scheme was used to effect this sorting as follows. On the first pass, all of the absorption data were used to obtain a first estimate of constants A, B, and C. These estimates were used in eq 1 to back-calculate predicted values of the transition energies $\hat{E}_{\mathrm{T}}$. The standard deviation between observed and calculated transition energies was obtained. If the standard deviation was less than 0.5 kcal/mol, processing terminated; otherwise the difference $|\hat{E}_{\mathrm{T}} - E_{\mathrm{T}}|$ was calculated for each solvent and the solvents were sorted into two classes depending upon whether the difference $|\hat{E}_{\mathrm{T}} - E_{\mathrm{T}}|$ was (1) larger than the standard deviation or (2) less than or equal to the standard deviation. Absorption data for solvents falling in the second class were then used to recalculate a new set of constants A, B, and C, and this new regression equation was used to calculate a new standard deviation and a new set of differences $|\hat{E}_{\mathrm{T}} - E_{\mathrm{T}}|$ and sorting into two classes was done again. This was continued until the regression gave a standard deviation less than 0.5 kcal/mol. Three to five regression trials sufficed to effect the regression analysis and sorting; standard deviations actually obtained were *ca.* 0.3 kcal/mol.

Statistical analysis of the regression results gave the following probabilities that random variation alone would produce the observed number of successful predictions by eq 1 (see Figures 7a and 7b): dye **1**, 0.02; dye **2**, 0.05; dye **3**, 0.44; dye **4**, 0.48; dye **5**, 0.08; dye **7**, 0.02. The predictions for dyes **1**, **2**, **5**, and **7** are therefore highly statistically significant. The predictions for dyes **3** and **4** are inconclusive. Taking all six experiments as a whole, the probability is about one part in 10,000 that four events out of six with probabilities of about 0.05 would occur on a random basis. This analysis shows that the computer routine can identify significant mathematical structure and that the observed successes did not result from fortuitous selection of random events. The inconclusive predictions for dyes **3** and **4** arise from an assignable cause—a factor of structure (occurrence of an N–H bond) not present in the other dyes. This assignment of cause for dyes **3** and **4** is made possible by the highly significant correlations obtained with the other four dyes.

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Electronically Excited Aromatic Carbonyl Compounds in Hydrogen Bonding and Acidic Media

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Abstract: In 85% H_3PO_4 several aromatic carbonyl compounds display remarkable though often weak fluorescence at room temperature (Table I) and long but multiple component phosphorescent decay times at 77°K (Table III). By subjecting benzophenone to extremes, namely nonpolar, weakly hydrogen bonding solvents and strongly acidic solvent glasses, and then many intermediate solvent conditions, a model for aromatic carbonyl solvation has been established in which the excited state (1) possesses n,π^* character in nonpolar and weakly hydrogen bonding solvents, (2) exhibits enhanced π,π^* character in very polar hydrogen bonding solvents, and (3) attains a protonated π,π^* state in strongly acid media.

It has been reasonably established that nearly complete reversal of excited state energy levels occurs in certain molecules which are very sensitive to moderate changes in solvent polarity and hydrogen bonding. For example, the fluorescence intensity of quinoline in solvents benzene, ethanol, and water is enhanced in the ratio 1:50:1000, respectively. The authors concluded that the lowest n,π^* state in solvent benzene is replaced by a nearby π,π^* state in water.[1] Singlet state inversion is apparently also a property of acridine[2,3] and pyrene 3-aldehyde[4] whose fluorescence behavior is similar to quinoline. Sensitivity to moderate variations in solvent polarity is often an indication that the lowest π,π^* energy level is almost isoenergetic with the n,π^* energy level. Within the triplet manifold, observations of multiple-component phosphorescence for indanone,[5] butyrophenone,[6] acetophenone,[7] and substituted acetophenones,[8,9] again indicates strong dependence on solvent with respect to the relative energies of n,π^* and π,π^* states. Here, however, triplet energy level reversal has been definitively documented only for butyrophenone[6] and acetophenone.[7]

It is a reasonable thesis that, in general, aromatic carbonyl compounds may be affected by polar, hydrogen bonding solvents, but to varying degrees depending upon the solvent system. To obtain complete inversion of n,π^* and π,π^* states, stronger hydrogen bonding solvents are required which may even lead to protonation of the carbonyl oxygen. In the present paper, through the use of very polar hydrogen bonding solvents and both weak and strong acid glasses at 77°K, we report a detailed examination of the excited singlet and triplet states for a number of carbonyl systems.

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(8) R. N. Griffin, *Photochem. Photobiol.*, **7**, 159 (1968).

