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The quenching of indolic compounds by monosubstituted benzenes and the photoreaction with chlorobenzene

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The quenching of the excited singlet of indole and its methyl derivatives by monosubstituted benzenes has been studied in three solvents of different polarities and bimolecular quenching rate constants have been determined. Below the diffusion limit the rate constants decrease when solvent polarity increases, with the exception of those for the quenching by benzonitrile. For the latter the rate constants are near the diffusion limit in all cases. The decrease may be understood in terms of a lower energy of the indole excited state in the more polar solvents. In cyclohexane the remnant emission in the presence of high concentration of the quencher is clearly red shifted, indicating the presence of a new emitting species that can be ascribed to the presence of an exciplex. In some cases the emission of the exciplex can be clearly separated from the molecular fluorescence. In the quenching by chlorobenzene in ethyl acetate and acetonitrile a new highly fluorescent product is formed. This photoreaction is observed with all the indole derivatives and the kinetics of the reaction was followed by the increase in fluorescence intensity at a wavelength were the reactants do not emit. Three major products were identified as phenyl substituted indoles by GC-MS and their fluorescence emission and excitation spectra.

1 Introduction

Although the number of papers on the excited state behaviour of the indole chromophore is impressive, most of them concern biologically relevant indole derivatives in an aqueous environment.[1] Nevertheless, several papers have focussed on the fluorescent behaviour of indolic compounds in non-aqueous environments. In particular, the effect of small amounts of alcohols in a non-polar solvent such as cyclohexane produce dramatic changes in the emission spectra of indole and its derivatives, and this has received the interest of several research groups during the last three decades.[2,3] The change from a structured emission in non-polar solvents to a red shifted structureless band in the presence of a polar co-solvent have been explained through the formation of exciplexes between one indole molecule and one or several molecules of the polar additive. At the same time it was observed that non-polar aromatics such as benzene also have a dramatic effect on the emission of indole and some of its derivatives. This was first reported by Van Duuren[4] who observed that in benzene the fluorescence intensity is greatly reduced and red shifted with respect to cyclohexane. This was attributed to the formation of an excited state complex in benzene solution and it was found that the presence of an N–H bond in the indole ring is essential for this to happen. This effect was further studied by Suwaiyan and Klein[5] by time resolved fluorescence spectroscopy. More recently we[6] investigated the effect of substituents on the benzene ring upon the fluorescence quenching of indole and its methyl derivatives in cyclohexane. In this solvent the quenching process may be explained by a mechanism that involves the intermediacy of an excited state complex. The binding forces in the exciplex are predominantly hydrogen bonding for the case of benzene and toluene, while a charge transfer interaction is more likely for chlorobenzene and benzonitrile. A preliminary investigation of the solvent effect on these processes was also carried out.[6] When quenching experiments were performed in acetonitrile a different behaviour was observed. The quenching by benzene is practically non-existant and this was attributed to the interaction of the excited indole molecules with this solvent. This interaction, which is reflected in the fluorescence lifetime of indole in acetonitrile, 3.7 ns, much shorter than in cyclohexane, is likely to prevent the formation of the hydrogen-bond stabilised exciplex intermediate. On the other hand, in acetonitrile, indole is quenched by benzonitrile or chlorobenzene with rate constants similar to those in cyclohexane, and this was explained in terms of a charge transfer character of the exciplex. These properties of the exciplex formed by indole derivatives and the benzene ring, were also used to sense properties of the microenvironments in reverse micellar systems.[7]

