

DECAY PROCESSES OF SINGLET EXCITED PHENOL IN SOLUTION

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Summary

The yields of fluorescence at 295 and 77 K and of phosphorescence at 77 K of phenol and anisole were determined in solvents of different polarities (hydrocarbons, ether, ethanol). Also intersystem crossing yields are reported for phenol and anisole in cyclohexane solution at 295 K. The data show that a non-radiative process, different from intersystem crossing, competes with the decay of S_1 phenol in liquid hydrocarbons. The nature of this deactivation pathway is discussed.

1. Introduction

The sum of the fluorescence and triplet yields of benzenoid compounds in dilute solutions is often less than unity [1 - 3]. For benzene and toluene the quantum yield deficit, assigned to a radiationless $S_1 \rightarrow S_0$ process, is greater than 40% at room temperature [4]. This internal conversion process is strongly temperature enhanced and, in low temperature glasses, fluorescence emission and intersystem crossing account for the S_1 decay. An *ortho* or *para* arrangement of alkyl substituents suppresses the efficiency of this third decay channel, whereas it is remarkably enhanced by an alkyl substituent on a carbon attached to the ring (the "α substitution effect") [3, 5].

For benzene derivatives with substituents other than alkyl groups, mechanisms and yields for the various decay processes of the fluorescent state are much less known [6]. Whereas mono-substituted benzenes with appended electron-accepting groups (*e.g.* CHO, NO₂) are poorly fluorescent, these benzene derivatives with one appended electron-donating group (*e.g.* OH, NH₂) mostly exhibit good fluorescence [6, 7]. For aniline solutions in hydrocarbons and alcohols, Q_F and the intersystem crossing yield have been reported recently to be independent of temperature and the sum of both yields is near to unity [8].

The fluorescence yields and lifetimes of phenol show that the decay mechanisms are strongly dependent on the solvent [9, 10]. This has been

attributed to the ability of phenols to form hydrogen bonds with appropriate solvent molecules [11, 12]. The yields for fluorescence ($Q_F = 0.4$) and phosphorescence ($Q_P = 0.37$) in diethyl ether–isopentane–ethanol (5:5:2) (EPA) glass at low temperature have been reported [13] and the total emission yield does not exceed unity. At room temperature the main photolytic processes are hydrogen atom release in hydrocarbon solutions and electron ejection in aqueous solutions [11, 14].

In the present work the S_1 decay properties of phenol in various solvents (especially hydrocarbons) at room temperature and at 77 K are reported and compared with those of anisole under identical conditions. The decay mechanisms of S_1 phenol and their dependence on the molecular environment are discussed on the basis of the experimental data.

2. Experimental details

The phenol (p.a., Merck) was purified by repeated sublimation in a vacuum; the anisole, toluene, *p*-xylene and *p*-cresol (p.a., Merck) were purified by repeated zone refining. 2,5-Diphenyloxazole (PPO) (the reagent for scintillation measurements, Merck) was used without purification. The solvents were generally of the best available quality. Hydrocarbon solvents were further purified by column chromatography on SiO_2 (Woelm, Akt. 1) and basic Al_2O_3 (Woelm, Akt. 1) and were kept under dry nitrogen. Ethanol was refined by repeated chromatography over a 10 Å molecular sieve and diethyl ether (DEE) by repeated distillation. The solutions were carefully kept free of moisture. Oxygen was removed by repeated freeze–pump–thaw cycles or by saturation with high purity nitrogen.

Absorption measurements were performed on a Coleman 545 spectrophotometer (Perkin–Elmer) at room temperature or point by point at various temperatures with a PMQ II (Zeiss, Oberkochen) equipped with a low temperature cell.

Fluorescence measurements were performed with an MPF 4A fluorimeter (Perkin–Elmer) equipped with the facilities for automatic emission correction and a quartz Dewar. Low temperature measurements were performed in rectangular cells whenever possible or in cylindrical cells. As fluorescence standards, several substances (toluene, *p*-xylene and *p*-cresol) with similar emission properties and known quantum yields (taken from refs. 9 and 15) were used. Corrections for the refractive indices of the different solvents and for the change in the refractive index with temperature were applied [15, 16]. Furthermore, the change in the absorbance with temperature due to density changes was taken into account.

