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Absorption and Emission Spectroscopy of Pyruvic Acids and Pyruvate Esters

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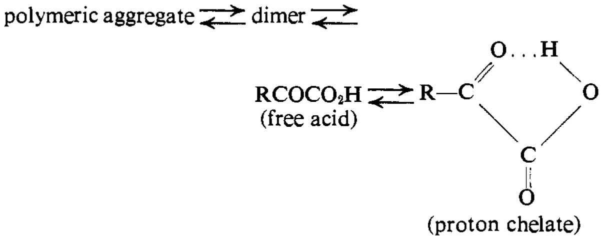
Abstract: The absorption and emission properties of pyruvic and trimethylpyruvic acid and their methyl esters have been investigated. Solutions of both α-keto acids are characterized by complex equilibria between monomeric and aggregated species which, individually, sample a varied geometric population. The spectroscopy of these compounds is a consequence of these equilibria. Absorption studies show that *all* entities in solutions of both acids and esters exist to some extent in a planar dicarbonyl geometry although the *preferred* geometry may be severely twisted. It is suggested that the relaxed emitting triplet possesses a planar dicarbonyl geometry with the energy of the emissions being a function of both solute–solute and solute–solvent interactions. Multiple emissions are observed at 77°K for both the keto acids in dilute 3-methylpentane glasses as well as in hydrogen-bonding glasses. Methyl trimethylpyruvate in a 3-methylpentane glass also exhibits multiple emissions which are attributed to variously aggregated species presumably bonded through dipole–dipole interactions. All observed luminescences are assigned as $^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$.

Despite extensive interest[1] in the biological and photochemical properties of α-keto acids, the absorption and luminescence characteristics of these compounds are neither well understood nor much investigated. Extensive infrared and cryoscopic studies[2] have indicated that solutions of α-keto acids are best described by the following equilibria.



(1)

Although the absorption spectra of dilute solutions of aliphatic α-keto acids have been described[3] in terms of the free and chelated acid, the effects of concentration and temperature on the observed absorptions are unexplored. No discussion of the absorption properties of aliphatic α-keto esters is extant. Such luminescence data[1,4] as are available are fragmentary at best, consisting of little more than the observation that luminescence is observed in rigid media at 77°K. In short, the consequences of the monomer–aggregate equilibria on the spectroscopic properties of solutions of α-keto acids have not been considered. Consequently, the emission and absorption characteristics of the following compounds have been investigated: pyruvic acid (PA), methyl pyruvate (MP), trimethylpyruvic acid (TMPA), and methyl trimethylpyruvate (MTMP).

Experimental Section

PA (Aldrich) and MP (Eastman) were obtained commercially. TMPA and MTMP were prepared by the method of Richard.[5] All compounds were repeatedly vacuum distilled prior to use and their purity confirmed by gas chromatography. All solvents employed were nonemissive in the region of experimental interest. Films were prepared by placing several drops of the compound between two quartz plates and rapidly cooling to 77°K. The polycrystalline film thus obtained had suitable optical properties for absorption and emission studies. Instrumentation and other techniques have been described previously.[6]

Prolonged irradiation of 10^{-3} *M* solutions in either EPA (*i.e.*, ether-isopentane-alcohol mixture) or 3-MP (*i.e.*, 3-methylpentane) with the full output of a G.E. AH-6 mercury arc lamp, both at ambient temperature and 77°K, did not alter the 77°K emission profiles. This fact indicates that the emissions observed are intrinsic to the keto acid systems and do not arise from photoproducts. Moreover, the known photoproducts[1,4] from the irradiation of PA and MP are nonemissive in the region of experimental interest. Esterification, by the addition of diazomethane, of a 3-MP solution of TMPA which exhibits multiple luminescences leads to the observation of the emission profile characteristic of MTMP