(9) R. N. Griffin, *ibid.*, **7**, 175 (1968).

Experimental Section

Reagents and Chemicals. Mineral acids were Baker analyzed reagent grade. EPA was obtained from Matheson. Methylcyclohexane (Harleco), silica-gel (Fischer) 28–200 mesh, Grade 12 (activated), and primary standard benzoic acid (Mallinckrodt) were used without further purification. Analytical reagent benzophenone (Eastman) was zone refined (16 passes.) Benzaldehyde (Baker) was washed three times with 10% Na_2CO_3 and water, and then vacuum distilled (55° (~10 mm)).[10] Acetophenone (Matheson Coleman and Bell) was carefully recrystallized (from the neat liquid). Chromatographic grade propiophenone (Analabs) and reagent butyrophenone (Eastman) were vacuum distilled (87 and 110°, respectively (~10 mm)) and then recrystallized three times. Anthraquinone (Eastman reagent grade) recrystallized from glacial acetic acid and was washed with ethanol. Xanthone[11] (Aldrich) was three times recrystallized from ethanol. 2-Acetonaphthone (Baker) was recrystallized from ethanol (three times) and from hexane (twice).

Quantum Yields of Fluorescence and Phosphorescence. Fluorescence quantum yields were determined relative to quinine sulfate (QS) in 0.1 *M* H_2SO_4 as a standard. The spectra were integrated by the cut and weigh technique. Prior to collecting emission data, the per cent transmission (% *T* in 1-cm^2 quartz cells) of all the solutions was adjusted to within 1% of that of QS for the 313-mm excitation band. The % *T*'s were determined on an Aminco Bowman spectrofluorimeter by attenuating the signal of the Hg-Xe source with a 1-mm path of silica gel behind the cell holder and situating the photomultiplier behind the cell block. As an additional precaution, a 313-nm Baird Atomic interference filter, employed to monochromate the excitation beam, was placed in front of the photomultiplier slit eliminating any fluorescence signal.

The 313-nm interference filter was moved in front of the cell holder and the fluorescence spectra were obtained from the 1-cm^2 quartz cell at an angle of 90°. All emission envelopes were uncorrected for instrumental inefficiencies, since the fluorescence spectrum of quinine lies in the same spectral region. Refractive index corrections for quantum yield comparison were also neglected.

Relative phosphorescence yields (Φ_p) were similarly determined by comparing unchopped total luminescence spectra at 77°K with that of standard benzophenone in EPA; $\Phi_p = 1$.[12] Solutions of ~40 OD/cm at 313 nm were placed in quartz 1-mm i.d. tubes and frozen (77°K) in an Aminco microdewar. Several runs were required to average the geometrical factors giving rise to variations. H_2SO_4 glasses cracked in many instances and produced unusually large variations (*ca.* 30%).

Lifetimes of Phosphorescence Decays at 77°K. Decay lifetimes were determined on the Aminco Bowman spectrophosphorimeter, employing an Aminco Photomultiplier battery pack no. 4-8275 and feeding the signal directly into a Tektronix 564 B storage oscilloscope.

Absorption Spectra. Absorption spectra and molar extinction coefficients were determined on a Carey Model 14 spectrophotometer.

Results and Discussion

Fluorescence and phosphorescence in a number of aromatic carbonyl compounds occurs in a solvent (85% H_3PO) capable of significantly altering the energy required for the excitation of the nonbonding electrons. Benzophenone triplet emission was more extensively studied in a number of hydrogen bonding and acidic glasses. Our observations are consistent with a model for carbonyl solvation in which the excited state (1) possesses n,π* character in nonpolar and weakly hydrogen bonding solvents, (2) exhibits enhanced π,π* character in very polar hydrogen bonding solvents, and (3) becomes a protonated π,π* state in strongly acidic media, *e.g.*

$$\mathrm{ArRC{=}O\cdots HA} \qquad (\mathrm{n},\pi^*) \tag{1}$$

$$\mathrm{ArRC{=}O\cdots H^{\delta+}\cdots A^{\delta-}} \qquad (\pi,\pi^*) \tag{2}$$