With the aim of obtaining a further knowledge on these excited state interactions and the related photochemical process, we undertook the present investigation. Here, we present a detailed study of the quenching of the excited singlet of several methyl substituted indoles by monosubstituted benzenes in cyclohexane, ethyl acetate and acetonitrile. The occurrence of exciplex emission was detected in several cases in the less polar solvent, and time-resolved experiments allowed the determination of the kinetic parameters for the quenching process. It was also found that in the quenching by chlorobenzene in acetonitrile or ethyl acetate a photochemical reaction occurs. The photochemistry of indolic compounds presents a large variety of reactions that depends on the substituents, the solvent and the presence of other substrates.[8] In the excited state the indole group is a good electron donor, and in the presence of other molecules acting as electron acceptors, several processes involving radicals or radical-ions may take place. These photoreactions include different types of additions to aromatic rings or double bonds.[9] Recently it was reported that photoexcited tryptophan reacts with aliphatic halocompounds in aqueous solution[10] and the proposed mechanism involves a radical addition to the indole moiety. However, the electron-transfer photochemistry of indole in organic solvents did not receive comparable attention.[8] Here we present results on the kinetics of the photoreaction of indole and 1-methylindole with chlorobenzene. It was found that the main products are phenyl substituted indoles and the process may be ascribed to a reactive electron transfer quenching process.

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Table 1 Singlet lifetime (ns) of indole derivatives measured at 298 K in air-equilibrated solutions

	Cyclohexane	Ethyl acetate	Acetonitrile
Indole	5.4	3.1	3.7
3-Methylindole	3.1	3.3	5.0
1-Methylindole	4.6	3.6	4.4
1,2-Dimethylindole	3.4	3.3	4.2

Estimated error ± 0.05 ns.

2 Experimental

Indole from Sigma or Aldrich 99+ % was used without further purification. 1-Methylindole from Aldrich was vacuum distilled and stored under nitrogen. 3-Methylindole and 1,2-dimethylindole, Aldrich or Sigma, were purified by sublimation. 2-Phenylindole was from Sigma and was used as received for identification of the photolysis products. Cyclohexane, benzene and toluene were from Sintorgan, HPLC grade and they were used as received. Chlorobenzene (Fluka) and benzonitrile (Merck) were purified by fractional distillation.

Fluorescence lifetime measurements were carried out with the time correlated single photon counting technique on an Edinburgh Instruments OB-900 equipment. The fluorescence spectra were measured with a Spex Fluoromax spectrofluorometer. The indoles were excited on the red edge of the absorption spectrum, 290–300 nm. In this way it was assured that, in the concentration range of the quenching experiments, the benzene derivatives do not absorb any appreciable amount of the exciting light. The emission wavelength varied with the indolic compound, and was in the range of 310–350 nm with a bandpass of 10 nm. Stern–Volmer constants for the quenching by chlorobenzene in ethyl acetate and acetonitrile were determined with 0.1 mm slits for the excitation beam to avoid photolysis of the solution during the measurements. All measurements were carried out with air-equilibrated solutions except where indicated.

The continuous photolysis for kinetics measurements were accomplished in the Fluoromax spectrofluorometer with 2 mm slit for excitation at 300 nm and an emission slit of 0.5 mm for emission at 400 nm. For product identification photolysis were carried out at 300 nm with a 150 W Xe lamp coupled to a PTI monochromator. The identification of photoproducts was performed with a Hewlett-Packard 5890 chromatograph equipped with a HP-1 crosslinked methyl silicone gum column and a HP 5972 mass selective detector.

3 Results and discussion

Fluorescence quenching

In the absence of quenchers, the fluorescence of indole and its methyl derivatives decay monoexponentially. The lifetimes of air equilibrated solutions in the different solvents are collected in Table 1. Our results are coincident with those available in the literature, provided that they were measured by the single photon counting technique under similar experimental conditions.[11] The quenching of the indoles by benzene, toluene, chlorobenzene and benzonitrile was studied in three solvents of different polarities, cyclohexane, ethyl acetate and acetonitrile. A different quenching behaviour is observed in the two more polar solvents as compared to cyclohexane. In ethyl acetate and acetonitrile the fluorescence decay is monoexponential and Stern–Volmer plots of fluorescence intensity presents in all cases an upward deviation from a straight line. As an example, the quenching of 3-methylindole by benzonitrile in ethyl acetate is shown in Fig. 1. This points to a static contribution to the quenching. In the red edge of the absorption spectra absorbances are additive. Therefore, ground sate interactions may be disregarded, and the static quenching may be ascribed to a Perrin's action sphere effect. The rate constants determined from the initial slope of Stern–Volmer plots coincide with those from the lifetime determinations. The quenching rate constants in these solvents are presented in Table 2.

