Electronically Induced Proton Transfer Reactions in Salicylic Acid Esters and Salicyloyl Chloride

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The multiple fluorescence emission spectra, excitation spectra, and lifetime of isopropyl salicylate, tert-butyl salicylate, and salicyloyl chloride have been analyzed in the gas phase and in cyclohexane and N_i -dimethylformamide solutions. Study of the electronic emission and IR absorption spectra of both esters and methyl salicylate gives further support to the hypothesis of a ground-state equilibrium between two intramolecular H-bonded conformers. The efficiency of the excited-state proton transfer reaction was determined from fluorescence and lifetime data of the 450-nm emission and found to be ca. 40% lower in tert-butyl than in methyl salicylate. On the other hand, the characteristic fast electronic energy relaxation of these compounds was not sensitive to the carboxyl substituent. Finally, the effect of solvent polarity on the radiationless rate was discussed in terms of the interaction between (π,π^*) and (n,π^*) states of the zwitterionic structures.

Introduction

The proton transfer reaction between two vicinal functional groups in electronically excited states is one of the few chemical reactions that can take place in the subnanosecond time range.^{1,2} This process was anticipated by Weller^{3,4} to account for the dual emission and the large Stokes shift that characterize the fluorescence of salicylic acid and its methyl ester. Based on the ideas put forward by Förster⁵ on the shift of the acid-base equilibrium produced by optical excitation, Weller assumed that a "protomeric" equilibrium was established during the lifetime of the excited molecules. Then, the dual emission from salicylic acid could be interpreted as originating in the "neutral" and "zwitterionic" forms derived from a single ground-state species. More recent investigations on methyl salicylate (MS) by Klöpffer and Naundorf⁶ and on methyl 2,6-dihydroxybenzoate by Kosower and Dodiuk⁷ have discovered that the relative intensity of the two emission bands depends on the wavelength of excitation. We extended these observations to a series of salicylic acid derivatives, either in the gas phase or in nonpolar solvents.⁸⁻¹⁰ Moreover, we postulated that, under these conditions, the dual fluorescence of MS is best explained if a ground-state equilibrium between two chelated H-bonded rotamers were established (Figure 7). This hypothesis received some confirmation from our recent finding of a single fluorescence in salicylaldehyde, salicylamide, and o-hydroxyacetophenone,¹⁰ compounds that can have only one rotamer.

The proposed ground-state conformers could be detected, at least in principle, by alternative techniques such as IR and NMR spectroscopies. In this paper we report the results of a search for this evidence, based on the analysis of the changes induced in the fluorescence and IR absorption spectra by substitution in the methyl group of MS.

In addition to the weak multiple fluorescence, methyl salicylate has the property of converting large amounts of electronic excitation energy into heat via an efficient picosecond process. This property is common to a number of complex aromatic molecules, also having intramolecular hydrogen bonds, widely used for protecting fibers and polymers from damage by UV radiation.¹¹ Thus, the investigation of the radiationless decay of salicylic acid esters, as the simplest prototype compound, could be invaluable to an understanding of the relationship between the intramolecular proton transfer reaction in the excited state and the UV-protecting efficiency. Some of the most recent work^{1,9,12} done on MS was also concerned with this point. Nevertheless, the exact mechanisms by which the excited-state proton motion mediates in the radiationless transitions or even the spin multiplicity of the intervening states are still a matter of conjecture. In this work we also show that important changes in the efficiency of the proton transfer reaction and in the decay of zwitterionic species are induced when the alkyl ester group in MS is changed from methyl to isopropyl and tert-butyl. The combination of steady-state and time-resolved fluorescence techniques made possible to study both effects separately, giving additional information on the electronic deactivation mechanism.

The emission of salicyloyl chloride is also included here, because of its utility for distinguishing between electronic and steric effects on the photophysical processes of the parent molecule MS.