$$\mathrm{ArRC{=}O^{+}{-}H} \quad \mathrm{A^-} \qquad (\pi,\pi^*)^+ \tag{3}$$

A. Fluorescence Spectra. Benzophenone and a number of other aromatic carbonyl compounds fluoresce in 85% H_3PO_4 at room temperature (Table I). With the exception of benzil, the phenomenon appears rather general and yields short-lived, structureless emission which is little affected by oxygen. The quantum yields of fluorescence in the H_3PO_4 solutions, when compared to normally nonexistent or extremely weak emission found in neutral solutions, are consistent with fluorescence from the protonated forms. Weller and Urban,[15] by monitoring fluorescence of the protonated forms of acetophenone and benzoic acid, have reported dramatic increases in the basicity of these compounds upon electronic excitation. Similar observations for 2-acetonaphthone,[16] anthrone,[17] and acridone[18] have been noted. The enhanced basicities of these excited carbonyls are easily rationalized. π,π* states are, or become, the energetically lowest states as hydrogen bonding or protonation increases the energy of n,π* states rendering the latter chemically and physically inert. (n,π* states are less basic than ground states.) Benzil, which does not measurably fluoresce in H_3PO_4, possesses two n,π* states of which only one should become energetically unfavorable due to hydrogen bonding or protonation.

Table I. Fluorescence Data in 85% H_3PO_4 at Room Temperature

Compd	λ_{max}, nm	Φ_f[a]
Acetone	~400	<0.001
2-Acetonaphthone	560	0.005 ± 0.001
Acetophenone	450	0.084 ± 0.008
Anthraquinone	462	0.006 ± 0.001
Benzaldehyde	470	0.020 ± 0.004
Benzil	485	<0.001
Benzoic acid	400	0.008 ± 0.001
Benzophenone	495	0.0062 ± 0.0006
Butyrophenone	453	0.11 ± 0.04
Propiophenone	453	0.085 ± 0.02
Xanthone	460	0.58 ± 0.06

[a] Quantum yields (Φ_f) are relative to quinine sulfate ($\Phi_f = 0.55$)[b] in 0.1 *N* H_2SO_4 with excitation at 313 nm. [b] W. H. Melhuish, *J. Phys. Chem.*, **64**, 762 (1960); **65**, 229 (1961).

B. Absorption Spectra. In the absorption spectrum of benzophenone, the expected solvatochromic shifts are observed, *i.e.*, red and blue shifts for the π,π* and n,π* bands, respectively, with increasing solvent polarity (Table II).[19] These spectral shifts are sufficient such that when benzophenone is adsorbed on silica gel,[20] the red-shifted π,π* band completely obscures the blue-shifted n,π* band, indicating that in this molec-

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[10] Arthur I. Vogel, "Practical Organic Chemistry," 2nd ed, Longman, Green and Co., New York, N. Y., 1951, p 663.

[11] See ref 10, p 703.

[12] Literature values are variable, ranging from 0.71[13] to 0.84,[14] with indications that it may be even higher, approaching unity.

[13] C. A. Parker and C. L. Hatchard, *Analyst*, 87, 664 (1962).

[14] E. H. Gilmore, G. E. Gibson, and D. S. McClure, *J. Chem. Phys.*, 23, 399 (1955).

[15] A. Weller and W. Urban, *Angew. Chem.*, **66**, 336 (1954).

[16] A. Trozzolo, private communication.

[17] A. C. Hopkinson and P. A. H. Wyatt, *J. Chem. Soc. B*, 1333 (1967).

[18] H. Kokubun, *Z. Electrochem.*, **62**, 599 (1958).

[19] M. Ito, K. Inuzuka, and S. Imanishi, *J. Amer. Chem. Soc.*, **82**, 1317 (1960).

[20] P. A. Leermakers and H. T. Thomas, *ibid.*, **87**, 1620 (1965).

Table II. Positions of (^1L_a) Transition for Benzophenone in Various Solvents[a]

Solvent	λ_{max}, nm	$\bar{\nu}$, cm^{-1}
Cyclohexane	248	40,300
Ethanol	251	39,800
Silica gel-cyclohexane	261.5	38,200
H_3PO_4 (85%)[b]	269	37,200

[a] Reference 20. [b] Present work.

ular environment the π,π^* singlet level is beginning to invert with the n,π^* level. In 85% H_3PO_4 the π,π^* band is even further red shifted with general characteristics of the spectrum remaining unchanged. However, the absorption spectrum is drastically altered (λ_{max} 292 (ϵ 1.4 × 10^4), 344 nm (ϵ 2.4 × 10^4) in 98% H_2SO_4, where the chromophore is protonated.[21] It is apparent that increasing solvent polarity produces a trend of inversion in the singlet levels with protonation becoming important in highly acidic media.