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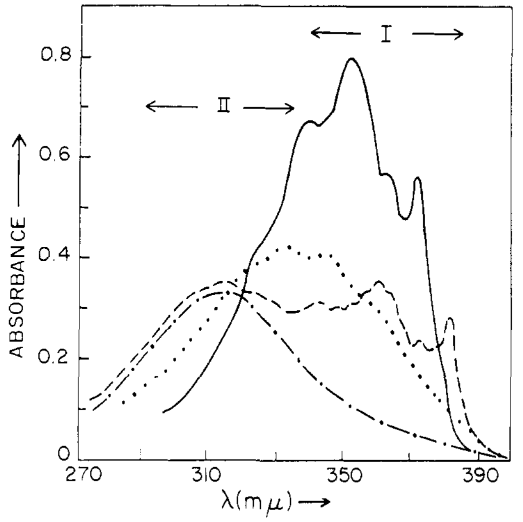

Figure 1. Lowest energy absorption band of PA, MP, TMPA, and MTMP in 3-MP solution at 300°K: (——) PA; (---) TMPA; (···) MP; (-··-) MTMP.

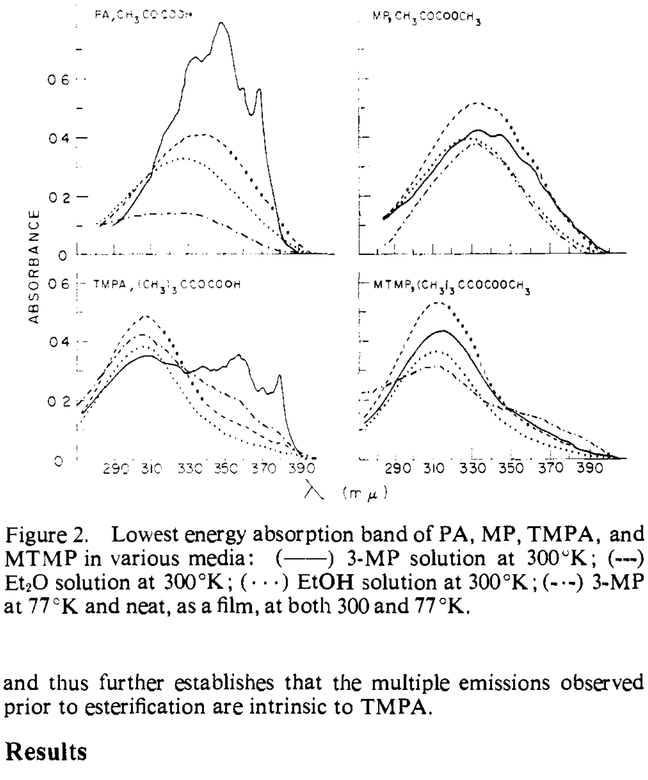

Figure 2. Lowest energy absorption band of PA, MP, TMPA, and MTMP in various media: (——) 3-MP solution at 300°K; (---) Et_2O solution at 300°K; (···) EtOH solution at 300°K; (-··-) 3-MP at 77°K and neat, as a film, at both 300 and 77°K.

and thus further establishes that the multiple emissions observed prior to esterification are intrinsic to TMPA.

Results

Absorption. Figure 1 is a composite of the absorption spectra of MP, PA, TMPA, and MTMP in 3-MP. All compounds exhibit weak absorption ($\epsilon < 100$) in the region $280 < \lambda < 400$ mμ, with the onset of absorption occurring at ~400 mμ. In the case of PA and TMPA, this first band is characterized by a well-defined vibrational structure in region I ($335 < \lambda \leq 400$ mμ), which becomes increasingly diffuse at shorter wavelengths. In contrast, only poorly resolved vibrational structure is discernible in the spectra of MP and MTMP; these spectra maximize at shorter wavelengths in the range designated region II in Figure 1. The absorption spectrum of TMPA is also observed to be red shifted ~700 cm^{-1} relative to that of PA, while the absorption maximum of MTMP is blue shifted ~630 cm^{-1} relative to that of MP.

