayed over a period of a few microseconds. After this rapid decay an absorption of different structure remained which lasted some tens of microseconds. The transient absorption intensities were directly proportional to the laser pulse energy, indicating one-photon excitation. The effects were the same in thoroughly dried cyclohexane as in the untreated solvent.
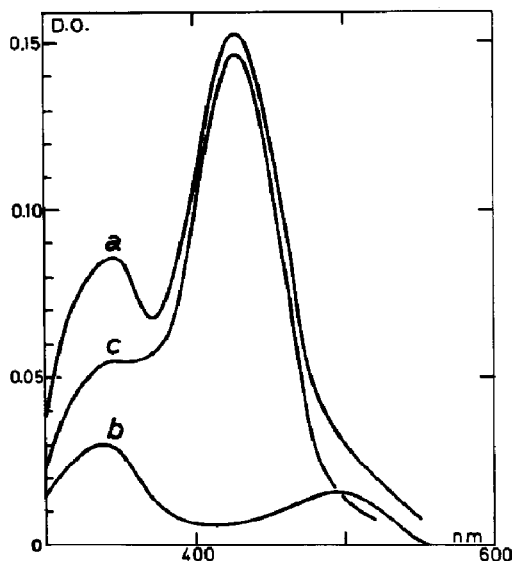
Fig. 1. Transient absorption spectra appearing after laser pulse excitation at 265 nm of 2×10^{-4} M indole in cyclohexane, at room temperature. (a) Absorption spectrum measured at the end of the laser pulse, degassed solution; (b) absorption spectrum measured 2 μs after laser excitation of an aerated solution (indole radical); (c) difference between spectra (a) and (b) (indole triplet).

In the presence of triplet quenchers such as *cis*-piperylene or oxygen, the rate of decay of the first transient spectrum was strongly enhanced whereas the longer-lasting absorption was unaffected. This result indicates that the strong absorption is due to the triplet state of indole; it also shows that the long-lasting spectrum is not formed from the triplet state.

The long-lasting spectrum is shown in Fig. 1 (b) as obtained in the presence of air. Under these conditions a higher precision (no triplet absorption overlap) was obtained than in the absence of oxygen. The difference between Fig. 1 (a) and (b) [Fig. 1 (c)] then represents the triplet absorption spectrum. This spectrum has a maximum at 430 nm and a pronounced shoulder at 350 nm. In water of pH 7, Bent and Hayon [6] reported an absorption maximum of the triplet state at about 440 nm.

We obtained the extinction coefficient of the indole triplet maximum at 430 nm using naphthalene in cyclohexane as reference. Degassed solutions containing indole and naphthalene, respectively, were prepared at concentrations such that the o.d. of both solutions was the same at 265 nm. The solutions were exposed to laser pulses of the same energy and the transient absorption intensities (D_T) due to triplet formation were measured. Under these conditions, the D_T values for indole (superscript I) and naphthalene (N) are related to the triplet extinction coefficients (ϵ_T) and the triplet quantum yields (Φ_T) by the expression $\epsilon_T^I = \epsilon_T^N \Phi_T^N D_T^I / \Phi_T^I D_T^N$. The naphthalene triplet was monitored at its 414 nm absorption peak ($\epsilon_T^N = 24{,}000$ M^{-1} cm^{-1}) [7] and that of indole at 430 nm. From $\Phi_F^N = 0.23$ in cyclohexane [8] and considering [9] that $\Phi_F^N + \Phi_T^N = 1$, one obtains from the experimental

results $\epsilon_T^I \, \Phi_T^I = 2000 \, M^{-1} \, cm^{-1}$. Assuming that the quantum yields of photochemical reactions and the probability of the excited singlet to ground state radiationless transition is negligible (see below), one obtains $\Phi_T^I = 1 - \Phi_F^I$. A Φ_F^I value of 0.49 in degassed cyclohexane has recently been reported [10]; this gives $\Phi_T^I = 0.51$. Arce and Ramirez [11], on the other hand, determined a lower value of 0.34 for Φ_T^I in MTHF at 77 K. Using the higher value, one obtains $\epsilon_T^I \approx 4000 \, M^{-1} \, cm^{-1}$ at the 430 nm maximum. Recently, Ghiggino *et al.* [12] reported for the similar compound tryptophan a triplet extinction coefficient of $3700 \, M^{-1} \, cm^{-1}$ at the triplet absorption peak at 480 nm, in a dry PVA film.

The assumption that internal conversion (radiationless transition from the excited singlet to the ground state) is absent was supported by the results of a study of the indole triplet yield as a function of temperature. Methylcyclohexane was used as a solvent in this case. It was found that the o.d. increase at 430 nm was independent of temperature to within 10% between 180 K and room temperature (after correction for concentration variations). As a general rule, internal conversion increases with temperature, thus affecting the triplet yield. The absence of temperature effect on the triplet yield then strongly indicates that internal conversion does not occur to a significant extent.

