

## TEMPERATURE EFFECTS ON THE PHOTOPHYSICAL BEHAVIOUR OF PHENOL AND ANISOLE IN VARIOUS SOLVENTS<sup>†</sup>

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### Summary

A photophysical study of phenol and anisole in polar and non-polar solvents performed at various temperatures is presented. The main mechanisms responsible for the deactivation of  $S_1$  are identified and are discussed in the light of radiationless transition theory. The results indicate that the lowest singlet state of these molecules deactivates via a triplet manifold. The type of final state reached, *i.e.* associative or dissociative, depends on the relative position of the energy surfaces and on the influence of the solvent on the molecular states.

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### 1. Introduction

The fluorescence quantum yield of phenol, like that of many other benzenoid hydrocarbons, depends on the initially excited electronic state [1 - 4]. Compounds exhibiting the same behaviour include phenols, anilines, indoles and most aromatic amino acids with benzenoid groups as chromophores. Solvents generally play an important role in the photophysical and photochemical properties of these substances [1, 4 - 6]. In fact it is well known that the deactivation of excited states in these compounds includes photochemical processes such as photodissociation or electron ejection accompanied by the production of a solvated electron [7 - 13] depending on the solvent used. Studies of these processes have been carried out for the photoionization of phenolic and indolic compounds in particular because of their role in biological systems. Various mechanisms have been proposed to explain the photodissociation of phenols and the formation of phenoxyl radicals. They include monophotonic or biphotonic processes [7 - 9, 13 - 15], the existence of a triplet state as the precursor of the photolysis [8, 9, 14] and charge transfer to the solvent [4].

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Extensive studies of phenols in various solvents by Getoff and coworkers have shown that the photochemical cleavage of the O—H bond is the main process responsible for the variation in the behaviour of the fluorescence quantum yield as a function of the excitation wavelength [3, 6, 16]. Owing to the formation of hydrogen bonds, this dependence is fairly weak in polar solvents such as alcohols and ethers (but not water) but is very strong in hydrocarbon solvents [1, 3, 12, 16].

The nature of the process which competes with the internal conversion  $S_2 \rightsquigarrow S_1$  and the nature of the non-radiative decay originating from the  $S_1$  state in phenols are not clear. The sum of the fluorescence and triplet yields is generally less than unity, and the balance can be assigned to a radiationless transition leading to photodecomposition [3, 16].

In order to obtain information about the radiationless routes by which the  $S_1$  state deactivates we measured the fluorescence lifetime of phenol and anisole in 3-methylpentane and in 1:1 methanol-ethanol at various temperatures. Several possible mechanisms for the deactivation of the excited states of phenol and anisole were identified from analysis of the experimental results and these are discussed with the aid of model calculations based on radiationless transition theory. In view of the unusual photophysical behaviour of phenol in hydrocarbons, we shall focus the discussion on the deactivation mechanism of the  $S_1$  and  $S_2$  states of this system. In particular, the energies of the states involved and the intersystem crossing integrals for phenol are estimated using the intermediate neglect of differential overlap/spectroscopic (INDO/S) approximation, whereas the dynamics of the processes are investigated using a localized model which has already been successfully applied to hydrogen abstraction from alkanes [17, 18] and the photodissociation of aryl halides [19].

## 2. Experimental details

Phenol (Carlo Erba, reagent grade) was purified by sublimation under vacuum and anisole (Carlo Erba, reagent grade) was passed three times through a column of freshly activated silica gel. The solvents used were ethanol, methanol and 3-methylpentane (3MP) (Carlo Erba, spectroscopic grade). The alcohols were purified by distillation and 3MP was purified by repeated column chromatography on silica gel.

Solutions of phenol and anisole in 1:1 ethanol-methanol and in 3MP with an optical density ranging from 0.1 to 0.3 were sealed under vacuum after repeated freeze-pump-thaw cycles in a 1 cm fluorescence cell.