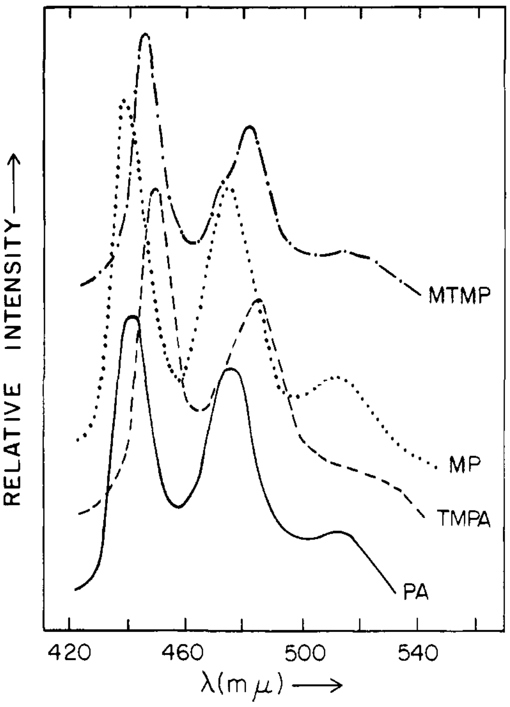

Figure 3. Emission spectra of thin films at 77°K. For notation, see caption to Figure 1.

In PA and TMPA a third, weak intensity absorption region which exhibits a vibrational splitting of ~1500 cm^{-1} is detected in the region $230 < \lambda < 280$ mμ; this absorptivity range is designated as region III and is merely a shoulder feature on a much more intense region IV ($\lambda < 230$ mμ) band. The region IV band maximizes below 200 mμ and is also present in the spectra of MP and MTMP, where its intensity precludes detection of the weak region III absorption present in the keto acids.

The spectra given in Figure 2 represent absorption in media of various polarities and hydrogen-bonding capabilities. Absorption spectra in the hydrogen-bonding media Et_2O (*i.e.*, diethyl ether) and EtOH (*i.e.*, ethanol) indicate that, in both solvent systems, the onset of the first absorption band remains constant at ~400 mμ for all compounds studied. Although the absorption profiles of MP and MTMP are only slightly blue shifted in the solvent progression 3-MP, Et_2O, and EtOH, those of PA and TMPA are dramatically altered. In fact, in their salient features, the acid spectra in hydrogen-bonding media are identical with those of their respective esters. Moreover, the weak region III absorptivity which is observed in the 3-MP solutions of the acid is no longer observable.

The absorption spectra of thin films and of 3-MP solution at 77°K coincide as shown in Figure 2. They differ from their ether and ethanol counterparts only in the degree of resolution and in the increased absorptive intensity of region I which is noted in the TMPA and MTMP spectra.

Emission. The emission spectra of *thin films* of PA, MP, TMPA, and MTMP, all at 77°K, are given in Figure 3 and are identical with those obtained from *concentrated* ($C > 10^{-3}$ *M*) solutions in 3-MP at 77°K. All spectra exhibit vibrational spacings which are characteristic of the symmetric carbonyl stretching frequency.[2] The observed vibrational splittings are:

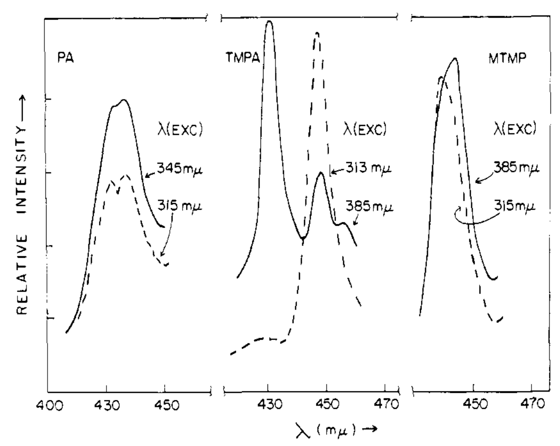

Figure 4. The dependence of emission spectrum on excitation wavelength for dilute solutions of PA, TMPA, and MTMP in 3-MP at 77°K. The excitation wavelength, in mμ, is indicated on the various emission spectra.

