Induction of Triplet-State Emission of the Transient Proton-Transfer Keto Form of Methyl Salicylate by Heavy-Atom Perturbation†

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The rare (third) example of a triplet-state emission from a transient phototautomer is reported here for the case of the keto form of methyl salicylate. This molecule satisfies two of the three essential criteria predicted for observation of a triplet−singlet emission under conditions of excited-state intramolecular proton transfer: (1) published spectroscopic data confirm a keto tautomer triplet below the stable enol tautomer triplet, and (2) an easily accessible spectroscopic region. The third criterion, (3) noninterfering radiationless transitions, is not satisfied, and the $T_1' \rightarrow S_0'$ transition is not observed. This difficulty is overcome by external heavy-atom perturbation using ethyl iodide matrices at 77 K, with time-resolved spectroscopy. The tautomer phosphorescence is observed at $\lambda_m = 560$ nm, with a lifetime in the microsecond range. Internal heavy-atom perturbation is demonstrated to be effective in 3,5-dibromo and -diiodo methyl salicylates, the enhanced $T_1' \rightarrow S_0'$ emission occurring in the latter in both steady-state and time-resolved emission.

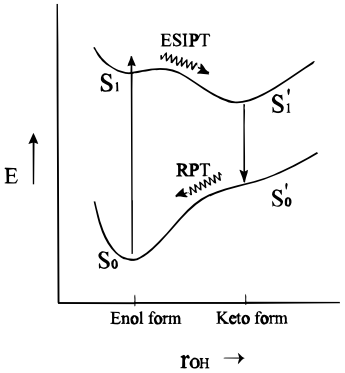
Introduction

Extensive research on excited-state intramolecular proton transfer over the last decades has revealed many examples of transient tautomer $S_1' \rightarrow S_0'$ fluorescence (Scheme 1). In contrast, observation of the corresponding $T_1' \rightarrow S_0'$ phosphorescence is reported in only two previous cases. This paper explores the transient $T_1' \rightarrow S_0'$ emission in methyl salicylate.

Almost 40 years ago, Weller[1] analyzed the fluorescence of methyl salicylate (MS) and established the foundation of what is currently known as the excited-state intramolecular proton-transfer (ESIPT) mechanism (see Scheme 1). This mechanism is widely used to identify useful substances with highly varied properties such as ultraviolet stabilizers[2] and laser dyes,[3] and others of potential use for storing information[4] or probing the properties of biomolecular moieties.[5]

The intramolecular proton-transfer mechanism has been studied extensively in theoretical and experimental terms, both in excited states[6] and in the ground state.[7] Studies involving excited electronic states have been focused on excited singlet states. Comparatively little research has been conducted on triplet states, largely because often they were assumed to be nonphosphorescent. There is no reported evidence for phosphorescence of 2-hydroxybenzoyl systems (I) in the keto form (III);[8] also, only a few such systems have been found to phosphoresce in their enol form (II)[10] or in forms (IV) containing no intramolecular hydrogen bonding (IMHB)[11,12] or including one as in the rotated form (V) of MS produced after long irradiation[9,12] (see Scheme 2). In fact, only three substances that evolve via the ESIPT mechanism have been found to possess phosphorescent keto forms, in all three, the receptor for the proton transfer is a nitrogen-containing heterocyclic system, viz. benzoxazole in 2-(hydroxyphenyl)benzoxazole (VI),[13] benzothiazole in 2-(hydroxyphenyl)benzothiazole (VII),[14] and pyridine in 2,2′-bipyridyldiol (VIII)[15] (see Scheme 2). In fact, the triplets for the keto forms of 2-hydroxybenzoyl compounds had to be examined by using the time-resolved EPR technique (TREPR) with laser excitation in order to elucidate the properties of nonphosphorescent short-lived triplet states.[16,17]

SCHEME 1: Schematic Potential Energy Diagram for the ESIPT Mechanism via Enol MS (II) to Keto MS (III) Phototautomerism



Recently, Kasha et al.[18] analyzed the behavior of the triplet-state potentials in the ESIPT mechanism and distinguished three different situations depending on the relative energy of the first triplet state for the enol (II) and keto forms (III) involved in the ESIPT mechanism; the most common situation should be that involving the most stable triplet for the keto form (III) so that reverse proton transfer to the enol form could not occur. This situation, which should produce the typical phosphorescence of proton-transfer spectroscopy, is rarely observed in practice; as noted earlier, there is little reported evidence for this type of emission (i.e., a $T_1' \rightarrow S_0'$ emission for the transient keto tautomer).

