

ISOTOPE EFFECT ON THE PHOTOPHYSICAL PROPERTIES OF PHENOL

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Summary

The photophysical properties of phenol and its deuterated derivatives have been investigated by measuring the lifetime and the quantum yield of fluorescence at various temperatures in 3-methylpentane. The differences observed in the lifetime values and in the quantum yields of fluorescence have been explained with localized potential energy surfaces and current theory on radiationless transition processes taken into account.

1. Introduction

As it is a prototype of a large class of molecules of biological interest, phenol has been the subject of several studies aimed at investigating the nature of its excited states [1 - 6]. Recent studies have shown that, beyond the usual ways of photophysical deactivation, this molecule undergoes different kinds of photochemical processes such as electron ejection or cleavage of the O-H bond. Electron ejection takes place in polar solvents [4, 7 - 9], whereas cleavage of the O-H bond is favoured in non-polar solvents, such as saturated hydrocarbons [2, 3, 10]. Moreover the quantum yields of fluorescence and of hydrogen production show a marked dependence on the initially excited electronic state [10 - 12].

In a previous note we reported a photophysical study of phenol and anisole at various temperatures, both in saturated hydrocarbons and in alcohols [3]. The kinetics parameters, deduced from the Arrhenius curves of the fluorescence lifetimes *vs.* the temperature, led us to infer that the main non-radiative route of deactivation of S_1 is an intersystem crossing (ISC) to the triplet manifold. The presence of a dissociative triplet with a highly favourable Franck-Condon factor from S_2 and a less favourable factor from S_1 was suggested and a comprehensive picture of the photophysical properties of phenol in different solvents and with different initial excitation was provided. In order to test the model proposed in ref. 3 and to obtain further insight into the photophysics of phenol, we extended this study to include the

deuterated derivatives. In particular we examined compounds isotopically substituted in the O—H bond as C_6H_5-OD and in the ring as C_6D_5-OH and C_6D_5-OD . The mass substitution of the hydroxyl hydrogen atom should be effective in the photochemical cleavage of the O—H bond [13], whereas the main effect of deuteration of the ring is expected to concern the internal conversion processes such as $S_2 \xrightarrow{h\nu} S_1$ and $S_1 \xrightarrow{h\nu} S_0$ [14].

2. Experimental details

Totally hydrogenated phenol C_6H_5-OH (C. Erba, reagent grade), partially deuterated phenols C_6H_5-OD and C_6D_5-OH (MSD Isotopes) and totally deuterated phenol C_6D_5-OD (Aldrich) were purified by sublimation into a dry-box filled with dry nitrogen.

Because of the sensitivity of phenol to water molecules in forming hydrogen bonds, particular care was taken in purifying and dehydrating the solvent used. 3-Methylpentane (3MP) (C. Erba R.P.E.) was twice chromatographed on activated silica gel and then dried over anhydrous Na_2SO_4 . In addition it was refluxed for some hours over metallic sodium and then distilled in a current of dry nitrogen. The purified solvent was kept under dry nitrogen. The purity was controlled fluorimetrically.

All the solutions were prepared in a dry-box soon after the sublimation of each sample and then sealed under vacuum after repeated freeze-pump-thaw cycles in fluorescence cells of path length 1 cm. Care was taken to avoid any contact with air during this last procedure.

For the lifetime measurements the absorbance of each sample was adjusted in the range 0.1 - 0.2 at the excitation wavelength. The measurements were made using a single-photon time correlation technique. 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. Further details on the single-photon apparatus and the deconvolution procedure are reported elsewhere [3, 15].

The fluorescence spectra were detected with an MPF44-B spectrofluorimeter equipped with a DCSU-2 differential corrected spectra unit (Perkin-Elmer). The absolute fluorescence quantum yields of the phenols in 3MP at 295 K and at $\lambda_{exc} = 265$ nm (4 nm bandwidth) were obtained using biphenyl and *p*-xylene in cyclohexane as standards [16]. Optically thin solutions were used (optical density, about 0.08 for a 10 mm pathlength) in a right-angle geometry and refractive index correction was made. The absorbances of the solutions were determined by the same optical system used to detect the emission and were adjusted to be very similar for the phenols and the standard to compensate for inner filter effects. The fluorescence quantum yields of phenols in 3MP at $\lambda_{exc} = 220$ nm (4 nm bandwidth) were obtained by comparing the corrected emission intensities of equally absorbing samples,