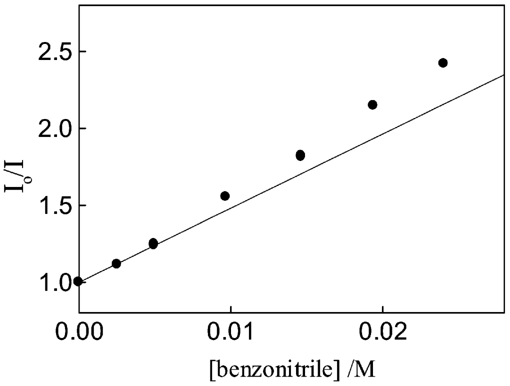


Fig. 1 Fluorescence quenching of 3-methylindole by benzonitrile in ethyl acetate.

In cyclohexane the quenching mechanism is more complex. In our previous work[6] we observed that in the quenching of indole by monosubstituted benzenes the mechanism involves the intermediacy of an exciplex. This is also found to be the case for the other indole derivatives investigated here. In all cases, at high quencher concentrations, the emission spectrum of the indoles becomes red shifted, as earlier observed by Van Duuren for the particular case of benzene.[4] Typical fluorescence spectra showing this effect are presented in Figs. 2 and 3. In all instances the exciplex emission is very low and

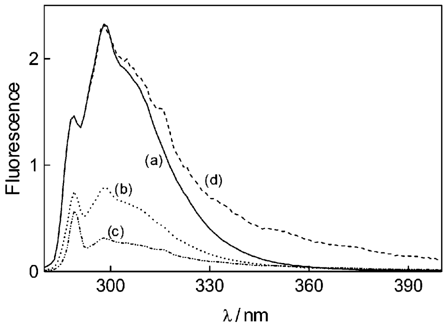


Fig. 2 Fluorescence emission spectra of indole in cyclohexane in the absence (a) and in the presence of 0.051 M (b) and 0.17 M chlorobenzene (c). Curve (d) is curve (c) scaled to the same maximum intensity that curve (a). Excitation wavelength 290 nm.

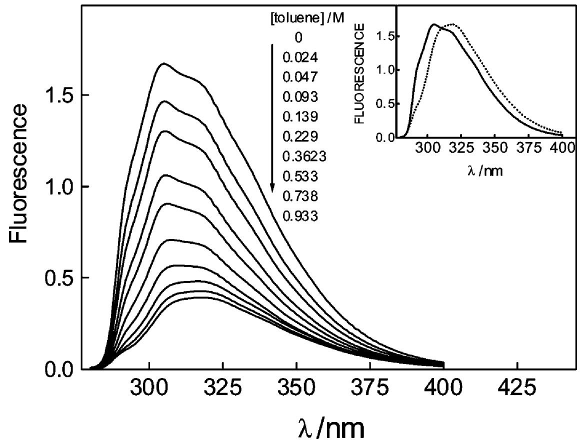


Fig. 3 Quenching of 3-methylindole by toluene in cyclohexane. Inset: Fluorescence emission spectrum in the absence (—) and the presence (···) of 0.93 M toluene scaled to the same maximum intensity. Excitation wavelength 290 nm.