† This paper is dedicated to Professor Michael Kasha as a tribute to his brilliant research into the photophysics of the triplet state.

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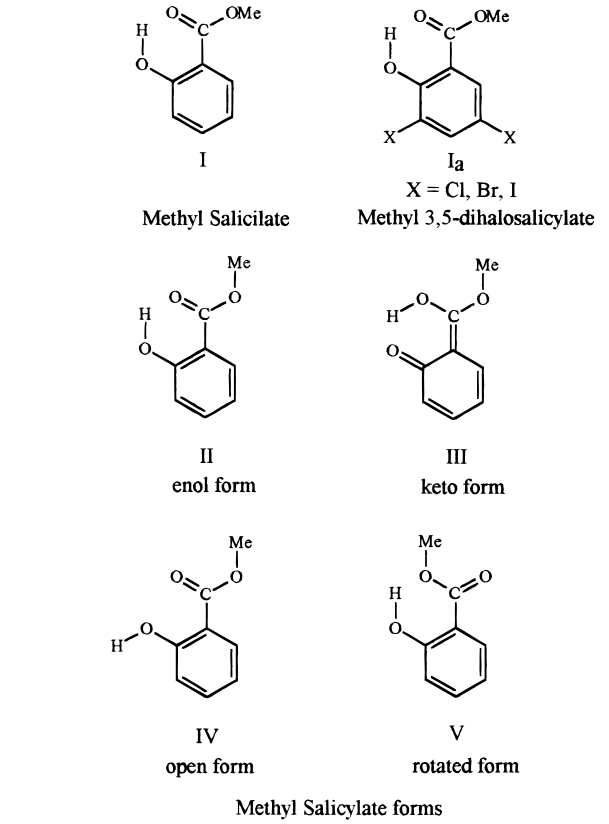
SCHEME 2



Inducing the phosphorescence of the keto form (III) in a system whose photophysics is governed by an ESIPT mechanism is obviously a major challenge if the compound concerned is markedly nonphosphorescent and exhibits a $S_1 \rightarrow S_1'$ proton phototransfer efficiency close to 100%. This precludes the existence of a significantly large population in the triplet state for the enol form reached by intersystem crossing (ISC) from the Franck−Condon (FC) state excited by the primary absorption $S_0 \rightarrow S_1$. The ultrarapid ESIPT precludes excitation of the enol form triplet; at the femtosecond range ESIPT rate greatly exceeds the ISC rate, restricted by spin−orbital coupling.

In this work, we used external and internal heavy-atom perturbations—the former are known as "the Kasha effect"[19]—that were introduced by replacing some hydrogen atoms by halogens in order to expose the phosphorescence of the keto form (III) in such an important system as MS, which has been shown to meet the previous two requisites, i.e., the generation of non-hydrogen-bonding molecular forms (IV) and the presence of a very efficient $S_1 \rightarrow S_1'$ process for precluding the formation of the T_1 state by $S_1 \rightarrow T_1$ ISC. Internal and external heavy-atom perturbations have proved effective in enhancing singlet−triplet transitions, whether radiationless[20−23] or radiative.[24,25]

Experimental Section

UV−visible absorption spectra were recorded on Cary 5 spectrophotometer at room and low temperatures.

Emission spectra corrected for instrument sensitivity were obtained on an Aminco−Bowman AB2 spectrofluorimeter using a continuous (CW) 150W xenon lamp for steady-state spectra and a 7 W pulsed xenon lamp for delayed spectra. Corrected excitation spectra were obtained at a constant excitation intensity. The sample temperature was controlled by means of an Oxford DN 1704 cryostat. Experiments at 77 K were normally performed with the aid of a liquid nitrogen accessory for cooling samples.

The solvents, methylcyclohexane (Mecyh, 99%, spectrophotometric grade), 2-methyltetrahydrofuran (99%), and ethyl iodide (99.5%), were all used from freshly opened bottles. Low-temperature experiments were conducted on Mecyh, 2:1 Mecyh/2-methyltetrahydrofuran (HF) and 2:1:1 Mecyh/2-methyltetrahydrofuran/ethyl iodide matrices (HFI), which possess excellent spectroscopic features. Fresh samples were used throughout.