excited at 220 and 265 nm. The uncertainty in the quantum yields derived using two different standards was within 10%. The ratio β between the fluorescence quantum yields exciting in S_2 and in S_1 , given by $\phi_F(S_2)/\phi_F(S_1)$, as a function of the temperature was determined by comparing the corrected emission intensities at a given temperature with those obtained at 295 K under the same experimental conditions. In the temperature range 230 - 295 K the shape of the absorption spectrum was controlled and found not to change appreciably. At lower temperatures a decrease in both the fluorescence intensity and absorbance was observed, indicating that molecular association probably occurs. Analogous behaviour has been reported for other molecular species following slow cooling of 3MP solutions [17].

Low temperatures were maintained using a Thor C610 nitrogen flow cryostat equipped with a Thor 3030 temperature controller and indicator. The absolute error is estimated to be ± 2 K.

3. Results

The lifetimes of phenol and its deuterated derivatives in 3MP were measured between 80 and 295 K by exciting each compound in the first singlet state.

Figure 1 shows the behaviour of the reciprocal lifetime $1/\tau$ (k) of the totally hydrogenated and the totally deuterated compounds as a function of $1/RT$. The curves of the partially deuterated compounds C_6H_5-OD and C_6D_5-OH overlap those of the totally deuterated C_6D_5-OD and of the totally hydrogenated C_6H_5-OH respectively.

For all the molecules investigated the decay rate constant is composed of a temperature-independent term and a thermally activated contribution:

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

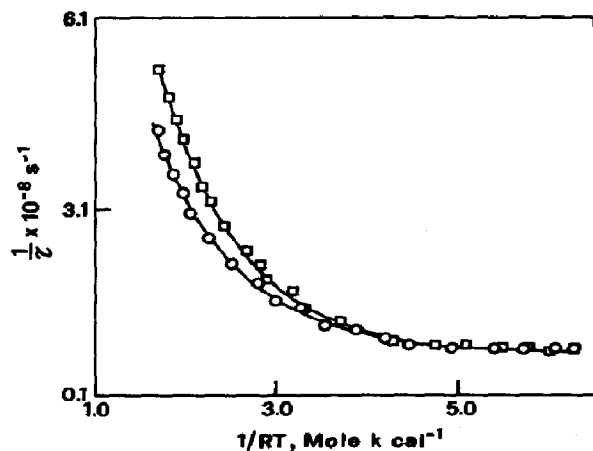


Fig. 1. Fluorescence rate parameters of phenol in 3MP: \circ , totally deuterated; \square , totally hydrogenated. Both the experimental points and the fitted curves are shown.

The full curves of Fig. 1 were calculated using a non-linear iterative least squares procedure and the values obtained for k_0 , A and ΔE for all the compounds in 3MP are given in Table 1. In a previous paper [3], a value of k_0 for C_6H_5-OH was reported which was about 1.5 times higher than the value we report in this paper. We attribute this difference to the poor dehydration of the solvent and to the formation of complexes of phenol with water molecules.

The fluorescence quantum yields of phenol and its deuterated derivatives obtained by excitation in S_2 ($\lambda_{exc} = 220$ nm) and in S_1 ($\lambda_{exc} = 265$ nm) in 3MP at 295 K are reported in Table 2. The ratio β at different temperatures in the range 230 - 295 K is also shown. The values for the quantum yields and β reported for totally hydrogenated phenol are in agreement with previous determinations [12, 16]. The quantum yields of the deuterated compounds for 265 nm excitation are well correlated with the lifetime values.

TABLE 1

Temperature-independent term k_0 , activation energy ΔE , pre-exponential factor A in 3-methylpentane obtained using eqn. (1) and experimental lifetimes τ at 295 K

Phenol derivative	k_0 (s^{-1})	A (s^{-1})	ΔE (kcal mol $^{-1}$)	τ (ns) ^a
C_6H_5-OH	7.6×10^7	2.9×10^9	1.1	1.9
C_6D_5-OH	7.8×10^7	2.7×10^9	1.1	2.0
C_6H_5-OD	7.8×10^7	1.9×10^9	1.0	2.4
C_6D_5-OD	7.7×10^7	1.9×10^9	1.0	2.4

^aAccuracy, $\pm 7\%$.

