(27) M. Anbar, S. Guttman, and R. Rein, J. Am. Chem. Soc., 81, 1816 (1959).
(28) R. A. Robinson and R. H. Stokes, Trans. Faraday Soc., 45, 612 (1949).
(29) E. S. Amis and J. F. Hinton, "Solvent Effects on Chemical Phenomena", Vol. I, Academic Press, New York, 1973.
(30) J. E. Prue, "Ionic Equilibria", Pergamon, Oxford, 1966. (Topic 15, 3, of "The International Encyclopedia of Physical Chemistry and Chemical Physics".)

Dual Fluorescence and Ground State Equilibria in Methyl Salicylate, Methyl 3-Chlorosalicylate, and Methyl 3-*tert*-Butylsalicylate

A. U. Acuña,* F. Amat-Guerri,† J. Catalán,‡ and F. González-Tablas‡

Instituto de Química Física "Rocasolano", C.S.I.C. Madrid, Spain *(Received August 6, 1979)*

Publication costs assisted by Comité Conjunto Hispano Norteamericano

Fluorescence spectra of methyl 3-chlorosalicylate, methyl 3-*tert*-butylsalicylate, and *o*-hydroxyacetophenone in cyclohexane and ethanol at room temperature have been measured, together with the corrected dual fluorescence excitation spectra of gas-phase methyl salicylate. Based on these observations a ground state equilibrium between two tautomers is proposed, both having an intramolecular hydrogen bond. This model is consistent with a number of methyl salicylate H-bond energy estimates. It also allowed an interpretation of the multiple fluorescence emitted from these and related compounds either in solution or in gas phase.

Introduction

The multiple emission of salicylic acid and a number of related *o*-hydroxyaromatic carbonyl compounds[1-4] has often been discussed in terms of proton transfer within the electronically excited states manifold[5] in order to explain the low yield fluorescence with two well-defined maxima in the UV (ca. 340 nm) and blue (ca. 450 nm) regions of the spectrum. In a recent paper[6] Smith and Kaufmann summarized some of the previous work carried out on these systems and provided picosecond experiments on methyl salicylate (MS) in nonpolar solvents. They suggested that in the ground state the location of the hydroxy proton relative to the carbonyl oxygen could be different for molecules which are UV emitters from those emitting fluorescence with a large Stokes shift. These experiments, together with the finding of Klöpffer[7] of a temperature-dependent double fluorescence of MS in gas phase depending also on the excitation wavelength, have displaced the quest of the origin of the dual emission from the electronically excited state to the ground state.

Here we report a number of experiments designed to identify more precisely which species can or cannot be responsible for that anomalous fluorescent behavior from the now rather comprehensive list of candidates[8-10] accumulated over the past 2 decades. It was also our intent to discuss some previous work done on closely related systems that has often been overlooked.

Experimental Section

Materials. Methyl salicylate (Merck) was purified by fractional vacuum distillation and analyzed by GC. *o*-Hydroxyacetophenone (Merck) after repeated vacuum distillation still showed an impurity on TLC plates ($60F_{254}$ Merck). By passing the redistilled product through a silica gel 60 column with purified chloroform we obtained a single spot on the TLC.

Methyl 3-*tert*-butylsalicylate was prepared from the acid[11] with diazomethane in methanol. It was purified by column chromatography and analyzed by TLC as above.

The previously described synthesis of 3-chlorosalicylic acid as the main reaction product between salicylic acid and *tert*-butyl hypochlorite could not be reproduced. In water[12,13] the reaction yielded 3,5-dichloro- and 5-chlorosalicylic acids while in Cl_4C[14] monosubstitution predominated, giving 5-chlorosalicylic acid as a major component and 3-chlorosalicylic acid. The latter was isolated by preparative TLC (precoated silica gel plates, 97:3 $CHCl_3$–AcOH) and recrystallized from water, mp 182–183 °C (lit.[14] 180 °C). The methyl ester was prepared finally by the NeOH–HCl method, because there was no reaction with diazomethane under usual conditions. After purification by column chromatography (vide supra) it was recrystallized from methanol, mp 35 °C (lit.[15] 38 °C).