The fluorescence lifetimes τ_M were determined with a nanosecond decay time SP 3X fluorimeter (Applied Photophysics Ltd., London). The values for k_{FM}° were calculated using the formulae given by Birks and

Dyson [17] and Strickler and Berg [18]. The lowest absorption bands were integrated throughout the wavelength range above the minimum value of the extinction curve between S_1 and S_2 .

The triplet quantum yields at room temperature were determined by the triplet-sensitized ketonization of ethyl acetoacetate. The method and procedure are described elsewhere [19, 20]. The photochemical degradation of phenol was taken into account by monitoring the reduction in the absorption of the enol form of ethyl acetoacetate compared with that of a sample without a triplet quencher irradiated under the same conditions. The changes in the phenol absorption spectrum were smaller than 5% in all cases.

H_2 yields were determined as described previously [11].

3. Results

The absorption spectra of phenol and anisole were measured at various temperatures between 295 K and the glass transition temperature of the solvent. At low temperatures the vibrational structure of the absorption spectra becomes generally more stressed, but spectral shifts were not observed except for phenol in ethanol solution. For this case the spectra at 295 and 191 K are given in Fig. 1.

Care was taken to avoid ground state dimer formation for phenol in hydrocarbons. When the sample (5×10^{-4} M phenol in 8:3 *n*-pentane: 2,2-dimethylbutane mixtures (P-DMB) or in 3-methylpentane (MP)) was cooled slowly, a slight blue shift of the spectrum ($\lambda_{\max 1} = 277$ nm and $\lambda_{\max 2} = 270$ nm at 77 K compared with $\lambda_{\max 1} = 278$ nm and $\lambda_{\max 2} = 271$ nm at room temperature) was observed. This effect was not seen when the sample cell was directly immersed in liquid nitrogen. The latter procedure was used for the luminescence measurements.

The corrected fluorescence and phosphorescence spectra of phenol and anisole in P-DMB and ethanol glasses for $\lambda_{\text{exc}} = 265$ nm are given in

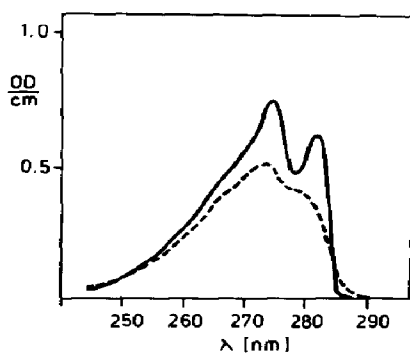


Fig. 1. The absorption spectrum of 2.6×10^{-4} M phenol in ethanol at $T = 295$ K (---) and at $T = 102$ K (—).

Figs. 2 and 3. Table 1 shows the wavelengths for the vibronic component of lowest energy observed in the absorption spectra and for the vibronic component of highest energy observed in the emission spectra of these systems at 77 K. For anisole, for which the vibronic structure of the phosphorescence spectra is not as well resolved as for phenol, the centre of the first small plateau was taken as λ_p . The yields of fluorescence and phosphorescence ($\lambda_{exc} = 265$ nm) are shown in Table 2. Luminescence yields were also determined for phenol in P-DMB glass at 77 K for $\lambda_{exc} = 225$ nm. As a standard for corrections to the changes in the intensity of the exciting light, a solution of PPO in cyclohexane was used. The value obtained agrees within the limits of error with the value obtained at $\lambda_{exc} = 265$ nm (see Table 2).