The methyl esters of the 3,5-dihalosalicylates were obtained by refluxing the corresponding acids with MeOH in the presence of 10% concentrated HCl for 2 days.[26]

Methyl 3,5-dichlorosalicylate and 3,5-dibromosalicylate were purified by silica gel column chromatography (using dichloromethane as eluent), and methyl 3,5-diiodosalicylate by recrystallization in *n*-hexane. The three compounds were used at a purity better than 99%.

Results and Discussion

Induction of Triplet-State Emission of Transient MS Keto Form via External Heavy-Atom Effect. The probability of proton phototransfer in the first excited singlet of MS has been estimated to be as high as 0.98.[26] Also, the compound has been shown to emit no phosphorescence; at least, Klöpffer[8] failed to detect it in a methylcyclohexane matrix at 77 K, nor did Orton et al.[9] in SF_6 at 12 K. According to Hirota et al.,[17] MS gives no open forms (IV) on exposure to light in a normal experiment; also, Orton et al.[9] claim that, based on spectroscopic evidence, irradiation in an SF_6 matrix for 48 h produces the form where the IMHB is established between the OH group and the ether oxygen in the carbonyl group (V).

TREPR studies of durene mixed crystals at 77 K[17] have shown that the triplet for the keto form (III) of MS decays at a roughly constant rate of 10^{-4} s^{-1}, on the assumption of a negligible effect of spin−lattice relaxation; also, Nishiya et al.,[27] from T−T absorption data at room temperature, estimated that the lifetime of the state must be about 10 μs. These results confirm that some excited singlets for the keto forms transform to the corresponding triplets via ISC. The fact that no phosphorescence was detected in this state was no doubt the result of the radiative constant rate being much lower than its $T_1' \rightarrow S_0'$ radiationless counterparts. It therefore seems logical to assume that, if both radiative and radiationless ISC processes are favored by a heavy-atom effect, the radiative process will probably be made more competitive and eventually render keto MS (III) phosphorescent.

Figure 1 shows the excitation and emission spectra for MS in the HF and HFI matrices at 77 K, obtained in the steady state and at a delay time of 45 μs. It should be noted that the *excitation spectrum* of Figure 1 (which closely parallels the *absorption spectrum* profile) has a band half-width (fwhm) of 2420 cm^{-1}, which significantly differs from the emission band

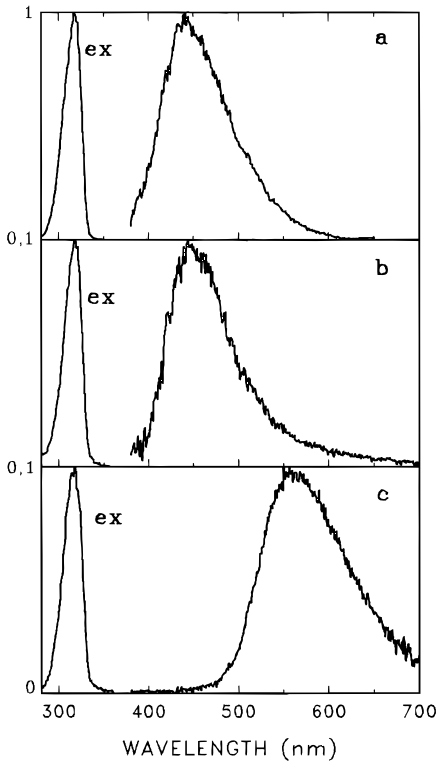


Figure 1. (a) Normalized emission and fluorescence excitation (ex) spectra of MS in HF (methylcyclohexane/2-methyltetrahydrofuran) at 77 K. (b) Normalized emission and fluorescence excitation (ex) spectra of MS in HFI (methylcyclohexane/2-methyltetrahydrofuran/ethyl iodide) at 77 K. (c) Normalized phosphorescence and excitation (ex) spectra of MS in HFI at 77 K obtained at 45 μs delay.

half-width (4150 cm^{-1}). Furthermore, both the absorption and emission bands are shifted ca. 9000 cm^{-1}.