Lifetime measurements were made using a single-photon time correlation technique. A thyatron-gated flash lamp filled with deuterium with a full width at half-maximum of about 2.5 ns was used. Excitation was performed at 265 nm using a monochromator. The emission was viewed at right angles using a Philips 56DUVP/03 photomultiplier and a 295 nm narrow-band interference filter (Balzers). The accumulated data were fed

into a PDP 11/23 microcomputer and were then processed. The single-exponential decay signals were analysed by deconvolution employing a non-linear least-squares procedure. The reduced  $\chi^2$  values were less than 1.3 in all cases and the resulting residuals were regularly distributed along the time axis. Further details of the single-photon apparatus and the deconvolution procedure are reported elsewhere [20].

Low temperatures were maintained using a Thor C600 nitrogen flow cryostat with appropriate modifications and a Model 3030 temperature controller.

The energies of the relevant singlet and triplet states of phenol were obtained using an INDO/S program with the parametrization proposed by Ridley and Zerner [21] and a configuration interaction limited to 50 mono-excited configurations. All calculations were performed on an SEL 27/32 computer.

### 3. Results

The lifetimes of phenol and anisole dissolved in 3MP and the alcohol mixture were measured between 77 K and room temperature by exciting each compound in the  $S_1$  state. The fluorescence decay was attributed, on the basis of the deconvolution procedure, to a single-exponential function which generally exhibited a good fit.

The reciprocal lifetimes  $1/\tau$  of phenol and anisole in the alcohol mixtures and 3MP are plotted as a function of  $1/RT$  in Fig. 1. For all the samples investigated the decay is composed of a temperature-independent contribution and a thermally activated contribution which can be described by

$$\frac{1}{\tau} = k_0 + A \exp\left(-\frac{\Delta E}{RT}\right) \quad (1)$$

The full curves were calculated using a non-linear iterative least-squares procedure and the values obtained for  $k_0$ ,  $A$  and  $\Delta E$  are given in Table 1.

It can be seen that in the case of phenol the frequency factor and, to a lesser extent, the activation energies vary depending on the solvent. In contrast, no differences in the photophysical parameters for anisole were present in the two solvents used. The lifetime of anisole was longer than that of phenol at both room temperature and 77 K.

The energies, oscillator strengths and compositions of the phenol states calculated using the INDO/S approximation are given in Table 2. It should be noted that, whereas the energies of the four low-lying  $\pi\pi^*$  singlets are reproduced well [22], the energies of the  $\pi\pi^*$  triplets are somewhat underestimated ( $T_1$  is about 1.0 eV lower than the literature value [23]). The energies of the lowest  $\pi\sigma^*$  triplets are calculated to be about 0.5 eV below the corresponding singlet states and we believe that their energy is more realistic; this conclusion is supported by previous calculations carried out using the same method for  $n\pi^*$  states of larger molecules [24].