Experimental Section

Materials. Methyl salicylate (MS) (Merck) was purified by several vacuum distillation cycles. Isopropyl salicylate (IPS) was obtained from salicylic acid and isopropyl alcohol in the presence of concentrated HCl. The ester was washed with aqueous 5% NaHCO₃, dried, and vacuum distilled (bp 110-112 °C, 15 torr). tert-Butyl salicylate (TBS) (from silver salicylate and tert-butyl chloride)¹³ was purified by column chromatography (silica gel, hexane) and vacuum distillation (bp 120-122 °C, 15 torr). Salicyloyl

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Figure 1. Gas-phase fluorescence spectra of isopropyl salicylate (p \simeq 0.1 torr). Dual emission (---), $\lambda_{\rm ex}$ = 300 nm. Excitation spectra at $\lambda_{\rm em}$ = 450 nm (---) and at $\lambda_{\rm em}$ = 350 nm (---).

chloride (SCl) was prepared from salicylic acid and thionyl chloride in benzene^{14,15} and distilled (bp 95 °C, 15 torr).

The purity of each ester was controlled by TLC with several eluents, while that of SCI was checked by chlorine analysis, IR spectrum, and refractive index $(n^{20}D) =$ 1.5812¹⁴). Only freshly distilled samples were used in the spectroscopic experiments. The solvents were purified and dried by standard procedures.

Methods. The vapors of the salicylic acid derivatives were handled in a grease-free vacuum line⁹ and transferred either to a 100-mm cylindrical absorption cell or to a 70mm spherical fluorescence cell. Emission and excitation spectra at room temperature were recorded with a SLM 8000 D photon-counting digital fluorimeter and processed with a PDP 11/05 minicomputer. All the spectra included here were corrected for the wavelength-dependent photomultiplier sensitivity and the energy distribution of the excitation setup, as described elsewhere.⁹ Fluorescence yields in the gas phase were estimated with reference to the benzene emission ($\phi_{\rm F} = 0.19$).¹⁶ The "absolute" visible $(\sim 450 \text{ nm})$ fluorescence quantum yields in solution were determined by using 10^{-5} M methyl salicylate in cyclohexane as a reference ($\phi_{\rm F} = 0.022$).⁹ The exclusion of oxygen from cyclohexane solutions of the salicylic acid derivatives results generally in a modest increase of the intensity of the visible fluorescence, well within our $\phi_{\rm F}$ experimental error of 10-20%. However, the UV emission, under such conditions, may increase by up to two times.

The emission lifetimes were measured by the singlephoton pulsed technique. A thyratron-controlled nanosecond flash lamp (Edinburgh Instruments E1 199) fitted with a 100-mm monochromator was used for repetitive excitation of the liquid samples. The emission was isolated with interference filters and the decay curves were analyzed on-line with the PDP 11/05 computer, using a nonlinear least-squares deconvolution routine. Frequent calibration of the instrument temporal response and "lamp shift" resulted in a time resolution of 300 ps for single exponential decays.

IR spectra (liquid films) were recorded with a Perkin-Elmer 580B spectrophotometer.

Results

Gas-Phase Emission. Figure 1 shows the room temperature fluorescence emission and excitation spectra of

TABLE I: Gas-Phase Absorption and Dual Emission Maxima^a (nm) of Salicylic Acid Derivatives $(p \leq 0.1 \text{ torr}; T = 20 \degree \text{C})$

compd	absorn	excitation	fluorescence
MS	303.5	298, 324	330, 445
IPS	303.5	300, 322	330, 450
TBS	304	300, 320	335, 455
SCI	324	302, 335	360, 505

^a The position of the visible fluorescence maximum depends on the excitation wavelength (see text).



Figure 2. Wavelength dependence of the relative fluorescence quantum yield of the visible band ($\lambda_{\rm max}\simeq$ 450 nm) in gas-phase methyl salicylate (MS), isopropyl salicylate (IPS), and tert-butyl salicylate (TBS). Absorption spectrum of gas-phase methyl salicylate (···).

the isopropyl ester of salicylic acid at low pressure (ca. 0.1 torr). The spectra of the tert-butyl ester, under the same experimental conditions, show similar characteristics. The collision-free regime results in a better resolution of the two excitation bands, as compared with that in the condensed phase. The small shoulder at 322 nm in the UV fluorescence excitation shows the amount of spectral contamination from emission in the visible at \sim 450 nm. These spectra are similar to but not identical with those of the methyl ester,⁹ as the relative contribution of the UV fluorescence to the total emission is quite different for the three esters. For example, when exciting at 300 nm, the fully corrected UV intensity for MS, IPS, and TBS is in the ratio 1:2:1.2, respectively.