But the excitation (absorption) band and the emission band of Figure 1 are not for corresponding transitions. It should be noted, however, that the band gap from 340 to 400 nm should be the position of the $S_1 \rightarrow S_0$ missing fluorescence, so that the "shifted band" at $\lambda_m = 440$ nm must be the $S_1' \rightarrow S_0'$ proton-transfer (keto form methyl salicylate) transient fluorescence.

From the spectra it follows that the Kasha effect exposes a new type of luminescence displaced bathochromically relative to MS fluorescence in HFI; this result, however, is analogous to that obtained by Linschitz et al.,[28] who, using the same matrix, detected $T_1 \rightarrow S_0$ phosphorescence in C_{60} for the first time. This weak luminescence is hidden in the spectrum obtained in the steady-state emission because it is masked by the fluorescence of the compound. In fact, the $T_1' \rightarrow S_0'$ band occurs at about 560 nm and has a lifetime of 1.40 ± 0.25 ms. Figure 2 shows the phosphorescence spectrum for MS in HFI at 77 K at a variable delay time; the spectrum confirms the lifetime for this phosphorescent emission.

Both the $S_1' \rightarrow S_0'$ fluorescence and the $T_1' \rightarrow S_0'$ phosphorescence excitation spectra ($S_0 \rightarrow S_1$) obtained were mimetic with the first absorption band for MS in the matrices used. Therefore, both types of luminescence must be produced by the electronic absorption $S_0 \rightarrow S_1$; the spectroscopic data also confirm that the new band is produced from the fluorescent state of the MS keto form (III), via ISC, as demonstrated by the heavy-atom perturbation effect.

Induction of $T_1' \rightarrow S_0'$ Emission of MS Keto Form via Internal Heavy-Atom Effect in Dihalosalicylates. Figure 3 shows the excitation and luminescence spectra for the 3,5-dichloro derivative (I_a) of MS in the Mecyh matrix at 77 K.

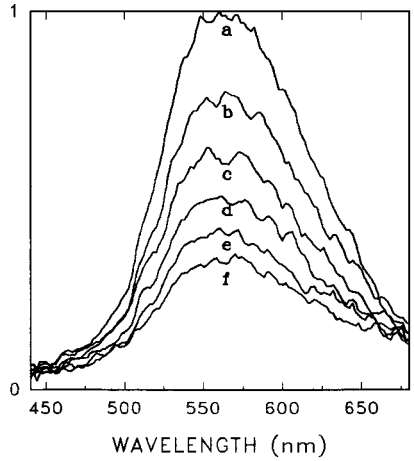


Figure 2. Time-dependent $T_1' \rightarrow S_0'$ phosphorescence spectrum of keto MS (III) in a 77 K HFI glass with a delay time of (a) 200 μs, (b) 500 μs, (c) 800 μs, (d) 1.1 ms, (e) 1.4 ms, and (f) 1.7 ms.

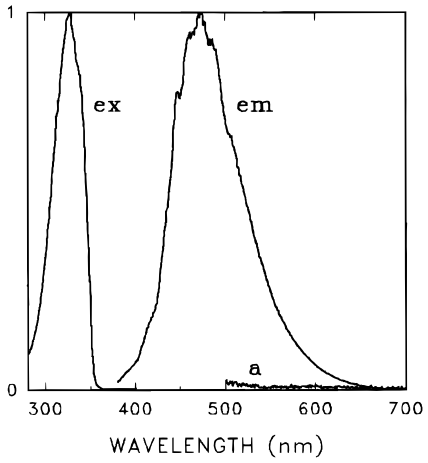


Figure 3. Normalized emission (em) and excitation (ex) spectra of methyl 3,5-dichlorosalicylate in a 77 K methylcyclohexane glass. (a) Emission spectrum of methyl 3,5-dichlorosalicylate in a 77 K methylcyclohexane glass obtained at 210 μs delay.

Figure 3 shows that the $S_1' \rightarrow S_0'$ fluorescence for the methyl 3,5-dichlorosalicylate is quite analogous to that for the nonhalogenated MS keto form (Figure 1). The excitation spectrum is mimetic with the first absorption band for the compound. Also, the spectrum obtained at a delay time of 210 μs confirms that the compound exhibits no phosphorescence.