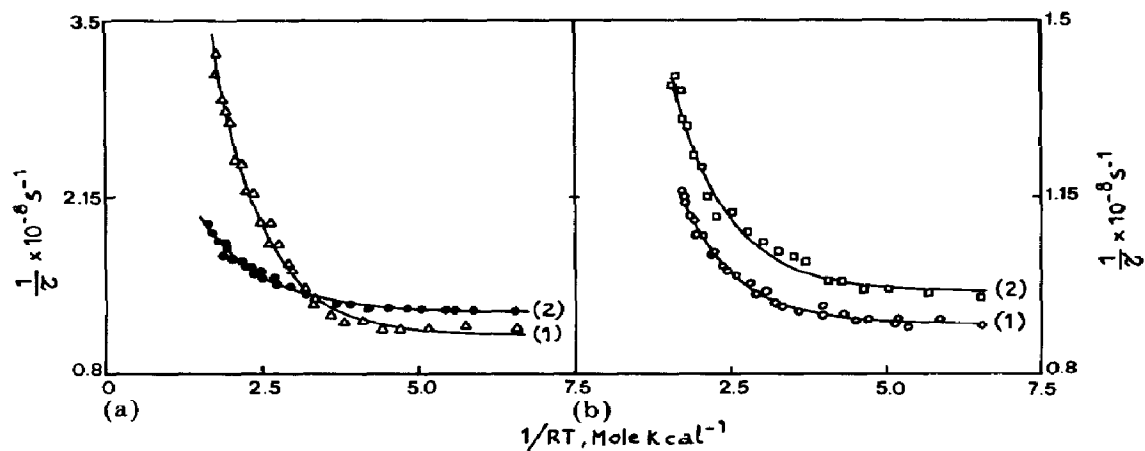


Fig. 1. Fluorescence rate parameters of phenol and anisole as a function of temperature: (a) phenol (curve 1, in 3MP; curve 2, in 1:1 ethanol-methanol); (b) anisole (curve 1, in 3MP; curve 2, in ethanol-methanol). Both the experimental points and the fitted curves are shown.

TABLE 1

Temperature-independent term  $k_0$ , activation energy  $\Delta E$  and frequency factor  $A$  obtained using eqn. (1)

Solvent	$k_0^a$ ( $s^{-1}$ )	$A^b$ ( $s^{-1}$ )	$\Delta E^c$ (kcal mol $^{-1}$ )
<i>Phenol</i>			
3MP	$1.2 \times 10^8$	$2.5 \times 10^9$	1.3
EtOH-MeOH <sup>d</sup>	$1.3 \times 10^8$	$2.8 \times 10^8$	0.9
<i>Anisole</i>			
3MP	$9.0 \times 10^7$	$2.0 \times 10^8$	1.2
EtOH-MeOH <sup>d</sup>	$9.7 \times 10^7$	$2.7 \times 10^8$	1.2

<sup>a</sup>Accuracy,  $\pm 7\%$ .

<sup>b</sup>Estimated error in  $\log A$ ,  $\pm 0.2$ .

<sup>c</sup>Estimated error,  $\pm 0.2$  kcal mol $^{-1}$ .

<sup>d</sup>1:1 ethanol-methanol.

The computed pattern of states forms a reasonable starting point for a discussion of the dynamics of the phenol deactivation processes.

#### 4. Discussion

It can be seen from the experimental results that the decay of the excited singlet state  $S_1$  in phenol and anisole in the two different solvents is composed of a temperature-independent term of the order of  $10^8$  s $^{-1}$  and a thermally activated component with a frequency factor of  $10^8 - 10^9$  s $^{-1}$  and an activation energy of the order of 1 kcal mol $^{-1}$ .

TABLE 2

Energies, oscillator strengths and compositions of the relevant states of phenol calculated using the INDO/S approximation

	$E_{\text{calc}}$ (eV)	$E_{\text{exp}}$ (eV)	$f$	<i>Composition</i> <sup>a</sup>
$S_1(\pi\pi^*)$	4.61	4.59 <sup>b</sup>	0.005	-0.64 (17 → 20) + 0.75 (18 → 19)
$S_2(\pi\pi^*)$	5.89	5.82 <sup>b</sup>	0.056	-0.54 (17 → 19) + 0.81 (18 → 19)
$S_3(\pi\sigma^*)$	6.26	—	0.000	0.98 (18 → 21)
$S_4(\pi\sigma^*)$	6.55	—	0.000	0.99 (17 → 21)
$S_5(\pi\pi^*)$	6.60	6.70 <sup>b</sup>	0.920	0.72 (17 → 20) + 0.61 (18 → 19)
$S_6(\pi\pi^*)$	6.64	6.93 <sup>b</sup>	1.010	-0.80 (17 → 19) + 0.53 (18 → 21)
$T_1(\pi\pi^*)$	2.41	3.55 <sup>c</sup>		0.70 (18 → 20) + 0.65 (17 → 19)
$T_2(\pi\pi^*)$	3.67			0.56 (17 → 20) + 0.81 (18 → 19)
$T_3(\pi\pi^*)$	3.71			-0.72 (17 → 19) + 0.67 (18 → 20)
$T_4(\pi\pi^*)$	4.65			0.81 (17 → 20) + 0.56 (18 → 19)
$T_5(\pi\pi^*)$	5.36			0.90 (18 → 22)
$T_6(\pi\pi^*)$	5.55			0.89 (17 → 22)
$T_7(\pi\sigma^*)$	5.66			-0.96 (18 → 21)
$T_8(\pi\sigma^*)$	5.90			0.98 (17 → 21)

<sup>a</sup>18, highest occupied molecular orbital ( $\pi$ ); 19, lowest unoccupied molecular orbital ( $\pi^*$ ); 21,  $\sigma^*$  orbital; 17 ( $\pi$ ); 20, 22 ( $\pi^*$ ).