The visible fluorescence excitation spectra show a large red shift (Table I) from the absorption spectra. We showed before for MS⁹ that under these conditions the light is absorbed almost exclusively by the molecular species responsible for this visible fluorescence. Therefore, the red shift should be produced by an energy-dependent emission efficiency, i.e., a rapid decrease of the quantum yield at shorter excitation wavelengths. Figure 2 shows the falloff of the normalized quantum yields of the three esters for higher excitation energies. In addition to that, λ_{max} of the 450-nm emission band depends on the excitation wavelength, an increase of the excitation energy resulting in a red shift of the fluorescence that, for MS, is ca. 250 cm^{-1} for every 1000-cm⁻¹ increase. A similar effect, although not as large, can be observed by increasing the temperature.⁹ The origin of this phenomenon may be related to the low height of the barrier for radiationless deactivation $(700-1000 \text{ cm}^{-1})^{9,17}$ of the emitting species. It is plausible that the molecules excited from the high-energy wing of the ground-state Boltzmann distribution disappear by nonradiative processes faster than the low-energy population.

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Figure 3. Gas-phase fluorescence of salicyloyi chloride ($p \simeq 0.1$ torr). Dual emission excited at 350 nm (—) and 300 nm (---). Excitation spectra at $\lambda_{\rm em} = 540$ nm (—) and at $\lambda_{\rm em} = 350$ nm (---).

TABLE II: Absorption and Dual Emission Maxima (nm) of Salicylic Acid Derivatives (10^{-5} M) in Degassed Cyclohexane Solutions and Fluorescence Quantum Yield ($\phi_{\rm F}$) and Lifetime (ns) of the Visible Emission

compd	absorn	excitation	fluorescence	$\phi_{\mathbf{F}}$	$\tau_{\rm F}$
MS	308	300, 308	335, 454	0.022^{a}	0.28^{b}
IPS	308	298, 308	$\sim 337, 455$	0.033	0.56
TBS	307	302, 307	$\sim 340, 460$	0.033	0.62
SCl	330	~335	$\sim 515^{'}$	10-4	
^a From	m ref 9.	^b From ref	1.		

Salicyloyl chloride vapor also shows a dual fluorescence band (Figure 3) in the collision-free limit, but with a very low efficiency, ca. two orders of magnitude less than MS

low efficiency, ca. two orders of magnitude less than MS and close to the detection limit of our experimental system. Two additional important differences relative to the salicylic acid esters were observed: the falloff of the fluorescence quantum yield at higher excitation energy is no longer abrupt, and the 505-nm emission bandwidth is almost 50% larger.

Solution Fluorescence Spectra. The relative intensity of the UV and visible components of the dual emission of the salicylic acid esters is solvent dependent. The room temperature excitation and emission spectra of the tertbutyl ester dissolved in a nonpolar solvent (cyclohexane) are shown in Figure 4. This is a representative example of the emission of most salicylic acid derivatives in a nonprotic medium with low dielectric constant. Under these conditions, the UV component of the fluorescence (Table II) might amount to only 5% of the total emission in contrast with the gas-phase spectrum. Hence, it can easily remain unnoticed in aerated solutions. The measured UV intensity shows no difference in the gas phase and in cyclohexane solution, within our experimental error. Therefore, the change in the relative intensity of the two bands results from the increased intensity of the visible band in solution. This is a consequence of the widely different quantum yield of the 450-nm fluorescence in both phases. Under collision-free conditions, the fluorescence yield was shown (Figure 2) to decrease very fast across the absorption band, eventually becoming zero, while in the liquid solution collisional stabilization⁹ gives a constant quantum yield, the 450-nm fluorescence excitation spectrum reproducing with fidelity the first absorption band (see, e.g., Figure 4). The smaller gap between the fluorescence excitation maxima of the two bands in solution $(700-900 \text{ cm}^{-1})$ as compared with that in the gas phase $(2000-2700 \text{ cm}^{-1})$ is also due to these changes in the visible quantum yield.



Figure 4. Emission spectrum of 10⁻⁵ M *tert*-butyl salicylate in degassed cyclohexane (---), $\lambda_{ex} = 300$ nm. Excitation spectra at $\lambda_{em} = 500$ nm (---) and at $\lambda_{em} = 360$ nm (---).



