reaction 12 proceeds with difficulty or not at all in anhydrous media. This appears reasonable in view of the fact that it is more difficult to reduce **1** than **2** or **3** by some 400–600 mV. Thus, in anhydrous media radical **11** could participate in a net back electron transfer process

$$RuL_3^+ + Et_3NH^+ + CH_3\dot{C}HNEt_2 \rightarrow RuL_3^{2+} + 2Et_3N \quad (18)$$

in which it functions as an oxidizing agent. In aqueous solution it has been found that reduced **1** and **2** can react with water in net redox processes[49] and the present results may indicate that a scavenging of the reduced **1** in competition with back electron transfer results in net chemistry via reactions 7, 8, and 17 in this case as well. Here, rapid reaction of **12** with water may divert the net reaction via reactions 16 and 17. Alternatively, **11** may participate in water reduction in aqueous media[43,49,51] (vide supra).

The observation of analogous products for the iron complex **5** is perhaps of even greater interest since **4** and **5** have relatively short-lived nonluminescent excited states. However, although no luminescence has been detected for **4** or **5**, indirect studies have suggested that the excited-state lifetime of **4** in solution is sufficiently long (1–23 ns)[54,55] to permit its participation in bimolecular reactions in solution. In recent investigations we have found that **4** and **5** participate in oxidative photoreactions analogous to their ruthenium(II) counterparts.[56] When solutions of **4** and **5** are irradiated in the presence of triethylamine and in dry acetonitrile, there is no direct evidence for buildup of a reduced FeL_3^+ species; however, the finding that irradiation of **5** in the presence of triethylamine results both in the trapping of radical **11** and in generation of acetaldehyde indicates that the same net photochemistry must be occurring with the iron as for the ruthenium complexes. However, studies with the simple bipyridine derivative **4** led to no detectable trapped radicals and to very low yields of acetaldehyde. In this case there is evidently insufficient generation of amine radical cation to permit the formation of a trappable concentration of **11**. The relatively small differences in efficiency of acetaldehyde formation between the corresponding iron and ruthenium complexes (**5** and **2**, respectively) suggest that analogous reactions such as water reduction[49] should be observable for a number of related metal complexes.

Acknowledgments. This work was supported by grants from the National Science Foundation (CHE-76-01074) and the National Institutes of Heatlh (GM 15,238). We are grateful to W. R. Grace and Co. and the North Atlantic Treaty Organization for grants in aid which supported travel and made possible the collaboration between the two laboratories. We thank Mr. Phillippe Maillard for a gift of several spin traps.

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Intramolecular Proton Transfer and Excited-State Relaxation in 2-(2-Hydroxyphenyl)benzothiazole

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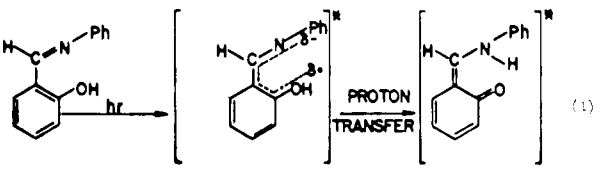
Abstract: The excited state vibrational and conformational relaxation of 2-(2-hydroxyphenyl)benzothiazole in solution has been studied as a function of temperature by means of picosecond spectroscopy, using a streak camera with <5-ps resolution. Three distinct relaxation processes were identified: (a) intramolecular proton transfer producing a cis-keto tautomer occurring within 5 ps from $T = 4$ to 300 K; (b) vibrational energy redistribution and/or relaxation into the medium at a rate of 10^{11} s^{-1} at 4 K and increasing rapidly with temperature; (c) radiationless decay (10^2–10^3 ps) induced by large amplitude torsional motion in solution at $T > 200$ K.