<sup>b</sup>Ref. 22.

<sup>c</sup>Ref. 23.

Since anisole in both solvents and phenol in the alcohol mixture phosphoresce with a high quantum yield [16], it is reasonable to assume in these cases that the radiationless decay of  $S_1$  is mainly due to intersystem crossing (ISC) to the triplet. The magnitude of the frequency factor is consistent with a deactivation process of the ISC type. The photophysical parameters reported in Table 1 are very similar in these three cases leading to the reasonable conclusion that no unusual differences exist in the deactivation of the  $S_1$  excited state. Moreover, since at room temperature the contribution of the non-activated process, which is mainly attributable to ISC, is larger than that of the activated process, typically by a factor of 3, we can infer that the radiationless decay of  $S_1$  occurs through an ISC process for phenol in the alcohol mixture and for anisole in the alcohol mixture and 3 MP.

In the case of phenol in 3MP, the most significant difference in comparison with the other systems is the frequency factor which is an order of magnitude greater. In contrast with previous cases, at room temperature the contribution of the activated process is a factor of 2 larger than that of the non-activated process.

It has been shown [3, 16] that, in addition to internal conversion (IC) and ISC processes, a further decay route from  $S_1$  must be operative in phenol dissolved in hydrocarbons. It is also well known that in hydrocarbons phenol undergoes photolytic processes originating from  $S_1$  and  $S_2$  with cleavage of the O—H bond [3]. Furthermore, the fluorescence quantum yield decreases

at room temperature when excitation is performed in the  $S_2$  state, *i.e.* a fast process competitive with IC from  $S_2$  to  $S_1$  is operative [3].

Model calculations taking into account both the singlet states  $S_1$  and  $S_2$  have been performed to investigate the general mechanism by which phenol in hydrocarbons undergoes photolysis and to clarify the real meaning of the photophysical parameters obtained.

The processes involved in the deactivation of phenol in hydrocarbons can be rationalized by assuming that both the photophysical deactivation of the states and the photochemical outcome are dependent on a radiationless transition law, *i.e.* the Fermi golden rule

$$k_{i,f} = \frac{2\pi}{\hbar} V^2 \rho F \quad (2)$$

where  $i$  and  $f$  denote the initial and final states,  $V$  represents an electronic factor,  $\rho$  is the density of states of the final manifold and  $F$  is the sum of the appropriate Franck-Condon (FC) factors. We take  $S_i$  ( $i = 1, 2$ ) for the initial state and  $T_n$  ( $n \equiv d \equiv$  dissociative for the photochemical detachment of a hydrogen atom,  $n = i$  for the intermediate associative triplet and  $n = 1$  for the lowest triplet state) for the final state (Fig. 2).

The presence of a photodissociative state  $T_d$  located on the C-H bond is strongly suggested by the detection of hydrogen formation in non-polar solvents [3] and is confirmed by the calculation reported in Table 2 where at least two triplet  $\pi\sigma^*$  states are located in the  $S_2$  region (at 5.65 eV and 5.90 eV respectively). Following eqn. (2) the crossing from  $S_1$  to  $T_d$  will be governed by the spin-orbit coupling integral  $V \equiv H_{so}$  and the FC factor which depends on the relative energy of the manifolds involved in the process. The spin-orbit coupling integral can be estimated by taking into account the monocentric part of the integral centred on the oxygen atom [23]. The computed value for  $H_{so}$  between  $S_1$  and  $T_7$ , which has the best configuration matching with  $S_1$ , is about  $2 \text{ cm}^{-1}$ .