Figure 5. Emission spectrum of 10^{-5} M isopropyl salicylate in dimethylformamide (---), $\lambda_{ex} = 300$ nm. Excitation spectra at $\lambda_{em} = 490$ nm (---) and at $\lambda_{em} = 340$ nm (---).

In Table II the yields and lifetimes of the visible fluorescence of the three salicylic acid esters in cyclohexane are included. The emission decay could be fitted to a single exponential. On the other hand, our attempts to resolve the lifetime of the UV emission were unsuccessful, although a biexponential decay with a long lifetime component (0.9–1.5 ns) was detected in this spectral region. With much more complex instrumentation, a lifetime of 0.967 ns for the UV fluorescence of MS in acetonitrile has been recently determined.¹²

The fluorescence spectra of IPS in N.N-dimethylformamide (DMF) is shown in Figure 5. The relative intensity of the two emissions is completely different from that in nonpolar solvents. There is a large increase in the intensity ratio of the two bands at 340/450 nm, showing that an excitation wavelength could be found where the UV fluorescence would dominate the spectrum. The spectra of the methyl and *tert*-butyl esters are similar to that in Figure 5. Table III summarizes the corresponding data for the three derivatives and SCl. The maximum of the visible band of methyl salicylate in DMF solution is 450 nm and not 382 nm, as was erroneously given before.¹⁰ The lifetimes of the 450- and 340-nm fluorescence of the esters in DMF are very short, <100 ps and 300-500 ps, respectively, and could not be measured accurately with our instruments.

Figure 5 also includes the fluorescence excitation spectra of the dual band. The shoulder at 360 nm is produced by a hidden contamination of the main band with phenolate

TABLE III: Absorption and Dual Emission Maxima (nm) of Salicylic Acid Derivatives (10⁻⁵ M) in Aerated Dimethylformamide Solution and Fluorescence Quantum Yield of the Visible Emission (ϕ_F)

compd	absorn	excitation	fluorescence	φ _F
MS	306	300, 306	$342, 450^a$	0.005
IPS	306	300, 306	$\sim 340, 455$	0.007
TBS SCI ^b	306.5 329 5	298, 306 ~ 335	$\sim 340, 460$	0.007

^a 382 nm was erroneously reported in ref 10. ^b In acetonitrile solution.

ion fluorescence with λ_{max} at 410 nm. The precursor of this emission is the ground-state phenolate ion derived from IPS. Although present in minute amounts, its quantum yield is almost a hundred times higher than that of the neutral molecule. This phenolate emission can be made dominant just by adding a small amount of a strong base to the DMF solution.

Salicyloyl chloride also shows the characteristic large Stokes-shifted fluorescence of salicylic acid derivatives in various polar and nonpolar solvents, but again with extremely low efficiency. On the other hand, the high chemical reactivity of this compound resulted in the fast contamination of the solutions with a variety of fluorescent products. As a consequence, in Tables II and III we included data only for the long wavelength emission that can be more easily isolated. This emission in cyclohexane is unusually wide, ~ 150 nm fwhm. As the DMF solution of SCl is not stable, the spectra were recorded in acetonitrile (Table III), a solvent with the same dielectric constant. The fluorescence quantum yield in that solvent is close to our detection limit for this particular compound.

Discussion

Origin of the Gas-Phase Dual Fluorescence. According to the model we proposed before,⁸⁻¹⁰ the gas-phase ground-state population of the salicylic acid esters described here is distributed between two different conformations where the hydroxyl substituent participates in two types of intramolecular H bonds.

The most probable conformation on energetic grounds has the carbonyl group included in a six-member ring (IC in Figure 7) and gives rise to the 450-nm emission, after a fast proton shift² from the phenol to the carbonyl group. The "normal" UV (330 nm) fluorescence is produced by the excitation of a small amount of the other conformer (IIC), with a weaker H bond between phenolic and ethereal oxygen atoms. Therefore, either the concentration or the quantum yield of species IIC increases from MS to IPS, according to the trend described in the Results.