TABLE 2

Fluorescence quantum yields ϕ_F and β values of phenol derivatives in 3-methylpentane

Phenol derivative	$\phi_F(S_1)$ ($\lambda_{exc} = 265$ nm)	$\phi_F(S_2)$ ($\lambda_{exc} = 220$ nm)	$\beta (= \phi_F(S_2)/\phi_F(S_1))$ ^a values at the following temperatures		
			295 K	251 K	230 K
C_6H_5-OH	0.08	0.03	0.37 ₅	0.43	0.46
C_6H_5-OD	0.10	0.04	0.40		
C_6D_5-OH	0.07 ₅	0.02	0.26 ₅		
C_6D_5-OD	0.09 ₅	0.02 ₅	0.26 ₅	0.28	0.30

^aEstimated error, $\pm 13\%$.

4. Discussion and conclusions

4.1. Deactivation processes following excitation in S_1

The kinetics parameters reported in Table 1 show some dependence on the isotopic substitution. Differences are observed between the lifetimes at

room temperature (see Fig. 1) and between the frequency factors. The differences observed depend in particular on the isotope substitution in the hydroxyl group. However, no deuterium effect is observed on the temperature-independent rate constants k_0 or for isotope substitution on the ring hydrogens. The values of the frequency factors found for all the compounds in 3MP are consistent with an activated process leading to the triplet manifold [3]. In particular the majority of the molecules at room temperature reach the dissociative triplet; the remaining molecules reach an associative triplet ($\phi_T = 0.32$) [2] or convert to the ground state by fluorescence and internal conversion. While we cannot exclude *a priori* the presence of a dissociative triplet isoenergetic with S_1 , we think that a natural candidate for this state is the $\sigma\sigma^*$ state localized on the O—H stretching coordinate, which correlates to the σ^2 ground state at long distances. By calculating the analytical dependence of this state on the distance $R(\text{O—H})$ [18, 19] and by describing the potential energy curves for the associative states S_0 , S_1 , S_2 and T_1 as Morse curves, with the minima located at the experimental spectroscopic energies and dissociative threshold at 88 kcal mol^{-1} [20], we obtain a state diagram such as that reported in Fig. 2.

We observe that the energy of S_1 , at about $37\,000 \text{ cm}^{-1}$ [3] occurs well above the dissociation limit of S_0 at $30\,791 \text{ cm}^{-1}$, but the high energy barrier to be overcome to reach $T_d(\sigma\sigma)^*$ does not permit a direct photodissociation from S_1 ($v = 0$). However, we observe that an intermediate triplet state, lying at favourable energy, can avoid the crossing to the dissociative triplet to give an adiabatic curve of the type drawn in Fig. 2 (full line). In analogy with the model proposed for the photodissociation of toluene [21], we suggest that this state can be identified with T_1 , with an equilibrium energy $E(T_1) =$

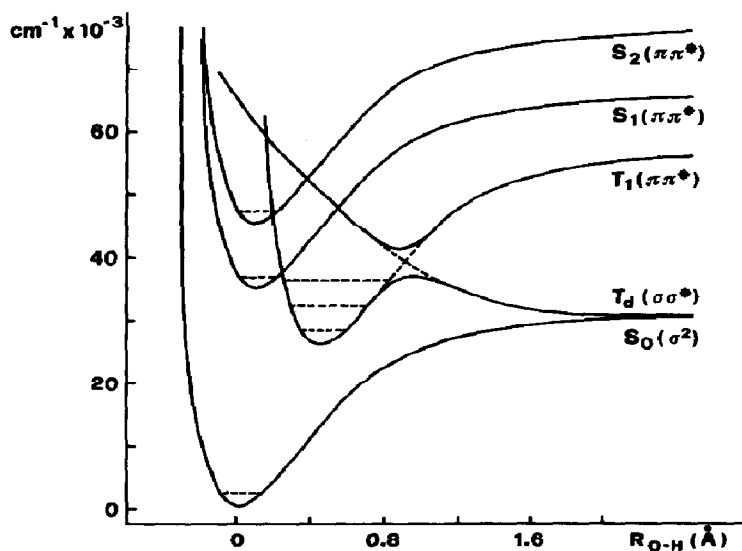


Fig. 2. Possible potential energy surfaces localized on the photodissociative coordinate.