Table 2 Quenching rate constants of indole derivatives by monosubstituted benzenes at 298 K ($k_q/10^9$ M^{-1} s^{-1})

		Solvent		
Indole derivative	Quencher	Cyclohexane	Ethyl acetate	Acetonitrile
Indole	Benzene	0.23	0.02	0.01
	Toluene	0.24	0.045	0.02
	Chlorobenzene	5.8	1.54	2.57
	Benzonitrile	10.0	16.1	13.8
1-Methylindole	Benzene	0.05	<0.01	<0.01
	Toluene	0.01	0.014	<0.01
	Chlorobenzene	0.13	0.19	0.50
	Benzonitrile	4.28	8.36	7.28
1,2-Dimethylindole	Benzene	0.06	–	–
	Toluene	0.20	–	–
	Chlorobenzene	4.1	–	–
	Benzonitrile	16.5	–	–
3-Methylindole	Benzene	3.7	0.02	<0.01
	Toluene	1.9	<0.01	0.1
	Chlorobenzene	12.5	0.91	1.2
	Benzonitrile	15.5	14.6	20.2

difficult to separate from the residual fluorescence of the indole. The only example where the exciplex emission can be observed as clearly separated is for the system 1,2-dimethylindole–benzonitrile in cyclohexane, Fig. 4. This is probably a consequence, among other factors, of 1,2-dimethylindole being the best electron donating of the indole derivatives and benzonitrile the strongest electron acceptor of the quenchers, which causes a larger red shift in the emission. In addition, in this solvent the fluorescence decay in the presence of quenchers follows a biexponential kinetics in the majority of the systems investigated.

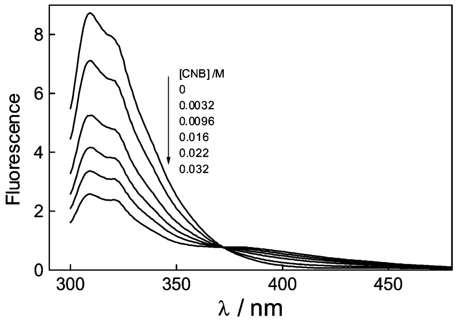
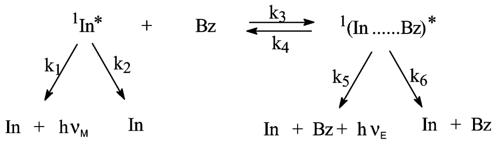


Fig. 4 Fluorescence emission of 1,2-dimethylindole as a function of benzonitrile concentration [CNB] in cyclohexane. Excitation wavelength 300 nm.

From the above considerations, the quenching mechanism in cyclohexane can be depicted by Scheme 1.



Scheme 1

In Scheme 1 In stands for the indole derivative and Bz for the substituted benzene. The exciplex ^{1}(In. . .Bz)* may decay to the dissociative ground state by a radiative or nonradiative process.

Solving the differential equation for the monomer decay the following equation results:[12,13]

$$[^1\mathrm{In}^*] = c[\exp(-\lambda_1 t) + A\exp(-\lambda_2 t)] \qquad (1)$$

From the decay of indole fluorescence in the presence of the quencher, the three relevant experimental parameters, A, λ_1 and λ_2 can be obtained. From A, λ_1 and λ_2 two quantities X and Y are defined:

$$X = (A\lambda_2 + \lambda_1)/(A + 1) \qquad Y = \lambda_1 + \lambda_2 - X \qquad (2)$$

and the rate constants are obtained as:

$$k_3 = (X - \tau_0^{-1})/[\mathrm{Bz}] \qquad (3)$$

$$k_4 = (X - \lambda_1)(\lambda_2 - X)/k_3[\mathrm{Bz}] \qquad (4)$$

$$k_p = Y - k_4 \qquad (5)$$

with $k_p = k_5 + k_6$; $\tau_o = (k_1 + k_2)^{-1}$ and where [Bz] is the molar concentration of the monosubstituted benzene. When the decay is monoexponential and the initial slopes of Stern–Volmer plots coincide with the rate constant from lifetime determinations, the same mechanism is valid with $k_4 \ll k_5 + k_6$ and in this case $k_3 = k_q$.

Eqn. (3) may be written as $X = \tau_0^{-1} + k_3[\mathrm{Bz}]$ and this may be used to determine the quenching rate constant when the decay is biexponential. Typical plots of X *vs.* quencher concentration are presented in Fig. 5 for the systems 1,2-dimethylindole–chlorobenzene and 1,2-dimethylindole–benzonitrile. In this way the rate constants $k_3 = k_q$ presented in Table 2 were evaluated in cyclohexane.