The IR spectra of the esters show a small shoulder at ca. 3450 cm^{-1} (Figure 6) which becomes more prominent with an increase in the alkyl group size. This absorption may be assigned to the O-H stretching of the phenol group bonded to the ether oxygen, according to the previously obtained data as follows: (i) the IR spectra of 2hydroxybenzyl alcohol and the corresponding methyl ethers, analyzed by Mori and Morioka,¹⁸ show bands in the range 3395-3429 cm⁻¹ that are assigned to the phenolic group internally H bonded to the alcoholic oxygen atom; (ii) the IR spectra of 2,6-dihydroxybenzoates¹⁹ show two hydroxyl absorptions: one of them ($\nu_{\rm OH} \sim 3200 \ {\rm cm^{-1}}$) was assigned to the "chelated" phenolic group (i.e., H bonded to the carbonyl oxygen), while the second one, at ca. 3470

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Figure 6. IR absorption spectra of liquid films of methyl salicylate (MS) and tert-butyl salicylate (TBS).



Figure 7. A model for some of the excited-state processes of salicylic acid derivatives. The proton shifts along the intramolecular H bond on excitation of rotamers IC to give Z states, which emit visible light (440-520 nm). Excitation of rotamers IIC gives rise to UV fluorescence. There is no measurable interchange of conformations in the excited state.

cm⁻¹, was assigned to a phenolic substituent bonded to the ethereal oxygen atom of the ester, just as in IIC; (iii) the IR spectrum of deuterated MS is consistent with these assignments.²⁰ In Figure 6 we also include an additional shoulder near 1730 cm⁻¹, tentatively assigned to the free C=O stretching of rotamer IIC, by analogy with methyl benzoate ($\nu_{\rm CO} = 1730 \text{ cm}^{-1}$).¹⁹

Thus, one can conclude that the increase in the molecular weight of the alkyl ester group in these salicylic acid esters produces a small shift toward the right in the ground-state equilibrium (Figure 7), following a similar trend in the H-bonding interaction between the phenolic proton and the ether oxygen. In fact, some evidence supporting this trend was obtained from the relationship²¹ of the gas-phase proton affinity with the O(1s) binding energy and the ionization potential of simple organic compounds. This correlation, when applied to the available photoelectron spectroscopy data^{22,23} of formic acid

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esters, shows that the basicity of both oxygen atoms in the ester group of the propyl and butyl esters is enhanced compared with that of methyl formate. Even more, the relative increase is higher in the ether than in the carbonyl oxygen atom. This result, by the way, confirms the qualitative predictions based on the well-known "inductive effect" of the alkyl groups. Hence, it is not unlikely that a similar change might take place in the salicylic acid esters studied here.

Radiationless Processes. The rapid electronic energy dissipation in all salicylic acid derivatives²⁴ studied to date is associated with the excited molecular species emitting visible (ca. 450 nm) fluorescence. Hence, the strong dependence of the quantum yield and lifetime of this particular emission on the excitation energy,⁹ temperature,^{1,9} solvent composition,¹² etc. is determined by the properties of the radiationless transitions. Figure 7 shows an idealized simple model where the most prominent excited-state processes of the compounds studied here have been identified. Excitation of rotamer IC results in the population of visible fluorescence emitters Z. In this model, $S_1(IC)$ is the "vertical" electronic excited state, i.e., the S_1 nuclear configuration is closer to S_0 than to Z. In particular, S_1 in MS apparently does not have a measurable lifetime.¹ Thus, it may be considered as the Franck-Condon configuration in the Z single minimum excited-state potential surface.²⁵ In other salicylic acid derivatives, $S_1(IC)$ might last long enough to emit fluorescence²⁶ (k_r') or to decay by nonradiative processes (k_n) , if the proton transfer rate constant $(k_{\rm Z})$ is of lower magnitude than in MS. In terms of the model, the probability of the proton transfer step $(\phi_{\rm Z})$ is

$$\phi_{\rm Z} = \frac{k_{\rm Z}}{k_{\rm r}' + k_{\rm n}' + k_{\rm Z}} \tag{I}$$

assuming an irreversible proton translocation. Once the molecule is trapped in the Z state, apparently there is no way of coming back to the initial excited-state configuration, as is discussed later. The exit channels available to Z states are emission (k_r) and nonradiative decay (k_n) . Thus, the fluorescence quantum yield of this species is

$$\phi_{\rm FZ} = \frac{k_{\rm r}}{k_{\rm r} + k_{\rm n}} \tag{II}$$

On the other hand, the experimental quantum yields of the visible fluorescence (ϕ_F) reported in Tables II and III were obtained from steady-state measurements of the emitted light $(Z \rightarrow S_0)$ absorbed in the transition $S_1 \leftarrow S_0$. According to this model