All the solvents used, even in the synthesis, were either commercial fluorimetric grade (Merck) or purified as described elsewhere.[16] Cyclohexane was dryed by distillation from sodium. The water content of ethanol was less than 0.02% by GC. Fluorescence was not observed from the neat solvents under the actual conditions of spectra recording.

Methods. Emission spectra were usually recorded on a Perkin-Elmer MPF-3 fluorescence spectrometer. Excitation and emission correction procedures have been described elsewhere.[17] High-resolution spectra from gas phase and/or low quantum yield samples were obtained in a photon counting SLM 8000 spectrofluorimeter, with a double grating excitation monochromator. Right-angle geometry, with front-surface illumination of thin cells when high absorbances could distort the spectra, was used in both systems. The solutions, freshly prepared for each experiment, were air equilibrated.

The corrected emission spectra presented here, in photon units, have been plotted on the same intensity scale, after having been corrected, when necessary, for the different sample absorbance and energy output of the exciting lamp. Thus, the ratio of their areas is proportional to the quantum yields ratio, within our experimental error (accuracy plus precision) of 10–20%. Fluorescence excitation spectra recorded at two different wavelengths, as in this case, need to be corrected for the wavelength dependence

† Instituto de Química Orgánica, C.S.I.C. Madrid, Spain.
‡ Departamento de Química Física, Universidad Autónoma de Madrid, Madrid, Spain.

0022-3654/80/2084-0629$01.00/0

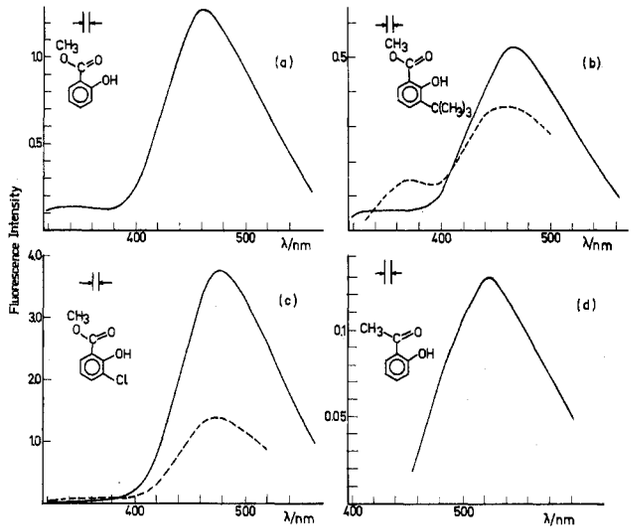

Figure 1. Corrected emission spectra on the same intensity scale (see text): (a) 10^{-5} M methylsalicylate in cyclohexane; (b) methyl 3-*tert*-butylsalicylate and (c) methyl 3-chlorosalicylate, both 10^{-5} M, in cyclohexane (—) and ethanol (- - -); (d) 10^{-5} M *o*-hydroxyacetophenone in cyclohexane. The excitation wavelength was 290 nm for (a), (b), and (c), and 320 nm for (d).

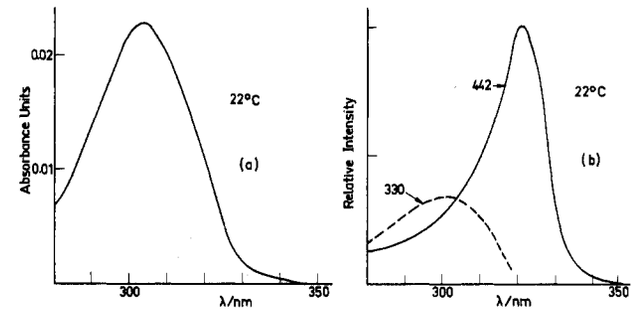

Figure 2. Absorption (a) and corrected fluorescence excitation spectra (b) including wavelength sensitivity factors (see text) or methylsalicylate in gas phase at equilibrium pressure, for the indicated emission wavelengths and temperature. The excitation slit was 1 nm.