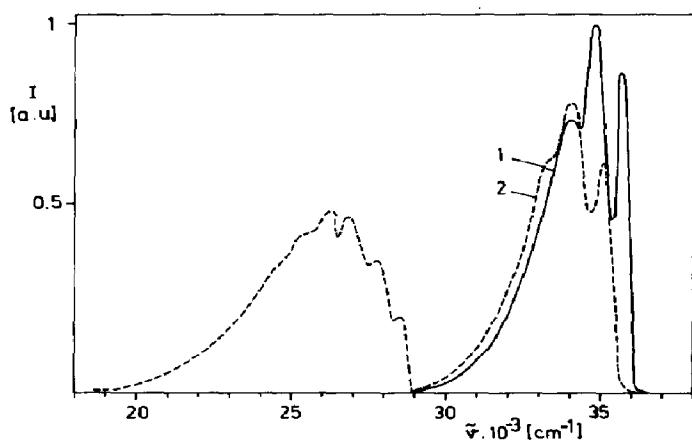


Fig. 2. Emission spectra of 10^{-4} M phenol in P-DMB (curve 1) and in ethanol (curve 2) at 77 K. The spectra are corrected for the response of the fluorescence unit.

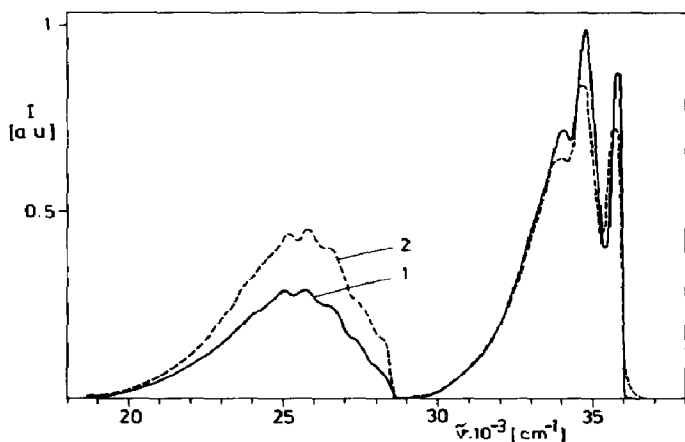


Fig. 3. Emission spectra of 10^{-4} M anisole in P-DMB (curve 1) and in ethanol (curve 2) at 77 K. The spectra are corrected for the response of the fluorescence unit.

TABLE 1

Absorption and emission maxima for phenol and anisole in various solvents at 77 K

| <i>Solute</i> | <i>Solvent</i> | λ_A (nm) | λ_F (nm) | λ_P (nm) |
|---------------|------------------|------------------|------------------|------------------|
| Phenol | P-DMB | 277.5 | 280 | |
| | P-DMB + 0.6% DEE | | 283.5 | 351 |
| | P-DMB + 4% DEE | | 284 | 351 |
| | P-DMB + 10% DEE | | 284 | 351 |
| | DEE | 281 | 285 | 351 |
| | Ethanol | 282 | 285 | 351 |
| Anisole | P-DMB | 278 | 279.5 | 357 |
| | DEE | 278 | 280 | 356 |
| | Ethanol | 278 | 280 | 356 |

TABLE 2

Emission and triplet yields of 10^{-4} M phenol and anisole in some solvents at 295 and 77 K

| <i>Solute</i> | <i>Solvent</i> | Q_F | | Q_P | Q_T |
|---------------|------------------|-------------|------------|-------|-------|
| | | $T = 295 K$ | $T = 77 K$ | | |
| Phenol | P-DMB | 0.075 | 0.44 | 0 | 0.32 |
| | P-DMB + 0.6% DEE | | | 0.02 | |
| | P-DMB + 4% DEE | | | 0.09 | |
| | P-DMB + 10% DEE | | | 0.17 | |
| | EPA ^a | | 0.40 | 0.37 | |
| | DEE | 0.22 | 0.40 | 0.60 | |
| | Ethanol | 0.22 | 0.37 | 0.38 | |
| Anisole | P-DMB | 0.29 | 0.45 | 0.22 | 0.64 |
| | DEE | | 0.41 | 0.50 | |
| | Ethanol | 0.24 | 0.40 | 0.35 | |

^aRef. 13.

The triplet yields for phenol and anisole at 295 K, determined by the sensitized ketonization of ethyl acetoacetate, are also listed in Table 2.