$$\phi_{\rm F} = \phi_{\rm Z} \phi_{\rm FZ} \tag{III}$$

Now, when 12 ns is used as the radiative lifetime²⁷ of Z and 0.28 ns as the 450-nm fluorescence lifetime of MS, eq II yields a value of $\phi_{\rm FZ} = 0.023$ for cyclohexane solutions. The steady-state quantum yield is $\phi_{\rm F} = 0.022$. Thus, we estimate from eq III a proton transfer probability close to 100% in liquid solutions, i.e., about 98% of the initially excited molecules decay by nonradiative routes connected with the Z state. The observed $\phi_{\rm Z}$ value requires that $k_{\rm Z} >> k_{\rm r}' + k_{\rm n}'$, which is consistent with the experimental

estimation¹ of a transfer rate greater than 10^{11} s⁻¹, even at 4 K. Furthermore, these figures imply that the proton transfer reaction actually is taking place in the electronically excited state, as Weller postulated.^{3,4} Therefore, a back-reaction should be physically possible, although in MS and other salicylic acid derivatives it is prevented by the much faster radiationless transitions. The deactivation mechanism in IPS and TBS shows interesting differences compared with that of MS. Assuming that all these compounds have the same radiative lifetime,²⁸ we can estimate $\phi_{\rm FZ}$ from the lifetimes of Table II in cyclohexane solution: 0.047 (IPS) and 0.052 (TBS). Thus, eq III gives a proton transfer probability of 70% and 63%, respectively, i.e., a substantial fraction of the initially excited molecules decays before populating the Z states. In addition to that, the nonradiative decay of these states is slowed down to some extent by the larger alkyl radicals in IPS and TBS. However, the fraction of molecules disappearing by nonemissive processes after reaching the Z state is still ca. 95%, practically the same as in MS. In conclusion, large amplitude internal rotational motions of the carboxylic group are unlikely to be responsible for the decay of those excited molecules in which proton transfer has taken place. On the other hand, these experiments suggest that the bulky alkyl radical may hinder the proton shift, probably by out-of-plane distortion of the hexagonal H-bonded ring.

The above results evidence that the efficient radiationless transitions in these molecules follow after the excited-state proton shift. However, we pointed out before¹⁰ that, in order to explain the large solvent effects on the fluorescence of some salicylic acid derivatives, an additional electronic factor must be present, which can modulate to some extent the ultrafast decay of the Z excited state. Thus, the 450-nm fluorescence quantum yield of MS is four times higher in cyclohexane than in DMF, while for salicylamide exactly the contrary happens.¹⁰ The fluorescence lifetimes are modified in a parallel way, symptomatic of the dependence of k_n on some solvent property. Recently,¹² it has been claimed that a positive correlation exists between the radiationless rate constant of MS and the solvent dielectric constant. For salicylamide, in contrast, this correlation does not hold.

It is possible¹⁰ that the relative energy of $(n,\pi^*)^{1,3}$ and $(\pi,\pi^*)^{1,3}$ states in the zwitterionic molecular species may be the crucial factor determining the efficiency of the radiationless transition. The energy of the (n,π^*) states made up from the carbonyl nonbonding electrons depends on the proximity of the phenolic proton and increases continuously as the proton approaches the carbonyl oxygen. In the limit, i.e., if the proton were completely transferred to the carbonyl group, these particular excited states should disappear, although new (n, π^*) states can be constructed from the n electronic density now available at the "phenolic" oxygen. On the other hand, the (π,π^*) singlet surface should be stabilized^{1,29} as the proton shifts from the phenolic to the carbonyl groups. Since in MS both kinds of electronic states are likely to be very close in energy,³⁰ the solvent dependence of their mutual interaction near the Z equilibrium position could be responsible for the changes¹² in the radiationless constant. In salicyloyl chloride, as in salicylaldehyde and o-

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⁽²⁷⁾ This is the 450-nm fluorescence lifetime at 4 K, measured in ref 25.