To determine the FC factor in eqn. (2) we fixed the origin of  $T_d$  at 5.90 eV in the region of the vibrationless level of  $S_2$ . The dependence of the energy of  $T_d$  on the stretching coordinate  $R_{O-H}$  can be approximately described by a straight line with a slope similar to that calculated for the photodetachment of hydrogen atoms from alkanes [17]. The vibrationless level of  $S_1$  is estimated to cross  $T_d$  at a distance of 0.15 - 0.25 Å from equilibrium, depending on the relative position of  $S_2$  with respect to  $S_1$ . The corresponding vibrational factor of eqn. (2) estimated in the  $\delta$  function approximation [17] is found to be  $10^{-3} - 10^{-4}$  which combined with the  $H_{so}$  factor gives a rate constant  $k$  of  $5 \times 10^8 - 5 \times 10^9$  for photodetachment from  $S_1$ .

However, crossing to an associative  $\pi\pi^*$  triplet  $T_1$ , which lies at a more favourable energy as computed for example for  $T_4$ , can exploit a much more favourable FC factor but an unfavourable electronic factor. In fact  $H_{so}$  between  $\pi\pi^*$  states is estimated to be about  $0.5 \text{ cm}^{-1}$  [25]. Taking into account a state density  $\rho = 1/\nu_{O-H}$  [26], a frequency  $\nu_{O-H}$  of  $3800 \text{ cm}^{-1}$  and an FC factor close to unity, we found a rate constant of the order of  $10^8 \text{ s}^{-1}$ .

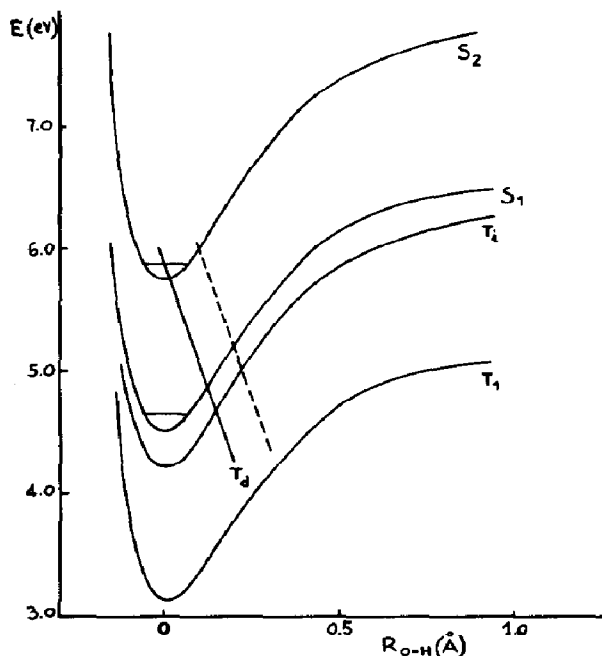
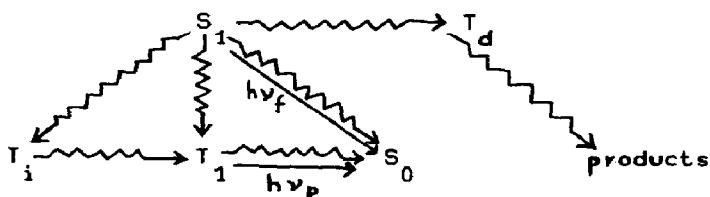


Fig. 2. Possible energy surfaces relative to photodissociation in the systems investigated: — — —, dissociative curve with an unfavourable addition of energy owing to the hydrogen bonding, *i.e.* phenol in ethanol-methanol.

for the process  $S_1 \rightsquigarrow T_i$ . Once the crossing has occurred  $T_i$  can deactivate by internal conversion to  $T_1$  or  $T_d$ , but the latter process becomes slow owing to the larger barrier to be overcome to reach  $T_d$  as shown in Fig. 2. The various processes of deactivation of  $S_1$  described so far can be summarized in the following scheme:



Comparing these estimates with the experimental values given in Table 1, we observe that, apart from a qualitative agreement of the order of magnitude for the rate constants, the higher spin-orbit coupling relative to the crossing  $S_1 \rightsquigarrow T_d$  is consistent with the higher frequency factor of phenol in 3MP relative to that of phenol in polar solvents. However, the small almost equal energy barriers detected in the two cases must be ascribed to the temperature-dependent vibrational part of eqn. (2) which is composed of an FC factor modulated by the state density of the final manifold. It is found that the high density of the dissociative state compensates the unfavourable FC factor relative to the  $S_1 \rightsquigarrow T_d$  crossing. This also agrees with the enhance-

ment of the rate constant observed for phenol in 3MP when the temperature is increased. This indicates the marked dependence of the vibrational part of eqn. (2) on temperature, which is typical of dissociative processes [18].