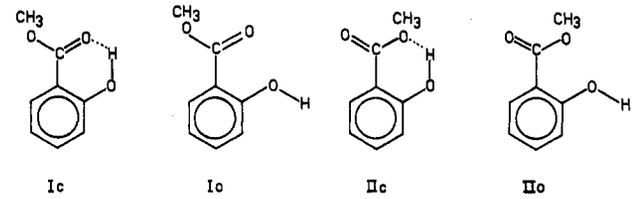

Figure 3. Tautomeric forms in ground state methylsalicylate.

of the emission setup, to make them comparable. These time-consuming correction techniques, although inevitably introducing additional errors in the final spectrum, are necessary to discuss the complex photophysics of these compounds.

Results and Discussion

The emission spectrum of methyl 3-*tert*-butylsalicylate (3BMS) in cyclohexane is similar (Figure 1) to the well-known dual luminescence of MS in nonpolar solvents, which are included in the same figure for intensity comparisons. Exitation along the first absorption band of 3MBS (280–340 nm) produces changes in the relative intensity of the UV and blue fluorescence bands of the same magnitude as those reported previously for MS[18] in the same solvent. On the other hand, a solution of methyl 3-chlorosalicylate (3ClMS) in cyclohexane shows (Figure 1) a large increase of the long wavelength fluorescence component, while the UV emission is now just a small shoulder.

The spectrum of the extremely weak luminescence of *o*-hydroxyacetophenone (oHAP) dissolved in cyclohexane is shown in Figure 1. This compound, which has strong phosphorescence in polar solvents,[19] retained that weak long-wavelength emission (Stokes shift = 10900 cm^{-1}) even after extensive column purification, although we cannot exclude the possible existence of trace amounts of water in the solvent.

The fluorescence excitation spectra of MS in the gas phase are presented in Figure 2. These spectra were fully corrected as described in the Experimental Section and therefor represent the product of the absorption spectrum times the quantum yield for each of the two emitting species.

The fact that a double excitation spectrum appears connected consistently with MS dual emission now seems well founded, either in polar[8,18] or nonpolar solvents[6-8] and in the gas phase. The simplest explanation of this behavior is then to assume that ground state molecules of MS and its derivatives can exist in at least two of the conformations[20,21] depicted on Figure 3. The absorption spectra would be close enough to make them appear as a single band, more so if their relative concentrations are widely different. Closed H-bond molecule Ic, the only species detected by IR spectroscopy[22] in MS, is most likely to favor proton tautomerization in the excited state,[23] so the blue emission has been traditionally assigned[2] to absorbing species of this geometry. This is also the conclusion of a recent high-resolution work[10] on MS at 4.2 K. The origin of the near-UV emission is, however, more confusing. Klöpffer proposed[7,8] that this fluorescence is due to molecules with open configuration Io (Figure 3) either in solution or in the gas phase. In the first case, in hydrogen bonding solvents, the intramolecular H bond is broken by competition of solvent molecules with the phenolic group. This increases the population of the Io tautomer and the UV emission consequently. In the gas phase the low-energy ascribed[7] to the intramolecular hydrogen bond, 3.6 kcal/mol, would allow the efficient buildup of Io isomers with modest increases in temperature.

Unfortunately this hypothesis leaves a number of experimental facts unexplained, including those reported here. This is the case for the lack of the UV emission in salicylamide,[24] oHAP, and salicylaldehyde,[25] all with different intramolecular H-bond strength. Also in 3BMS the bulky alkyl substituent would be expected to shift the equilibrium even more toward the Ic tautomer and, consequently, decrease the UV emission compared with MS, taking into account the similar equilibrium shift described[26] for *o*-*tert*-butylphenol.

In 3ClMS, on the other hand, the opposite effect should be produced, i.e., the Io species should increase in the equilibrium mixture because the chlorine atom can form a competing intramolecular H bond[27] with the phenolic group. These changes in the relative emission of the UV band were not observed; rather, a change in the opposite direction was detected (Figure 1) for this last compound. The increase in the intensity of the blue emission in 3ClMS and the inhibition in 3BMS compared with that from MS also contradicts the proposed equilibrium Ic $\rightleftarrows$ Io.