PA, 1670 cm^{-1}; MP, 1650 cm^{-1}; TMPA, 1620 cm^{-1}; and MTMP, 1650 cm^{-1}. Luminescence decay times lie in the range $1 \leq \tau \leq 3$ msec and clearly connote a phosphorescence (*i.e.*, $T_1 \rightarrow S_0$) process. The phosphorescence excitation spectra correlate well with the first two absorptive regions (*i.e.*, regions I and II) and no changes in the emission spectra were observed upon selective excitation within these absorption ranges.

The emissive properties of *dilute* ($C < 10^{-3}$ *M*) 3-MP solutions of the acids and MTMP are complex, as illustrated by the excitation-dependent emissions of Figure 4. In these dilute 3-MP solutions, PA exhibits a dual luminescence that is readily discernible in the increased asymmetry and eventual splitting of the band occurring at $\sim$440 mμ in concentrated solutions. The shorter wavelength emission component becomes more pronounced with both decreasing concentration and increasing excitation energy. Excitation spectra of these two emissions, however, have profiles identical with that exhibited by the thin film. Experimental difficulties precluded the determination of the relative lifetimes of the two emissions; however, the observed over-all emissive lifetime is $\sim$2 msec.

This dual luminescence of PA, somewhat blue shifted, is also evident in hydrogen-bonding solvents and is shown in Figure 5. The short-wavelength emission component is significantly shorter lived ($\tau < 1$ msec) than the long-wavelength component ($\tau \simeq 2$ msec), and substantial differences are detectable in the excitation spectra (Figure 5). The vibrational splitting in the two emission regions approximates those of the film spectra.

Excitation-dependent multiple luminescences (*i.e.*, more than two) are also evident in the spectra of TMPA in dilute 3-MP solutions and are shown in Figures 4 and 6. The shorter wavelength emission is characterized by a vibrational splitting of $\sim$1620 cm^{-1} and is the shorter lived ($\tau < 1$ msec). The longer wavelength emission, however, has a vibrational spacing of $\sim$1740 cm^{-1} and a lifetime of $\sim$2 msec. The contrasting excitation spectra are also shown. The more structured spectrum correlates well with the solution absorption of Figure 1, while the spectrum maximizing at $\sim$330 mμ is similar to *neat solution* spectra. The observed emission and excitation characteristics are unaltered in hydrogen-bonding solvents.

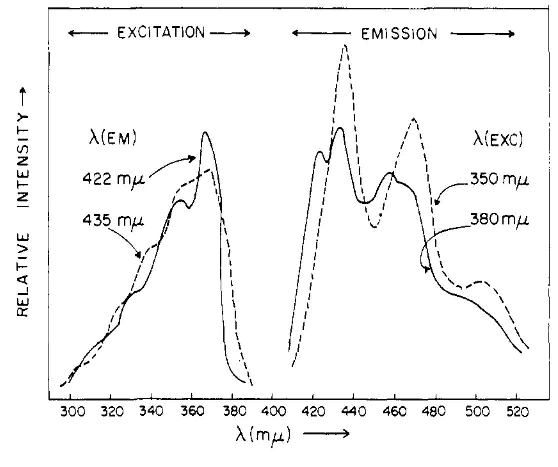

Figure 5. Emission and emission-excitation spectra of PA in EP glass at 77°K.

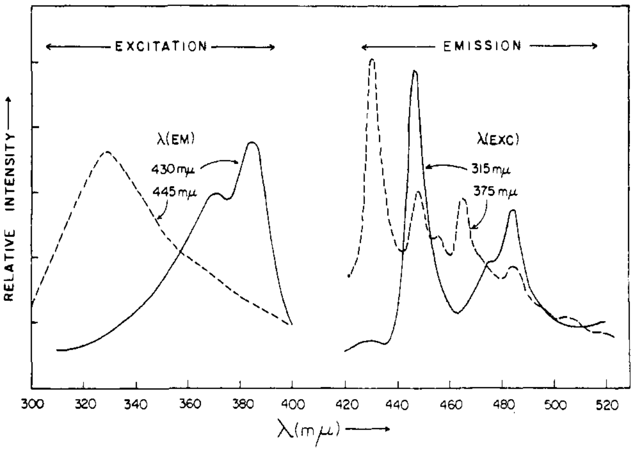

Figure 6. Emission and emission-excitation spectra of a dilute solution of TMPA in 3-MP at 77°K.