Indole triplet kinetics

The decay kinetics of the indole triplet state were monitored at 430 nm, at a range of indole concentrations and laser energies. The kinetic analysis was based on the hypothesis that the following deactivation processes may occur:

$$I_T \quad \rightarrow I \qquad (\text{rate constant } k_1) \qquad (1)$$

$$2I_T \quad \rightarrow 2I \qquad (k_2) \qquad (2)$$

$$I_T + I \rightarrow 2I \qquad (k_3) \qquad (3)$$

Reaction (1) includes phosphorescence and quenching by solvent impurities, reaction (2) is the net result of triplet–triplet annihilation, and reaction (3) is concentration quenching of the triplet state.

At low laser energies, the triplet decay was independent of the laser energy and also of the overall indole concentration. Values of $k_1 = 6.2 \times 10^4$ s^{-1} (triplet lifetime = 16 μs) and $k_3 < 10^8 \, s^{-1} \, M^{-1}$ were obtained. At higher laser energies, T–T annihilation increased the rate of decay. It was in this case important to render the laser light homogeneous by placing a depolished quartz plate in front of the sample cell. A kinetic analysis according to Linschitz and Sarkanen [13] gave a value of $k_2/\epsilon_T^I = 1.8 \times 10^4 \, s^{-1}$ cm. Using $\epsilon_T^I = 4000 \, M^{-1} \, cm^{-1}$ as found above, one obtains $k_2 = 7 \times 10^9 \, s^{-1} \, M^{-1}$. Values in the range $2 - 5 \times 10^9 \, s^{-1} \, M^{-1}$ are commonly observed in fluid solutions. The slightly high value found for indole may indicate that our ϵ_T^I value is somewhat overestimated.

A striking result is the short indole triplet lifetime. The phosphorescence lifetime of indole is several seconds at 77 K [14, 15]. A reason for the low

triplet lifetime of 16 μs in fluid solution may be impurity quenching. Some support for this possibility was obtained from a study of k_1 for indole in methylcyclohexane as a function of temperature, from 180 K to room temperature. We found that k_1 is inversely proportional to the viscosity in this temperature range, as expected if quenching is due to the diffusion of an impurity. However, we also studied the lifetime of the triplet in water and methanol, and found approximately the same lifetime in all solvents. Other authors [2] also obtained similar values to ours in water. It therefore seems as though the low triplet lifetime is a characteristic property of indole in fluid solution.

The indole radical

The laser photolysis study showed that a longer-lived species appears in addition to the fast-decaying indole triplet state. This specie has absorption maxima at ~340 and ~500 nm [(Fig. 1 (b)]. Pailthorpe and Nicholls [16] found maxima at 350 and 519 nm on flash photolysis of indole in ethanol; they attributed these to the indole radical formed by dissociation of the N–H bond. Their argument was that N-methylated indole derivatives do not give rise to such an absorption. We studied 1-methylindole by laser photolysis, and only obtained the triplet state spectrum (identical to that of indole), without any indication of longer-lasting species. One may conclude that the same type of radical is formed in cyclohexane as in ethanol. Our piperylene quenching runs showed that the indole radical is not formed from the triplet state, but by direct dissociation from the excited singlet. The reaction apparently is monophotonic since the radical yield was found to be independent of the laser energy.

We determined an approximate value for the quantum yield of radical formation using a value of 4000 M^{-1} cm^{-1} for the extinction coefficient of the radical at 500 nm. This value was obtained by laser excitation of indole in water. We found in this case, as other authors [2, 3], absorption due to the hydrated electron and the indole radical. One may assume that the radical concentration is equal to that of the hydrated electron formed in the photoionization process. Since the extinction coefficients of this species are known [17] (its concentration was monitored at 720 nm) it was then possible to determine the extinction coefficients for the indole radical. (Using the same method, Bryan *et al.* [3] obtained an extinction coefficient for the tryptophan radical in water of 1800 M^{-1} cm^{-1} at 510 nm.)

Comparing the triplet absorption intensities with those of the radical (Fig. 1), and using the value $\Phi_T^I = 0.5$ (see above), one obtains a value of 0.05 for the quantum yield of indole radical formation in cyclohexane. This small yield was neglected in the approximate triplet yield calculation described in a preceding paragraph. On the other hand, although the photodissociation yield is small, the radical formation cannot be neglected in the kinetic analysis of the transient absorption spectra. The photodissociation reaction may possibly also occur in water, and this process thus should be included in the analysis of data on the laser photolysis of indole (and

tryptophan) in aqueous solution [2, 3] in addition to the intersystem crossing and photoionization processes.

Acknowledgements

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