Klöpffer's hypothesis rests on a value for the MS intramolecular H bond in the ground state that is significatively lower compared with the energies obtained from other techniques or predicted theoretically.[28,29] Thus, by means of the relationship between IR shifts and H-bond strength of Zadorozhnyi et al.[30] and by using the most recent frequencies[31,32] we can compute a value of 7 ± 0.1 kcal/mol for this bond. Alternatively, by introducing in

Schaefer's correlation[33] the NMR chemical shifts of the phenolic protons of MS, δ = 10.6 ppm,[5] and of phenol, δ = 4.29 ppm,[34] we obtained an energy of 6.7 kal/mol for this intramolecular bond. To our knowledge there is only one experimental determination, carried out by ultrasonic absorption,[35] that gives the low energy value (2.4 kcal/mol). It is very likely that these measurements were affected by some systematic error because the intramolecular H-bond energy in salicylaldehyde, also published in the same paper (3.5 kcal/mol), has been evaluated recently from NMR and far-IR data[33] to be 7.1 kcal/mol.

A comprehensive explanation of the experimental evidence available can be reached if rotamer IIc with an intramolecular H bond were responsible for the UV fluorescence in MS and related compounds. As this species cannot exist in OHAP, salicylamide,[36] and salicylaldehyde these molecules only show the long wavelength emission. On the other hand, when MS is in the presence of hydrogen bonding solvents the weakening action of the solvent molecules on the intramolecular bond of Ic and the additional stabilization of species IIc by carbonyl solvation results in a shift of the equilibrium toward the last isomer. This has been detected by an increase in the UV emission.[8,18] In the excited state the respective emitting singlets cannot interchange before emission takes place, because the blue and UV fluorescences have very different lifetimes,[6] at least in MS. It is also interesting to note that, if the excitation spectra of Figure 2 corresponds to species Ic and IIc, it suggests that the emission quantum yield of Ic must drop abruptly when going to the short wavelength side of its absorption.

Moreover, the ground state equilibrium Ic $\rightleftarrows$ IIc we are proposing is consistent with the finding[18] that the intensity ratio between the UV and blue emissions of MS in a number of alcohols increases in the same order as do the stabilities of the hydrogen bond complexes between alcohols and esters.

Finally, that low enthalpy previously assigned[7] to the intramolecular hydrogen bond dissociation in MS might correspond to the equilibrium between Ic and IIc, i.e., to a *difference* between two intramolecular H bonds. However, one should be cautious about these assignments. It has been found[6] that the radiationless rate constant of the blue emission has an activation energy of the same magnitude (4 kcal/mol). This, together with our own observations showing that MS vapor adsorption on the silica cell walls (a fact already noted by Klöpffer) has a strong influence in fluorescence intensity measurements, may render the interpretation of the temperature dependence of gas phase fluorescence intensity for these compounds extremely difficult.

Acknowledgment. We thank Mr. F. Toribio for his collaboration in setting up the experimental systems and Dr. J. González for laboratory facilities. This work was supported by Project IIIP-3042 of the C.C.H.N. and by the Comisión Asesora Científica y Técnica.