As noted previously, the emission and excitation spectra of MP in 3-MP, at *all concentrations*, are identical with the thin film counterparts (see Figure 3). In EP (*i.e.*, ether–isopentane mixture) and EtOH solutions, the origin bands of the emissions are blue shifted to 425 and 420 mμ, respectively; however, a similar shift is not detectable in the excitation spectra. The vibrational splittings and emission lifetimes in the hydrogen-bonding solvents approximate those observed in 3-MP solutions.

Unlike MP, MTMP exhibits a dual luminescence in dilute 3-MP. This duality is shown in Figure 4 *via* the excitation dependency of the first emission band. Although the asymmetry is sensitive to excitation energy as well as concentration, excitation spectra taken on either side of the first band have profiles essentially identical with the thin film counterparts. The observed emission lifetime is $\sim$2.5 msec. Experimental difficulties, however, precluded determination of the relative lifetime of the two observed emission components. Vibrational spacings again approximate those observed in the film spectra. Emission and excitation spectra of EP and EtOH solutions are identical with their counterparts in dilute 3-MP solutions.

Discussion

Absorption. Extensive experimental generalization[7] and theoretical correlation[6,8] of the absorption spectra of α dicarbonyls have established that the first three electronic transitions of PA and TMPA, in order of increasing energy, are assignable as: (1) ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ in regions I and II; (2) ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ in region III; and (3) ${}^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ in region IV. Similarily, the observed transitions of MP and MTMP are assignable as ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ in regions I and II and ${}^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ in region IV. The rationale for the assignment of both regions I and II as only one transition is provided later. These assignments, when coupled with the equilibria of eq 1 and with steric and electronic considerations, provide a suitable framework for discussion of both the absorption and luminescence spectra.

In the isolated molecule, coplanarity of the α dicarbonyl moiety is favored by the formation of an intramolecular hydrogen bond. Steric interactions, however, will distort these otherwise planar geometries and the intercarbonyl dihedral angle, θ, will assume some value $0 < \theta < 180°$.

The importance of θ in determining the spectroscopic behavior of α diketones has been demonstrated by several workers.[9] In particular, Leonard and coworkers found that as the dicarbonyl subunit deviates from planarity, the lowest energy transition (${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$) undergoes a substantial blue shift. Examination of models of PA, MP, TMPA, and MTMP establish the following order of deviation from planarity in the nonchelated entities PA $\simeq$ MP $\ll$ TMPA $\simeq$ MTMP. Thus, MP and MTMP are expected to mimic the behavior of their respective *free* parent acids and the $\lambda_{\max}$ absorption of the TMPA/MTMP couple to occur at shorter wavelengths than that of the PA/MP couple. Characteristics consistent with these expectations are readily discernible in the absorptions of region II and suggest that absorption in this region is to be identified with nonchelated structures.

The region I absorption is associated with the planar chelate. This hypothesis is supported by the similarity of vibrational structure of PA and TMPA in region I and the failure to observe significant absorption in this region for MTMP. The observation that MP and MTMP have the same onset of absorption as do PA and TMPA necessarily implies that these compounds also exist to some extent in planar conformations, with the contrast in the relative absorptivities of region I/region II emphasizing the differences in the most probable ground state geometries. Clearly, the smaller interval between region I and II maxima for the MP/PA couple relative to the TMPA/MTMP couple indicates that MP and the nonchelated PA deviate less from planarity than do MTMP and nonchelated TMPA.