Since the two  $S_1$  deactivation mechanisms ( $S_1 \rightsquigarrow T_d$  and  $S_1 \rightsquigarrow T_i$ ) are assumed to be competitive, it is expected that additional barriers to one of the processes will favour the other. In fact the presence of hydrogen bonding, which introduces additional barriers to the crossing to  $T_d$ , will favour the deactivation of  $S_1$  to  $T_i$  in the case of phenol in the alcohol mixture, and this is confirmed by the absence of hydrogen production [3]. This feature is shown in Fig. 2 by a broken line parallel to  $T_d$  but located at higher energies with respect to the associative states  $S_1$  and  $S_2$ .

The kinetic parameters found for anisole in both solvents are almost equal to those of phenol in the alcohol mixture, and they indicate that in this case also the preferred mechanism of deactivation of  $S_1$  is crossing to an associative triplet  $T_i$ . In fact phosphorescence is observed for both phenol in the alcohol mixture and anisole in the alcohol mixture and 3MP [16]. The absence of photodissociation in anisole has to be ascribed to the much more delocalized nature of the O—C bond which shares its electronic density distribution with all the other bonds in the molecule. As in the case of hydrocarbons where the C—C bonds are delocalized and their rupture is unfavourable compared with that of the localized C—H bonds, the energy necessary to break the O—C bond in anisole is much higher than that required for the cleavage of the more localized O—H bond [17, 27].

Finally, we observe that the presence of dissociative triplet states along the O—H coordinate of phenol located at an energy very close to  $S_2$  explains the different quantum yields of fluorescence obtained in hydrocarbons when the  $S_1$  or  $S_2$  states are directly excited [3]. This feature can be ascribed to direct photodissociation occurring from  $S_2$  and competing with the internal conversion process  $S_2 \rightsquigarrow S_1$ . In fact, from the calculated value of  $2.5 \text{ cm}^{-1}$  for  $H_{so}$  for  $S_2 \rightsquigarrow T_d$  and the estimated value of about  $100 \text{ cm}^{-1}$  for the vibronic coupling term of the IC process [25], we obtain  $k_{ISC} = 7 \times 10^{11} \text{ s}^{-1}$  and  $k_{IC} = 3 \times 10^{11} \text{ s}^{-1}$ . This means that the ISC and IC processes are competitive and hence the high quantum yield for hydrogen production obtained by exciting the  $S_2$  manifold directly is justified. Also, the addition of further energy barriers to  $T_d$ , such as hydrogen bonding for phenol dissolved in the alcohol mixture or electronic delocalization for anisole, renders the photodissociation with respect to the IC process to  $S_1$  much slower and finally uncompetitive.

This feature agrees with the weak dependence of the fluorescence quantum yield on the excitation wavelength for phenol in hydrogen-bond-forming solvents and for anisole in all the solvents investigated.

## 5. Conclusions

In this work we have investigated the photophysical behaviour of phenol and anisole by varying the temperature in two different solvents. The



experimental kinetic values indicate that the main routes of deactivation of  $S_1$  are radiationless transitions to triplet states. Model calculations based on radiationless transition theory helped to identify the nature and relative energies of the final states reached during the deactivation process. Despite the approximations introduced in this model we found that the main experimental features were reasonably reproduced, and we believe that explicit inclusion of further details such as hydrogen bonding and delocalization effects will produce a marked improvement in our understanding of these molecules.

Studies of deuterium and substituent effects which are now in progress will provide a deeper insight into the photophysical properties of these and related systems.

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