Figure 4 shows the excitation and luminescence spectra for the brominated derivative of MS in the Mecyh matrix at 77 K, recorded both in the steady state and at a delay time of 210 μs. As can be seen, there is a new type of luminescence displaced bathochromically relative to the fluorescence of the compound. The band appears at ca. 586 nm and corresponds to a lifetime of 146 ± 11 μs; also, the excitation spectrum is mimetic with the first absorption band for the compound.

Figure 5 shows the excitation and luminescence spectra for the iodinated derivative of MS in the Mecyh matrix at 77 K, obtained in the steady state and at a delay time of 210 μs. As can be seen, the compound exhibits a new type of emission at ca. 605 nm that is not only visible in the steady state but also comparable in intensity to the fluorescence; the corresponding lifetime is 62 ± 5 μs. A degassed sample gave a slightly increased phosphorescence-to-fluorescence intensity ratio for this compound but contributed nothing else of spectroscopic relevance. Figure 6 shows the luminescence spectra for this compound in an air-equilibrated Mecyh matrix at a variable

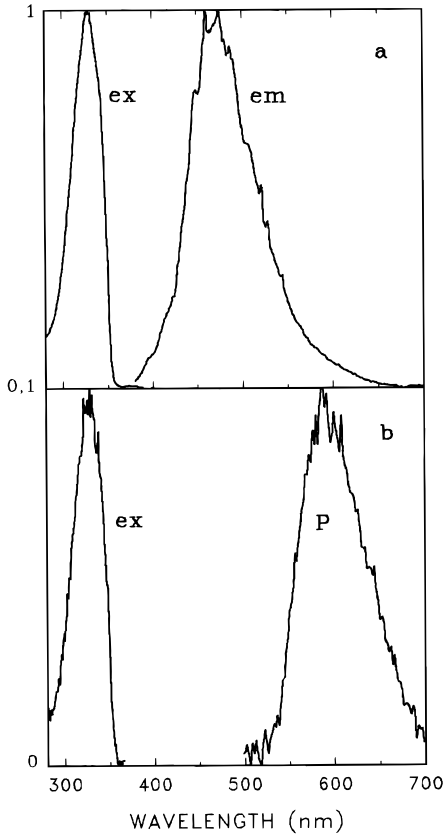


Figure 4. (a) Normalized emission (em) and fluorescence excitation (ex) spectra of methyl 3,5-dibromosalicylate in methylcyclohexane at 77 K. (b) Normalized $T_1' \rightarrow S_0'$ phosphorescence (P) and phosphorescence excitation (ex) spectra of the keto form of methyl 3,5-dibromosalicylate in methylcyclohexane at 77 K obtained at 210 μs delay.

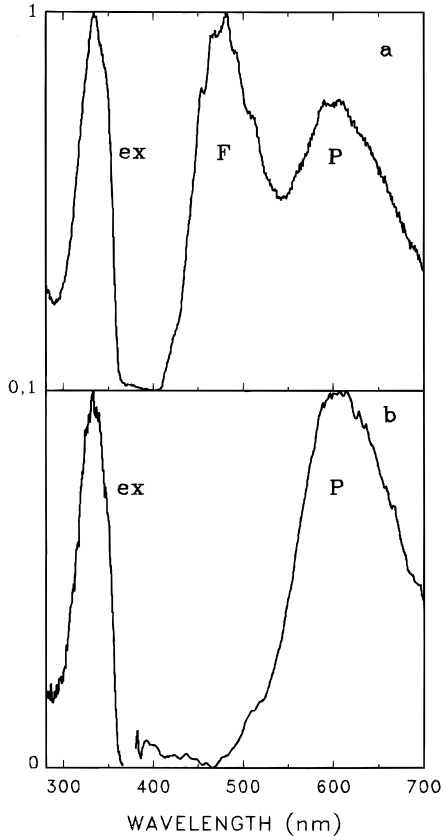


Figure 5. (a) Normalized emission (F and P) and excitation (ex) spectra of methyl 3,5-diiodosalicylate in methylcyclohexane at 77 K. (b) Normalized phosphorescence (P) and phosphorescence excitation (ex) spectra of the keto form of methyl 3,5-diiodosalicylate at 77 K obtained at 210 μs delay (F: $S_1' \rightarrow S_0'$ fluorescence emission, P: $T_1' \rightarrow S_0'$ phosphorescence emission).

temperature. As can be seen, the new band only appears at a temperature low enough to avoid quencher diffusion on the compound.