The dramatic contrast in the solvent dependency of the absorption spectra of the ester and parent acid is illustrated in Figure 2. Although the absorption maxima of MP and MTMP undergo only a small blue shift in hydrogen-bonding solvents (a blue shift which might be associated either with the normal solvent shift for ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transitions or with a change in the most probable ground state geometry), the absorption properties of PA and TMPA are dramatically altered. In fact, the absorption profiles of PA and TMPA in both ethereal and ethanolic solutions are nearly indistinguishable from those of their respective esters. This similarity is a consequence of the destruction of the intramolecular hydrogen bond of the proton chelate and the concomitant loss of dicarbonyl coplanarity. The loss of vibrational structure and absorption intensity in region I is consistent with assignment of the primary absorption in this region in noninteracting media to the proton chelate and implies that region II absorptivity is associable with intermolecularly hydrogen-bonded structures of nonplanar nature. Again, as in 3-MP, the broad range spanned by region I and II absorptions in polar solvents is indicative of the varied geometric population sampled. However, since the onset of absorption remains constant at $\sim$400 mμ for all compounds in all media (Figure 2), the existence of planar entities is implied in all instances, regardless of molecular environment or degree of molecular association.

The similarity of the film and polar-media absorption spectra of the keto acids at 77°K requires consideration of the consequences of eq 1. These equilibria dictate that with decreasing temperatures and increasing concentrations the relative population of associated species or aggregrates will increase. In fact, neat solutions necessarily consist solely of aggregrates. The correspondence between these two types of acid spectra and those of the appropriate esters demonstrates that acid aggregrates contain a predominance of nonplanar dicarbonyl species. It must be reemphasized, however, that the constancy of absorbance onset at $\sim$400 mμ confirms the constant existence of a small population of planar entities.

The effects of eq 1 are also found at ambient temperatures in the spectra of 3-MP solutions of TMPA where increasing concentration of TMPA causes a substantial increase in the absorptivity of region II relative to that of region I. Thus, in the case of the α-keto acids, absorption in region II must be attributed to both free and aggregrated nonplanar entities.

Emission Spectra of Films and Concentrated Solutions in 3-MP. The experimental data identify[10] the luminescence of films and of concentrated ($C > 10^{-3}$ M) solutions in 3-MP as ${}^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$. Although the correspondence between the phosphorescence-excitation and low-temperature absorption spectra indicates that a large and geometrically varied population is excited, a single, excitation-independent emission is observed for each compound. This phenomenon, together with the similar phosphorescence energies, suggests that all relaxed emitting triplets possess a common well-defined geometry. Certainly, if emission were to occur from triplets of varying intercarbonyl dihedral angle, the emission spectrum would be expected to be diffuse and to show a critical dependence upon excitation energy. No such phenomena were observed.

The most probable geometry of the relaxed emitting

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triplet is one in which a coplanar configuration of the dicarbonyl entity is attained. This supposition follows from the observation that the energy separation between the absorption maximum (which provides information about the most probable ground state conformation) and phosphorescence origin band lies in the range 8,000–10,000 cm^{-1}, whereas only a 3000–4000 cm^{-1} separation exists between the *onset* of absorption and the phosphorescence origin band. As established in the discussion of the absorption spectra, the 400-mμ absorption (*i.e.*, region I) of MP, PA, TMPA, and MTMP is associated with a planar ground state conformation, while absorption at shorter wavelengths (*i.e.*, region II) involves twisted geometries. In compounds such as biacetyl, 2,3-pentanedione, and camphorquinone where both absorption and emission occur from a planar conformation,[11] the splitting between the absorption and phosphorescence maxima is 2–4000 cm^{-1}. These molecules are $^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$ emissive and the 2–4000 cm^{-1} separation is generally characteristic[10] of $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1/{}^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$ separations for such compounds. Accepting, then, this 2–4000 cm^{-1} separation as the norm for α dicarbonyls in which there is no significant difference between the ground and emitting state geometries, it follows that the assignment of a planar conformation to the relaxed emitting triplet is not unreasonable. This conclusion is also consistent with the observations of Evans and Leermakers[11] regarding the preference of α diketones to emit from planar conformations. Moreover, these latter model compounds emit in a narrow energy region (18,000–20,400 cm^{-1}) as do MP, TMPA, PA, and MTMP (22,400–22,500 cm^{-1}). This approximate constancy of emissive energy is particularly striking when contrasted with the broad absorption energy range spanned by the preferred ground conformations of the α-keto compounds.