References and Notes

(1) A. Weller, *Z. Elektrochem.*, **60**, 144 (1956).
(2) A. Weller, *Prog. React. Kinet.*, **1**, 189 (1961).
(3) H. Beens, G. M. Grellmann, and A. Weller, *Discuss. Faraday Soc.*, **39**, 183 (1965).
(4) M. Kondo, *Bull. Chem. Soc. Jpn.*, **49**, 2679 (1976).
(5) W. Klöpffer, *Adv. Photochem.*, **10**, 311 (1977).
(6) K. K. Smith and K. Kaufmann, *J. Phys. Chem.*, **82**, 2286 (1978).
(7) W. Klöpffer and G. Kaufmann, *J. Lumin.*, **20**, 283 (1979).
(8) W. Klöpffer and G. Naudorf, *J. Lumin.*, **8**, 457 (1974).
(9) E. M. Kosower and H. Dodiuk, *J. Lumin.*, **11**, 249 (1975/76).
(10) J. Goodman and L. E. Brus, *J. Am. Chem. Soc.*, **100**, 7472 (1978).
(11) The sample of methyl 3-*tert*-butylsalicylic acid was kindly donated by Professor C. J. W. Brooks, Chemistry Department, University of Glasgow.
(12) B. F. Clark, *Chem. News*, **143**, 265 (1931); *Chem. Abstr.*, **26**, 1591 (1932).
(13) J. M. Schackelford, *J. Org. Chem.*, **26**, 4908 (1961).
(14) D. Ginsburg, *J. Am. Chem. Soc.*, **73**, 2723 (1951).
(15) R. Anschütz, *Annalen*, **346**, 313 (1906).
(16) A. U. Acuña, A. Ceballos, J. Garcia-Dominguez and M. J. Molera, *An. Quim.*, **71**, 22 (1975).
(17) A. U. Acuña, A. Ceballos, and M. J. Molera, *J. Phys. Chem.*, **81**, 1090 (1977).
(18) K. Sandros, *Acta Chem. Scand., Sect. A*, **30**, 761 (1976).
(19) A. A. Lamola and L. J. Sharp, *J. Phys. Chem.*, **8**, 2634 (1966).
(20) J. Catalán and J. I. Fernández-Alonso, *Chem. Phys. Lett.*, **18**, 37 (1973).
(21) J. Catalán and A. Macias, *J. Mol. Struct.*, **38**, 209 (1977).
(22) N. Mori, Y. Asano, and Y. Tsuzuki, *Bull. Chem. Soc. Jpn.*, **42**, 488 (1969).
(23) J. Catalán and F. Tomás, *Adv. Mol. Relaxation Processes*, **8**, 87 (1976).
(24) (a) B. A. Zadorozhnyi, *Zh. Prikl. Spectrosk.*, **5**, 349 (1966); *Chem. Abstr.*, **66**, 60510*p*; (b) P. J. Thistlethwaite and G. J. Woolfe, *Chem. Phys. Lett.*, **63**, 401 (1979).
(25) A. U. Acuña and J. Catalán, to be submitted for publication.
(26) N. L. Allinger, J. J. Maul, and M. J. Hickey, *J. Org. Chem.*, **36**, 2747 (1971).
(27) G. L. Carlson, W. G. Fateley, A. S. Manocha, and F. F. Bentley, *J. Phys. Chem.*, **76**, 1553 (1972).
(28) J. Catalán, E. Canadell, and J. I. Fernández-Alonso, "Progress in Theoretical Organic Chemistry", Vol. 2, I. G. Csizmadia, Ed., Elsevier, Amsterdam, 1977, p 106.
(29) E. Canadell, J. Catalán, and J. I. Fernández-Alonso, *Adv. Mol. Relaxation Processes*, **12**, 265 (1978).
(30) B. A. Zadorohnyi and I. K. Ischenko, *Opt. Spectrosc.* (*Engl. Transl.*), **19**, 306 (1965).
(31) ν(OH) = 3185 cm^{-1} and ν(CO) = 1680 cm^{-1} for methyl salicylate in ref 13.
(32) Phenolic ν(OH) = 3610 cm^{-1} from E. A. Robinson, H. D. Schreiber, and J. N. Spencer, *J. Phys. Chem.*, **75**, 2219 (1971). Methyl benzoate ν(CO) = 1728.4 cm^{-1} from C. Lawrence and M. Berthelot, *J. Chem. Soc., Perkin Trans. 2*, **98** (1979).
(33) T. Schaefer, *J. Phys. Chem.*, **79**, 1888 (1975).
(34) A. J. Dale and T. Gramstad, *Spectrochim. Acta, Part A*, **28**, 639 (1972).
(35) T. Yasunaga, N. Tatsumoto, H. Inoue, and M. Miura, *J. Phys. Chem.*, **73**, 477 (1969).
(36) The single emission of salicylamide in water has been recently time resolved in to two overlapping components as described in ref 24b. They were assigned to the zwitterion and phenolate ion spectra. This is another example where Klöpffer's open form should be present but no UV fluorescence was detected, giving further support to our model.