The emission of MS in HFI at 77 K, and those of the brominated and iodinated derivatives (also in the Mecyh matrix), can unequivocally be assigned to the $T_1' \rightarrow S_0'$ phosphorescence of the keto form of MS; in fact, it cannot be assigned to any other form containing no IMHB (IV) nor to the rotated form (V) since, as shown by Orton et al.,[9] this latter form exhibits a phosphorescence band at 420 nm with a much longer lifetime (2.3 ± 0.2 s in SF_6 at 12 K) and gives an excitation spectrum not resembling the first absorption band for MS. This phosphorescence cannot be assigned to the enol form (II) either because it must be energetically similar to that for the rotated form (V), which Orton et al.[9] found to appear at 420 nm.

ESIPT Diagram for Methyl Salicylate (I). Constructing an energy diagram for the levels involved in the ESIPT mechanism for MS entails prior knowledge of the energies of the states concerned relative to the normal form (II) of MS (S_0), viz. for the keto form in the ground state (S_0') and its singlet (S_1') and triplet (T_1') in the excited state, as well as the excited states for the normal form [singlet (S_1) and triplet (T_1)].

According to Nishiya et al.,[29] the energies for states S_1 and S_1' in durene mixed crystals at 4.2 K are 32 300 and 29 162 cm^{-1}, respectively. We used the energy for the 0−0 component of the phosphorescence for the rotated form (V), viz. 26 950 cm^{-1} as measured by Orton et al.[9] in SF_6 at 12 K, as the energy for state T_1. Based on a theoretical computation at the B3LYP6-31G** level,[30] state S_0' is 5800 cm^{-1} apart from S_0; if this energy is increased by the energy for the onset of the phosphorescence for MS in HFI (Figure 1), i.e. ca. 20 000 cm^{-1}, T_1' turns out to be at ca. 25 900 cm^{-1}. This information was used to construct Chart 1, which clearly demonstrates that MS belongs to the third triplet-state potential situation proposed for ESIPT by Kasha et al.,[18] i.e. efficient proton transfer via a singlet state that leads to the formation of the keto form and, subsequently, to the filling of the T_1' triplet via $S_1' \rightarrow T_1'$ ISC and, eventually, to the $T_1' \rightarrow S_0'$ phosphorescence of the keto form, as demonstrated in this work.

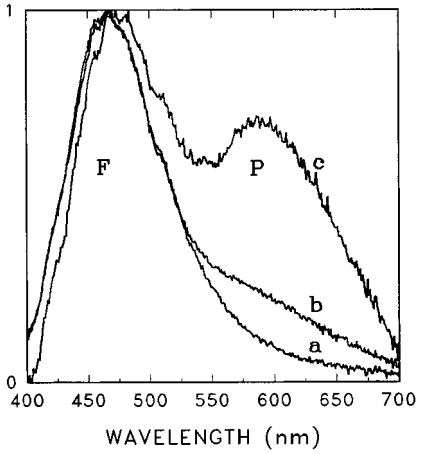
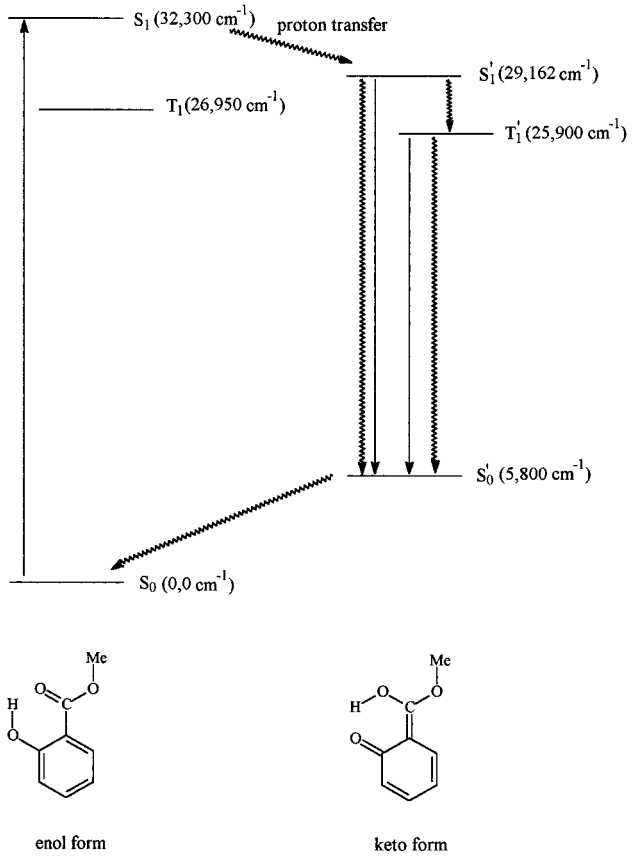