Emission Spectra of Dilute Solutions in 3-MP and Hydrogen-Bonding Solvents. With the exception of MP, all compounds investigated exhibited multiple luminescence in dilute 3-MP solution. Indeed, as shown in Figures 5 and 6, PA and TMPA exhibit dual luminescence even in hydrogen-bonding solvents.

On the basis of the experimental data, the long-lived emissions of PA, MTMP, and TMPA, as well as all luminescences of MP, must be identified[10] as $^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$. The short-lived (*i.e.*, $\tau < 1$ msec) emissions of PA and TMPA are also tentatively assigned as $^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$ on the basis of the observed separation of ~3000 cm^{-1} between the excitation and emission *origins*. The possibility that these short-lived emissions are fluorescence processes may be discounted because the large Stokes shifts predicated by this model can be accommodated only by assuming a significant change between the geometry of a planar ground state and that of the emitting singlet. On the basis of the earlier work of Leermakers[11] and the absorption and emission data discussed above, such a geometric change is improbable.

The genesis of the multiple luminescence lies in the demonstrated complexity of the emitting solutions and the observation[12] of aggregation-dependent emissions in other systems. As discussed earlier, solutions of PA and TMPA are best described by the equilibria of eq 1. Although low temperatures will shift these equilibria toward associated species, as indicated by the absorption spectra of Figure 2, decreased concentration and increased hydrogen-bonding capability of the solvent will shift the equilibria toward monomeric species. That at least two species of varying absorptive (geometric) properties are responsible for the multiple luminescence of PA and TMPA is demonstrated in Figures 5 and 6. Unfortunately, the stoichiometry of the emitting states cannot be obtained from the data available here.

The multiple luminescence of MTMP as shown in Figure 4 cannot be rationalized in terms of the equilibria of eq 1 and insufficient data are available to do other than speculate. We note, however, that both MP and MTMP possess nonnegligible dipole moments[3b] and that association may occur in either the ground state or the excited state or both. That such association can give rise to several luminescences has been adequately demonstrated in other systems.[13] The failure to observe multiple luminescences in MP solution, then, may be ascribed either to its smaller dipole moment or to insufficient resolution.

Summary

The absorption studies confirm the presence of various monomeric and associated species in solutions of the α-keto acids, the dominant entity present being determined by the interplay of numerous factors. These factors include concentration, temperature, and both solute–solute and solute–solvent interactions. Each discrete entity of the equilibria of eq 1 may sample, in turn, a varied geometric population which is composed of both *planar* and *twisted* conformations, each of which possesses differing absorptive properties. Despite the varied ground state geometries, however, all phosphorescence occurs from relaxed triplets which possess a planar intercarbonyl geometry; the multiple luminescences must then be ascribed to the diverse environments of various emitting molecules.

The absorption spectra of the α-keto esters are readily rationalized in terms of absorption by molecules with varying intercarbonyl dihedral angles. The presence of multiple luminescence in dilute solutions, of MTMP, however, again requires the invocation of associated species which emit only from planar configurations of the dicarbonyl group, as do the keto acids. Thus, the complexity of the emission spectra of both the keto acids and esters is attributed to complexes involving various degrees of solute and solvent participation.

Acknowledgment. This work was supported by contract between the United States Atomic Energy Commission–Biology Branch and The Louisiana State University.

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[11] T. R. Evans and P. A. Leermakers, *J. Amer. Chem. Soc.*, **89**, 4380 (1967).

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[13] O. S. Khalil, R. H. Hofeldt, and S. P. McGlynn, *Chem. Phys. Lett.*, **17**, 479 (1972).