C. Phosphorescence Spectra. By analogy, effects similar to those observed in the singlet state are not unexpected for the triplet state. Lamola[7] has reported inversion of n,π^* and π,π^* triplet levels of acetophenone at 77°K with increasing solvent polarity and concomitant increased lifetimes. We have observed that a number of aromatic carbonyl compounds display very markedly increased triplet lifetimes (τ_p) in 85% H_3PO_4 glasses at 77°K. Although the phosphorescent decays are not strictly first order, approximate (±5%) values are collected in Table III.

Table III. Phosphorescence Decay Times at 77°K in 85% H_3PO_4[a] and EPA

Compd	τ_p, sec, H_3PO_4	τ_p, sec, EPA[b,c]
Acetophenone	2.6 (1.51)[d]	0.008
Anthraquinone	0.10	0.004
Benzaldehyde	0.53	0.0015
Benzil	0.005	0.005
Benzophenone	0.66	0.006
Butyrophenone	2.8 (0.80)[e]	0.001[f]
Propiophenone	1.6–2.1	0.1–0.01[g]
Xanthone	1.9	0.02

[a] Decays monitored at λ_{max}. [b] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 297. [c] C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968, p 281. [d] Reference 7. [e] R. D. Rauh and P. A. Leermakers, *J. Amer. Chem. Soc.*, **90**, 2246 (1968). [f] In hexane. [g] R. Shimada and L. Goodman, *J. Chem. Phys.*, **43**, 2027 (1965).

The phosphorescent lifetime of benzophenone is increased by two orders of magnitude in a H_3PO_4 glass with only a slight reduction in the quantum yield of emission ($\Phi_p \sim 0.55$ in 85% H_3PO_4 relative to 1.0[12] in EPA). The lifetime is seen in Table IV to increase continuously with solvent glasses of increasing hydrogen bonding strength and acidity and is indicative of a trend for enhanced π,π^* character in the triplet state. Some information regarding the nature of the emitting state may be gleaned from emission spectra. At 77° the typical vibrational structure of benzophenone phosphorescence is lost with increasing solvent polarity. In Table V and Figures 1a and 1b it is seen that the near edge of the benzophenone emission shifts to the blue with increasing solvent polarity up to and including H_3PO_4 (in which benzophenone is only slightly, if at all, protonated, even in the excited state). In stronger acids, 70% $HClO_4$ and 98% H_2SO_4 the spectrum is significantly altered and shifted to the *red* (Table V, Figure 1b).

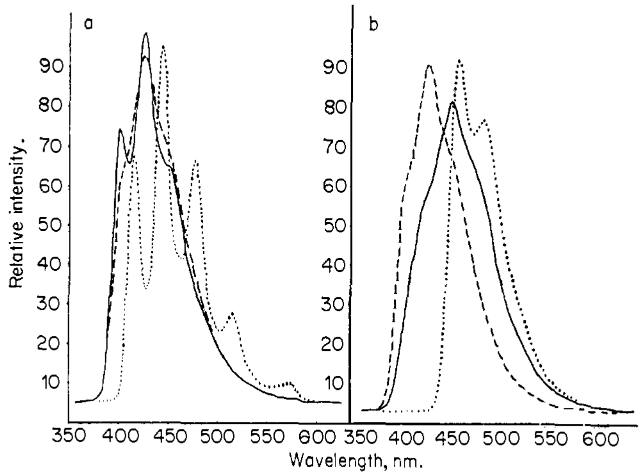

Figure 1. Phosphorescence spectra for $(C_6H_5)_2CO$ in various glasses at 77°K: (a) · · ·, methylcyclohexane; ——, ethylene glycol–water (1:1); - - -, silica gel–methylcyclohexane; (b) - - -, silica gel–methylcyclohexane; ——, 85% H_3PO_4; · · ·, 98% H_2SO_4.

Table IV. Observed Phosphorescence Lifetimes for Benzophenone in Various Solvent Glasses at 77°K

Solvent	τ_p, sec[a]
Methylcyclohexane (MCH)	0.005
EPA	0.006
Ethylene glycol-water (1:1) (EGW)	0.077
Silica gel-MCH	0.12
85% H_3PO_4	0.66
85% H_3PO_4-70% $HClO_4$ (1:1)	0.80
(1:4)	0.88
(1:24)	0.94
70% $HClO_4$	0.95
98% H_2SO_4	1.03

[a] Measured at λ_{max}.