28 634 cm^{-1} . Moreover, this hypothesis requires either a triplet surface quite displaced with respect to S_0 and a reasonable vibronic coupling integral or an undisplaced surface but a very large non-adiabatic matrix element. In the absence of experimental data or more detailed calculations supporting one of these hypotheses, we choose the model which better fits the overall observations (see Fig. 2), but we cannot exclude *a priori* in this region the presence of an intermediate triplet different from T_1 and quite displaced along the $R(\text{O}-\text{H})$ coordinate as recently pointed out in the case of chlorobenzene photodissociation [22]. The presence of an intermediate triplet state reached from S_1 with a very favourable Franck-Condon factor is consistent with the lack of deuterium effect observed on the k_0 values, which would be certainly mass dependent in the case of direct tunnelling to T_d . However, the only deuterium effect observed concerns the lifetimes at high temperature of the molecules isotopically substituted in the O-H group. The analysis of the kinetics parameters shows that this difference arises substantially from different values of the frequency factors. Since the frequency factors are directly related to the density of states of the final manifold reached and to the electronic factor, which is mass independent [23], the somewhat larger value found for the -OH molecules has to be related to a larger probability of dissociation of these molecules. Along the model of surfaces proposed above, the dynamics of this process at room temperature can proceed as follows. A vibronic level of S_1 , at about 1 kcal mol^{-1} above the zero energy level and delocalized on the whole molecular skeleton, for example along the low frequency, isotopically independent out-of-plane modes of b_1 and a_2 symmetries [24], is thermally populated and goes to an excited level of T_1 through an activated intersystem crossing. In this state part of the energy is concentrated on the localized OH stretching to give dissociation, whereas the remaining part is lost thermally. Such a dynamical model seems to be in agreement with recent measurements of the triplet lifetime of the isolated molecule in supersonic jets, which show an anomalously short triplet lifetime (300 ns) by excitation in the region of S_1 ($v = 0$), compared with other aromatics in the same conditions [6]. In the OH stretching surface, therefore, the $\nu_0^{\text{OH}} + \Delta E$ level would result more coupled to the dense vibrational continuum of T_d than the corresponding $\nu_0^{\text{OD}} + \Delta E$ level, because of the different zero level energies, and this feature would be reflected in different values of frequency factors and rate constants for internal quenching of fluorescence at high temperatures.

4.2. Deactivation processes following excitation in S_2

Table 2 shows the fluorescence quantum yields obtained by exciting into S_2 and S_1 the compounds dissolved in 3MP. In this case the compounds can be divided into two categories, depending on the deuteration of the ring. In fact it turns out that the compounds deuterated in the ring show a smaller $\phi_F(S_2)$ with respect to the ring-hydrogenated counterparts and this feature is reflected in the β values at room temperature, ranging from about 0.39 for the lighter compounds to about 0.26 for the heavier compounds. This isotope

effect is small when the experimental uncertainties are considered, but it is very reproducible on repeated independent runs and it is therefore taken as reliable. This isotope effect is expected on the basis of different rate constants of the internal conversion $S_2 \rightsquigarrow S_1$ radiationless process for the two classes of compounds. In fact, it is well known that the C—H (C—D) stretchings are very effective accepting modes as a result of the relatively high frequency [25].

A slight temperature dependence of the ratio β is observed for the totally hydrogenated and deuterated phenols by varying the temperature from 230 to 295 K. This means that for the single molecule of phenol the photodissociation process occurring from S_2 has a very small barrier to overcome and that the process can take place in times comparable with the fast internal conversion process $S_2 \rightsquigarrow S_1$, as suggested in ref. 3. The observed independence of β of the deuterium substitution in the O—H group (Table 2) can be explained within the model of potential energy curves proposed to explain the photophysical deactivation of S_1 . In fact the crossing of S_2 ($v = 0$) to a high level of T_1 , well above the dissociation limit, occurs with a very favourable Franck-Condon factor and it is consistent both with the high quantum yield of direct dissociation from S_2 and with the lack of selection between the O—H and the O—D cleavage in this energy region.

In conclusion, the qualitative model proposed appears to be able to explain most of the basic features of the photophysics of this system. In order to get insight more deeply into the details of these processes more calculations on the potential energy curves and more experimental information on the lowest triplets are required.

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