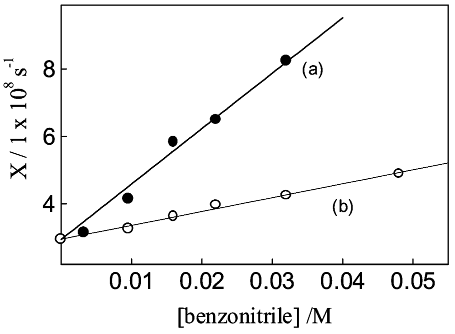


Fig. 5 Plot of the function X, (eqns. (2) and (3)), for the quenching of 1,2-dimethylindole in cyclohexane as a function of quencher concentration for benzonitrile (a) and chlorobenzene (b).

It can be seen in Table 2 that for the quenching by benzene and toluene the rate constants decrease when the solvent polarity increases. The same is true for the quenching by chlorobenzene of indole and 3-methylindole, except than in this case the rate constants in ethyl acetate and acetonitrile are similar. The emission of the indole chromophore in the absence of quencher undergoes a red shift on going from cyclohexane to acetonitrile. Therefore, the decrease in the rate constants may be explained in terms of a lower energy of the indole excited state in the more polar solvents. In a given solvent the rate constants increase with the acceptor capability of the quencher and they are near the diffusion limit for the quenching of indole and 3-methylindole by benzonitrile. The rate constants for the quenching of 1-methylindole are similar in the three solvents and they are much lower than those for indole. Since these two molecules have similar oxidation potential, the difference may be understood by a hydrogen-bonding contribution to the stabilisation of the exciplex. In the case of indole this contribution is present, while for the N-methyl substituted derivative the hydrogen bond cannot be established and the exciplex is less stable. A similar comparison can be established between 1,2-dimethylindole and 3-methylindole.

Photoreaction of the indoles with chlorobenzene

During the quenching by chlorobenzene in the more polar solvents, ethyl acetate and acetonitrile, a new fluorescent product is formed. This photoreaction is only observed with chlorobenzene and for all the indole derivatives. The photoproducts are highly fluorescent and the reaction may be followed by the increase in fluorescence intensity. The time profile of the increase in the fluorescence at 400 nm in ethyl acetate and acetonitrile are shown in Fig. 6. For both solvents the concentration of chlorobenzene is such that the same fraction of singlet quenching is obtained. It can be seen that the relative yield is higher in the more polar medium. In a non-polar solvent such as cyclohexane the reaction does not take place. Typical fluorescence excitation and emission spectra of the photoproducts are shown in the inset in Fig. 6. They are very similar to those obtained for a pure sample of 2-phenylindole in the same medium.

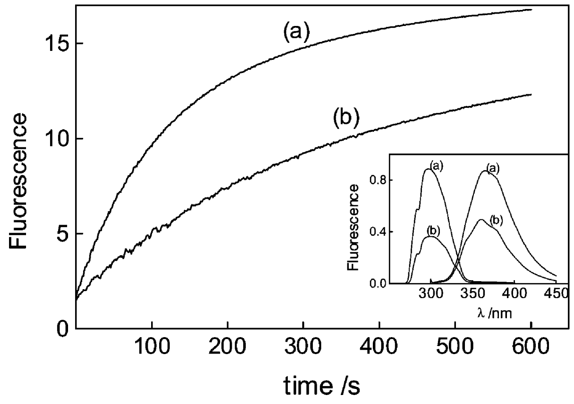


Fig. 6 Time profile of fluorescence intensity at 400 nm for the system indole–chlorobenzene (ClB): (a) in acetonitrile, [ClB] = 0.1 M; (b) in ethyl acetate, [ClB] = 0.24 M. Inset: Fluorescence excitation and emission spectra of the product of the photoreaction in acetonitrile and in ethyl acetate.