Table 3 shows the decay parameters for the S_1 state of phenol and anisole in cyclohexane and ethanol. In addition to the fluorescence lifetimes τ_M , the first-order rate constants for radiative decay (k_{FM}) and for inter-system crossing (k_{TM}) and the natural radiative decay constant k_{FM}^0 are also given. k_{FM} and k_{TM} were calculated from the respective values for the yield and the lifetime:

$$k_{FM} = \tau_M^{-1} Q_F \quad k_{TM} = \tau_M^{-1} Q_T \quad (1)$$

The values obtained for τ_M and k_{FM}^0 are in good agreement with the data given in ref. 9.

TABLE 3

 S_1 decay parameters for phenol and anisole in cyclohexane and ethanol at 295 K

| <i>Solute</i> | <i>Solvent</i> | τ_M ($\times 10^{-9}$ s) | k_{FM} ($\times 10^7$ s $^{-1}$) | k_{FM}^0 ($\times 10^7$ s $^{-1}$) | k_{TM} ($\times 10^7$ s $^{-1}$) |
|---------------|----------------|-----------------------------------|-----------------------------------------|-------------------------------------------|-----------------------------------------|
| Phenol | Cyclohexane | 2.4 ± 0.5 | 3.1 | 3.0 | 13.3 |
| | Ethanol | 7.0 ± 0.5 | 3.1 | 3.1 | |
| Anisole | Cyclohexane | 8.0 ± 0.5 | 3.6 | 3.4 | 8.0 |
| | Ethanol | 7.5 ± 0.5 | 3.3 | 3.0 | |

For the symbols see text.

The yield $Q(H_2)$ of photochemically produced H_2 from phenol in cyclohexane (concentration, 10^{-2} M) at 303 K is 0.12 [11]. This value is not affected by the concentrations of ethyl acetoacetate necessary to quench the phenol triplet completely.

4. Discussion

The spectral shifts of the absorption and fluorescence spectra of phenol when a hydrocarbon solvent is replaced by alcohol or ether reflects the formation of hydrogen-bonded ground state complexes in these media [11, 12, 21]. For anisole, hydrogen bond formation is of minor importance and solvent shifts of the spectra are therefore small (Table 1). The red shift of the absorption maximum of phenol in ethanol on cooling (Fig. 1) can be explained by a stabilization of the hydrogen bond in which phenol acts as the proton donor, compared with that in which phenol is the acceptor. This is supported by the close resemblance of the absorption spectra in the low temperature alcohol and in ether [21]. No solvent shifts are observed, however, for the phosphorescence spectra. Also for phenol in chloroform the first maximum has been reported to appear at $\lambda_P = 351$ nm [9]. The difference between the sensitivities of the relaxed S_1 and T_1 to the solvent environment might be explained by the different molecular geometries of these two states. The singlet is most probably a $^1B_2(\pi, \pi^*)$, whereas the triplet is orbitally $^3A_1(\pi, \pi^*)$ [6].

Because of the lack of phosphorescence of phenol in P-DMB glass we are not able to calculate the triplet yield under these conditions. The results, however, are in accordance with the findings for α - and β -naphthole under comparable conditions [22, 23]. No phosphorescence was reported for these compounds in hydrocarbon glass.

It is proposed that a non-radiative intersystem crossing process competes with phosphorescence. This process shows different characteristics from the S_1 decay route (discussed below) since $Q_F + Q_P$ is also smaller than unity for anisole in P-DMB glass and the process is not primarily enhanced by the formation of hydrogen-bonded complexes (Table 2).

The S_1 decay of phenol and anisole in solution is characterized by the following main properties.

(1) In cyclohexane as the representative hydrocarbon solvent the sum of Q_F and Q_T for anisole is near to unity ($Q_F + Q_T = 0.93$ at 295 K). For phenol, however, fluorescence and intersystem crossing account only for 40% of the S_1 deactivation ($Q_F + Q_T = 0.395$). A further decay route, not leading to the triplet, must be operative from the S_1 state of phenol. This non-radiative decay is strongly suppressed by the methylation on the oxygen.