⁽²⁸⁾ The extinction coefficients differ by less than 3% and the emission spectra are also very similar. (29) The π -electronic distribution is sensitive to the hydrogen atom

⁽²⁹⁾ The π -electronic distribution is sensitive to the hydrogen atom position along the intramolecular bond, as, e.g., in keto/enol equilibrium. (30) This relative ordering of (π,π^*) and (n,π^*) states is based on the

⁽³⁰⁾ This relative ordering of (π,π^*) and (π,π^*) states is based on the experimental data for simple carbonyl and benzoic acid derivatives. Permanent dipole moments of the excited states were obtained by CNDO/S methods.

hydroxyacetophenone,¹⁰ (n,π^*) states should be at much lower energy³⁰ and, as a consequence, their very weak fluorescence is not solvent sensitive. Salicylamide, although from this last group according to our estimations, exhibits a strong solvent effect on the quantum yield. This can be explained because in this particular compound the dipole moment of the $(n,\pi^*)^{1,3}$ states of the Z configuration is much lower³⁰ than in the ground state, while that of the (π,π^*) states does not change appreciably. Greater relative destabilization of the (n,π^*) states would occur with increasing polarity of the solvent. This can decrease the energy gap between the interacting electronic states giving rise to a solvent-dependent fluorescence yield. Since this mechanism is different from that taking place in MS, the correlation of $k_{\rm p}$ with the dielectric constant of the solvent is not expected to be the same. This scheme is more consistent with a Z radiationless decay starting with intersystem crossing from the $(\pi,\pi^*)^1$ to a $(n,\pi^*)^3$, as Klöpffer suggested before.²⁴ Nevertheless, much information about the nature and multiplicity of the intermediate states (if any) in the zwitterion decay to the ground state is need before the mechanism of this process can be understood.

Summary and Conclusions

The dual fluorescence and IR spectra of isopropyl and tert-butyl salicylates give further support to the hypothesis of two different ground-state molecular conformations of salicylic acid esters in the gas phase and in nonpolar liquid solution. The efficiency and lifetime of the visible fluorescence of these derivatives show that the out-of-plane rotation of the carboxyl group may limit the efficiency of the proton transfer reaction. However, large amplitude internal rotation is not considered to be a critical factor in the deactivation chain of salicylic acid esters. Steadystate and time-resolved changes in the fluorescence of the excited state produced by the proton transfer reaction are examined as a function of solvent and carbonyl substituent. These observations show that the superfast radiationless channel is always connected with this particular electronically excited state. Finally, the involvement of interacting $(\pi,\pi^*)^1$ and $(n,\pi^*)^3$ states is invoked to explain the solvent-dependent fluorescence quantum yield and the first stages of the zwitterion decay.

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Registry No. Isopropyl salicylate, 607-85-2; tert-butyl salicylate, 23408-05-1; salicyloyl chloride, 1441-87-8; methyl salicylate, 119-36-8.

Carbon-13 Nuclear Magnetic Resonance Relaxation in Microemulsions. Aggregation in the Extensive Solution Phase of the Sodium Octanoate-Octanoic Acid-Water System

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The longitudinal NMR relaxation time for ¹³C is determined at three different magnetic fields in the extensive solution phase (L_2 region) of the system sodium octanoate-octanoic acid-water. This phase serves as a suitable simple model for microemulsions. The data are analyzed by using a model that emphasizes the separation of the fast internal motions within the aggregates and slow motions on a time scale characteristic of the aggregate dimensions. Three important parameters are derived from the relaxation data: a correlation time characteristic of the fast motion, an order parameter, and, finally, a correlation time for the slow motions. These three parameters show that the internal motion is fast (time scale, 2×10^{-11} s), that the packing is insensitive to water content, and, finally, that the aggregates grow in size up to a certain water content. At higher contents, the simple model with closed water domains does not apply.

Introduction

In three-component systems surfactant-solubilizatewater, several different phases with different structures appear.¹ Of these, the normal micellar solutions and the liquid crystalline phases have been studied extensively (for several reviews, see refs 2 and 3). Two very important generalizations emerge from these studies: first, one can rationalize and predict the phase behavior from arguments concerning the geometrical structure of the molecules⁴⁻⁶ and, second, local molecular interactions are quite independent of changes in aggregate size and geometry.⁷⁻⁶

In certain amphiphilic solutions, isotropic solutions can simultaneously contain relatively large amounts of hydrocarbon and water. For a four-component system with surfactant + cosurfactant having this feature, one often uses the term microemulsion.¹⁰ Many other surfactant

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