Fig. 7 shows a plot of the fluorescence of the photoproduct *vs.* time for the photolysis of 1-methylindole at three concentrations of chlorobenzene. It can be seen that the kinetics follows a typical first-order growth. A double inverse plot of the first-order kinetic coefficient *vs.* chlorobenzene concentration is presented in the inset and a linear behaviour is observed. In Fig. 7 also shows the effect of oxygen on the photoreaction. While the fluorescence emission of the products is the same as that for the reaction in air-equilibrated solution, when the solution is deoxygenated by bubbling with argon, an acceleration of the reaction takes place. This may be explained by the interception by oxygen of the intermediate radicals.

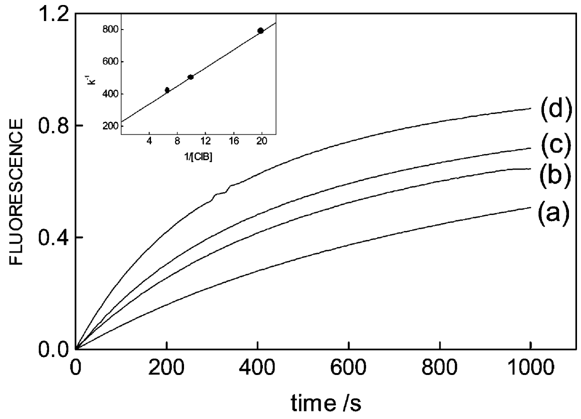


Fig. 7 Photolysis of 1-methylindole (1 × 10^{-4} M) in the presence of chlorobenzene. Fluorescence intensity at 400 nm as a function of time for three different concentrations of chlorobenzene: (a) 0.05 M; (b) 0.1 M; (c) 0.15 M; (d) 0.1 M in the absence of oxygen. Excitation wavelength 320 nm. Inset: Double inverse plot of the first-order kinetics coefficient *vs.* chlorobenzene concentration.

These observations may be rationalized by considering the simple kinetic mechanism shown in Scheme 2:

$$\mathrm{In} \xrightarrow{h\nu} {}^{1}\mathrm{In}^{*}$$

$${}^{1}\mathrm{In}^{*} \xrightarrow{\tau_0^{-1}} \mathrm{In}$$

$${}^{1}\mathrm{In}^{*} + \mathrm{ClB} \xrightarrow{k_\mathrm{q}} \mathrm{X}$$

$$\mathrm{X} \xrightarrow{k_\mathrm{b}} \mathrm{In} + \mathrm{ClB}$$

$$\mathrm{X} \xrightarrow{k_\mathrm{R}} \mathrm{Products}$$

Scheme 2

In the mechanism ClB stands for chlorobenzene, ^{1}In* for the indolic compound in its singlet excited state, and X is an intermediate formed in the quenching process that may proceed to products or revert to the starting compounds in the ground state.

The rate of formation of the photoproduct P may be written as:

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = \Phi_\mathrm{R} I_\mathrm{a} \qquad (6)$$

Where Φ_R = reaction quantum yield and I_a = actinic light absorbed = $I_\mathrm{o}(1 - 10^{-\varepsilon lc})$ where I_o is the incident light intensity, ε is the molar absorption coefficient at the irradiation wavelength and C is the molar concentration of the indole derivative.

Under the present experimental conditions, the chlorobenzene concentration may be considered constant, and at the exciting wavelength (300 nm) the absorbance of the indole is very low. With these limitations the time evolution of the photoproduct may be obtained by integration of eqn. (6) and is given by eqn (7):