Figure 6. Normalized emission (F and P) spectrum of methyl 3,5-diiodosalicylate in methylcyclohexane at (a) 197 K, (b) 167 K, (c) 137 K. (F is the $S_1' \rightarrow S_0'$ fluorescence and P is the $T_1' \rightarrow S_0'$ phosphorescence of the keto form.)

CHART 1: Relative Energy Levels of the Enol and Keto Forms of MS



Discussion

The rarity of the observation of the $T_1' \rightarrow S_0'$ phosphorescence emission in transient tautomers excited in ESIPT experiments has been analyzed by Kasha et al.[18] In their classification, case C applies to observability of this emission, for which three criteria are given: (1) a $T_1' < T_1$ state energy relationship (cf. Figure 7), (2) an expected spectral region for the appearance of the phosphorescence which is readily accessible instrumentally, and (3) freedom from interfering radiationless transitions, so that a moderate quantum yield of phosphorescence can be observed. The fact that only two $T_1' \rightarrow S_0'$ transitions are recorded to date[18] of the many known cases of ESIPT indicates the difficulty involved (one of the cases reported being by multiple indirect stages).

The keto tautomer of methyl salicylate satisfies the first two criteria (cf. Figure 7). It is fortunate that for keto methyl salicylate the $S_1' \rightarrow S_0'$ fluorescence occurs at $\lambda_m = 440$ nm, allowing spectral room for the $T_1' \rightarrow S_0'$ emission within the visible region (the $S_1 \rightarrow S_0$ fluorescence is missing in the band gap 340−400 nm, overpowered by the ultrarapid rate of the ESIPT enol → keto photoconversion).

However, the $T_1' \rightarrow S_0'$ emission for keto methyl salicylate does not appear, even in the time-resolved spectrum. Nevertheless, as has been shown in the previous section, the intermolecular heavy-atom perturbation technique, using a solvent glass matrix containing ethyl iodide, does permit the observation of the sought-after $T_1' \rightarrow S_0'$ emission, using time-resolved spectroscopy in the microsecond range.

In addition, the internal heavy-atom effect proves to be as expected a still more powerful tool, with greatly enhanced $T_1' \rightarrow S_0'$ emission in the dibromo and especially the diiodo methyl salicylate. For the diiodo derivative, the sought-after emission appears even in the steady-state rigid methylcyclohexane glass solution at 77 K, without the use of time resolution.

It is clear that the elusive nature of the keto tautomer $T_1' \rightarrow S_0'$ *emission* of methyl salicylate was occasioned by the dominant $T_1' \rightarrow S_0'$ *radiationless* ISC, which required that the radiative rate should be accelerated by the enhanced spin−orbital perturbation techniques applied.

Conclusion

It is ironic that for methyl salicylate, the first molecule for which *excited-state intramolecular proton transfer* (ESIPT) was demonstrated,[1] the first demonstration of the $T_1' \rightarrow S_0'$ emission remained to be observed so many decades later. This delay indicates the subleties of the triplet manifold excitation mechanism, in addition to the principal preoccupation with only the singlet-state manifold for the tautomerization potentials. The analysis of three possible energetic sequences for the S_0, S_1, T_1, S_0', S_1', and T_1' states (Chart 1), and the recognition of the criteria for each of the three possible resultant tautomerization reactions[18] potential diagrams, has led to the logical resolution of the cause of the current rarity of $T_1' \rightarrow S_0'$ emission for the transient tautomer.

As demonstrated in the current research, direct application of experimental spin−orbital perturbation techniques, using both intermolecular and intramolecular "heavy-atoms" effects (actually, high-*Z*, atom effects), has proved to be a facile method of generating the desired $T_1' \rightarrow S_0'$ emission. This case should prove to be the most common of the three possible cases.

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