(2) Since k_{FM} is slightly higher for anisole than for phenol, the fluorescence is slightly favoured in the methoxy compound, but the intersystem crossing to the triplet manifold is more efficient in phenol.

(3) The third deactivation pathway of S_1 phenol is considerably less efficient in the polar solvents ethanol and ether. The Q_F values for phenol and anisole in these two solvents are nearly equal (Table 2). It has been shown previously [12] that the increase in the fluorescence yield of phenol in hydrocarbon-alcohol mixtures correlates with the formation of hydrogen-bonded solute-solvent aggregates. Therefore the formation of hydrogen bonds efficiently suppresses this non-radiative pathway.

(4) In low temperature glasses the fluorescence yields of phenol and anisole are equal in the hydrocarbon mixture (P-DMB) and only slightly smaller in ether and ethanol (Table 2). This further non-radiative deactivation channel of S_1 must therefore be enhanced strongly by the temperature of the solution.

(5) The main photolytic process originating from the S_1 state of phenol in cyclohexane at room temperature is the cleavage of the O-H bond. No bond-splitting processes have been observed in hydrogen-bonding solvents (alcohols, ether) [11, 12]. Ground state complexation prevents this photochemical pathway.

The main feature of the S_1 properties of phenol is the occurrence of an important non-radiative decay channel in hydrocarbon solutions at room temperature. As is stressed above, this decay route is inefficient when phenol is complexed by hydrogen bonding, when the hydrogen atom on the -OH group is replaced by -OCH₃ or in low temperature glasses. These characteristics suggest that the S_1 non-radiative decay might be predominantly an -O-H bond cleavage, possibly followed by an inhomogeneous recombination of the resulting phenoxyl and hydrogen radicals (Fig. 4). For a quantitative explanation of the non-radiative decay route by the latter process, the quantum yield q_{RP} for the formation of the radical pair should be 0.6. Since the measured yield $Q(H_2)$ is 0.12 in cyclohexane, 80% of the radical pairs should recombine in this solvent.

It should be pointed out that O-H bond cleavage is a very important process for the S_2 deactivation of excited phenol with a yield $Q(H_2) = 0.55$ (corrected for S_1 processes) [11]. However, 85% of the radicals escape recombination in this case. Since no wavelength effects on Q_F are found in the P-DMB glass, the S_2 deactivation by O-H bond cleavage is suppressed under these conditions.

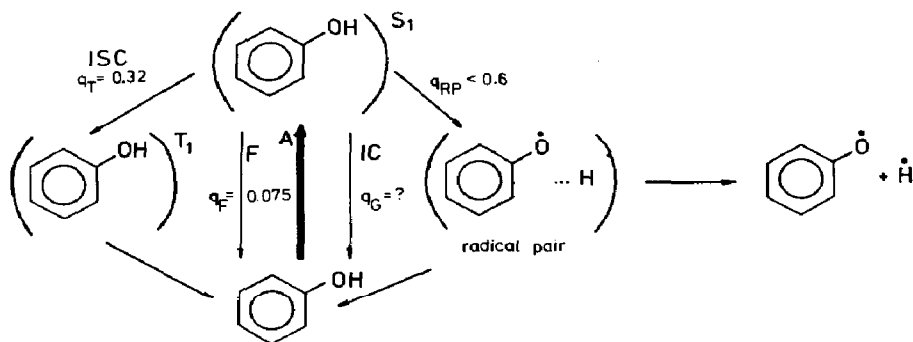


Fig. 4. Proposed S_1 deactivation mechanisms for phenol in hydrocarbon solution. (The q values give the quantum yield for the processes at 295 K.)

This comparison gives further evidence that a rupture of the O—H bond followed by non-homogeneous recombination of the radicals is an efficient route in the S_1 to ground state conversion of phenol in hydrocarbon solutions. The value of q_{RP} , however, remains unknown and the question whether other non-radiative pathways contribute to the S_1 deactivation is still unsolved.

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