$$[\mathrm{P}] = [\mathrm{P}]_\mathrm{max}[1 - \exp(-kt)] \qquad (7)$$

with

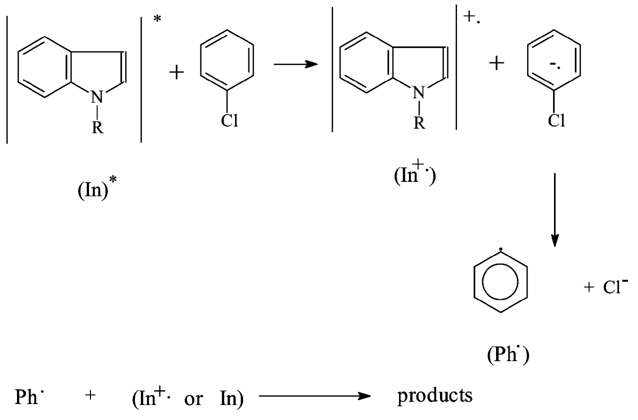
$$k = 2.303 I_\mathrm{o} \varepsilon l \Phi_\mathrm{R} \qquad (8)$$

From the plots of fluorescence intensity of the photoproduct *vs.* time, values of k were obtained for different concentrations of chlorobenzene. Now, according to Scheme 2 the quantum yield may be written as:

$$\Phi_\mathrm{R} = \left(\frac{k_\mathrm{R}}{k_\mathrm{R} + k_\mathrm{b}}\right) \frac{K_\mathrm{SV}[\mathrm{ClB}]}{1 + K_\mathrm{SV}[\mathrm{ClB}]} \qquad (9)$$

where $K_{SV} = k_q\tau_o$. Since the kinetic constant k is directly proportional to the quantum yield, eqn (8), a double inverse plot of k and [CB] should be linear. That this is the case is shown in the inset in Fig. 7. From the intercept/slope ratio a value of 8.0 M^{-1} results for K_{SV} This value is higher than that determined from the fluorescence quenching experiments. However, considering the several assumptions and approximations made, it may be taken as evidence for a singlet mechanism for the photoreaction.

Using the GC-MS technique several photoproducts of the reaction between indole and chlorobenzene were detected. The mass spectrum of the three major products gave a parent peak that can be assigned to phenyl substituted indoles. For one of them the spectrum corresponds to 2-phenylindole. The yield of 2-phenylindole relative to the other isomers was only 12%. An electron transfer mechanism followed by phenyl radical addition to the indole ring may explain the formation of these products, and this is illustrated in Scheme 3. In the first reaction the indole in its excited singlet state transfers an electron to chlorobenzene, to give the indole radical cation ($In^{+\bullet}$) and the chlorobenzene radical anion. It is well known that the chlorobenzene radical anion undergoes a very fast decomposition into chloride ion and phenyl radical.[14] The latter may combine with the indole radical cation or add to indole itself, affording the different phenyl indoles as final products after proton or hydrogen atom elimination.



Scheme 3

This mechanism is similar to that recently proposed by Edwards *et al.*[10] for the photoreaction between *N*-acetyl-L-tryptophan and chloroform in aqueous medium. In this case the observed products were explained by a reaction scheme that involves an initial electron capture by the halocompound. Then the radical-anion of chloroform eliminates chloride ion affording small aliphatic radicals that add to the indole ring.

The mechanism is also in agreement with the observed solvent effect. The lack of reaction in cyclohexane is due to the unfeasible charge separation process in this solvent and instead exciplex emission is observed in this solvent as shown in Fig. 1. The effect of the lower polarity of ethyl acetate as compared to acetonitrile is evidenced in the plots in Fig. 6.

The photochemical reaction was observed with indoles both substituted and unsubstituted at the N atom. However, the product analysis was only performed for the case of indole. A more complete characterisation of the several products, for different indoles and in the two solvents, is necessary in order to establish a more detailed mechanism.

In summary, the singlet excited state of indole and its methyl derivatives is quenched by monosubstituted benzenes with rate constants that depend on the structure of the quencher and the indole. For the quenching by benzene and toluene the rate constants decrease when solvent polarity increases, but they are close to the diffusional limit for benzonitrile. When quenching experiments were performed in cyclohexane an exciplex emission was observed and the decays were biexponential. A new interesting finding is a reactive electron transfer process in the quenching by chlorobenzene in ethyl acetate and acetonitrile. The major products were identified as phenyl substituted indoles by GC-MS and their fluorescence emission and excitation spectra.

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