Table V. Near Edges of the Phosphorescence Spectra in Various Solvents for Benzophenone

Solvent	λ, nm	$\bar{\nu}$, cm^{-1}
MCH	390	25,640
EPA	390	25,640
EGW	385	25,970
SG-MCH	380	26,320
H_3PO_4 (85%)	375	26,670
$HClO_4$ (70%)	432	23,020
H_2SO_4 (98%)	432	23,020

Three observations indicate that the emissions in 70% $HClO_4$ and 98% H_2SO_4 arise from the protonated triplet: (1) the alteration of the spectral shape, including the red shift of the near edge, as compared to emission in polar but neutral solvents; (2) the very similar lifetimes of benzophenone triplet in these glasses; and (3) the lack of significant deviation from first-order kinetics for these glasses. This lends substance to an intuitive expectation of a protonated triplet since the ground state is also protonated in these solvents. However, emission in 85%

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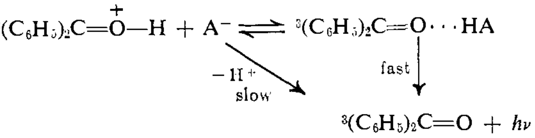
(21) R. Stewart, M. R. Granger, R. B. Moodie, and L. J. Muenster, *Can. J. Chem.*, 41, 1065 (1963).

H_3PO_4 at 77° more nearly resembles that for ethylene glycol–water (1:1) or silica gel–cyclohexane. Examination of Figure 1 will reveal that a significant portion of the emission in H_3PO_4 is of higher energy than that expected from a fully protonated state. Although definitive evidence as to the extent of protonation in 85% H_3PO_4 is lacking, it is clear from Table VI that much of the benzophenone emission arises from a long-lived nonprotonated species. The multicomponent decays of benzophenone adsorbed on silica gel or dissolved in 85% H_3PO_4 (Table VI) deviate slightly from first-order kinetics with no evidence of a very short lived (6 msec) component. The components could arise from benzophenone in different molecular environments, *i.e.*, different extents of mixing n,π* and π,π states and different extents of protonation. The system very probably is subject to a dynamic equilibrium between protonated and unprotonated species producing multicomponent spectra with the observed lifetimes a function of the extent of deprotonation (eq 4 and 5). However, we must note that the *fluorescence* yield of benzophenone in H_3PO_4 is less than 0.01 (Table I), so that intersystem crossing of neutral benzophenone competes overwhelmingly with possible intersystem crossing of the protonated species (in H_3PO_4). In the stronger acids it is likely that substantial intersystem crossing does take place in the protonated species.

Table VI. Approximate Phosphorescence Decay Times for Benzophenone at Various Monitoring Wavelengths (Excitation at 313 nm)

H_3PO_4		SiO_2-MCH	
λ, nm	τ, sec	λ, nm	τ, sec
400	0.14	393	0.081
425	0.53	434	0.11 to 0.21
452	0.66		
475	0.62	500	0.11 to 0.17
560	0.69		



$$\begin{tikzcd} {}^3(C_6H_5)_2C{=}\overset{+}{O}{-}H + A^- \arrow[r, shift left] \arrow[dr, "-H^+"', "slow"] & {}^3(C_6H_5)_2C{=}O\cdots HA \arrow[l, shift left] \arrow[d, "fast"'] \\ & {}^3(C_6H_5)_2C{=}O + h\nu \end{tikzcd}$$

(4)

(5)

It is unlikely that protonation is important in the ethylene glycol–water and methylcyclohexane–silica gel glasses; thus, the benzophenone phosphorescence in these glasses very likely arises from an unprotonated triplet with considerable π,π* character. At present the nature of the states producing the apparent continuum of phosphorescent lifetimes collected in Table IV has not been unambiguously established for each case. However, it is evident that the trend toward enhanced π,π* character and ultimate protonation, noted for the singlet state in solvents of increasing hydrogen bonding strength and acidity, also holds for the triplet state.

Summary

In conclusion, we have cited evidence that benzophenone and presumably other normally n,π* aromatic carbonyl compounds possess enhanced singlet π,π* character in very polar and acidic media. The enhanced basicity of the singlet state observed by Weller and Urban[15] most reasonably arises from a π,π* type state. The fluorescence noted for a number of aromatic carbonyl and carboxyl compounds in 85% H_3PO_4 suggests that enhanced basicity of the singlet state is rather general when there exist suitable π,π* levels. Similarly, the phosphorescent lifetimes of benzophenone at 77°K are consistent with a shift from n,π* to π,π* to protonated π,π* states with increasing solvent polarity and acidity. Spectral evidence strongly suggests that benzophenone triplet is protonated in 70% $HClO_4$ and 98% H_2SO_4, but only partially so, if at all, in 85% H_3PO_4. A number of other aromatic carbonyl compounds, benzil excluded, possess increased phosphorescent lifetimes in 85% H_3PO_4 at 77°, illustrating the generally enhanced π,π* character of these triplets in polar and acidic media.

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