Introduction

Recently we have investigated the picosecond kinetics of intramolecular proton transfer in the lowest $^1\pi$–π^* state of salicylidenaniline (SA).[1] The enol form of this molecule was found to tautomerize (eq 1) into a cis-keto form with a rate of $k \geq 2 \times 10^{11}$ s^{-1} following Franck–Condon excitation at 355 nm. The time-resolved fluorescence emitted from the cis-keto product was monitored by a streak camera with <5-ps resolution. We have shown that this molecule tautomerizes within 5 ps at temperatures above 4 K in both protic and aprotic solvents. We also observed that the kinetics were unchanged when the phenolic proton was deuterated. The fluorescence of the cis-keto form was found to be biexponential at 4 K. A variety of experiments led us to conclude that the excited cis-keto conformer must undergo vibrational or conformational relaxation on the ~10-ps time scale. This is a novel observation because energy decay from vibrational levels of large molecules is normally thought to be a much faster process.

Equation 1 shows that SA may undergo several different torsional motions. Torsional relaxation naturally occurs on the picosecond and longer time scales in fluid environments, and might possibly influence the decay rates even in frozen solutions. Torsional relaxation in SA is complicated owing to the existence of at least three different torsional normal modes: two rotations about different C–N single bonds and rotation about the C_1–C_7 bond. We have now investigated the decay kinetices of a similar molecule, 2-(2-hydroxyphenyl)benzothiazole (HBT), which has only the C_1–C_7 torsional degree of freedom shown in Scheme I.



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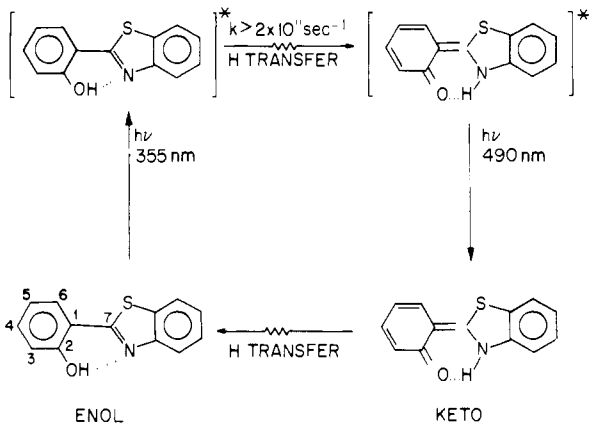
Scheme I



2-(2-HYDROXYPHENLY) BENZOTHIAZOLE PHOTOTAUTOMERIZATION

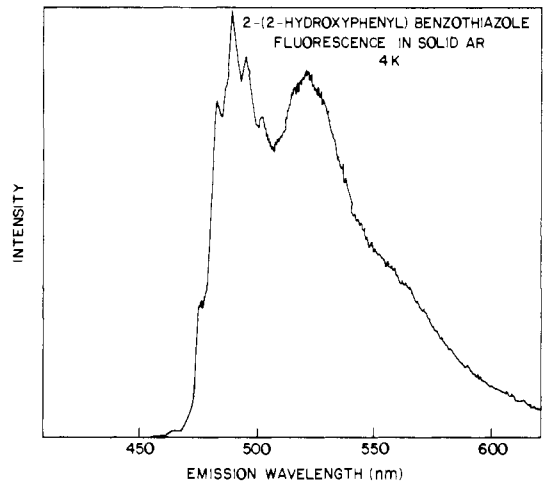


Figure 1. Total emission spectrum (0.2-nm resolution) of an HBT in argon matrix excited by nanosecond pulses at 361 nm.

The relaxation data of HBT might be expected to be different than the SA 4 K 10-ps kinetics if we assume that the transient observed represents torsional relaxation. To examine this effect, we measured that fluorescence kinetics of HBT over a wide range of temperature (4–300 K) and time (5–5000 ps).

Experimental Section

The nanosecond fluorescence apparatus and experimental techniques have been described in detail previously.[2,3] The picosecond apparatus and data processing system are similar to the one used and described by us in earlier papers.[1,4] Briefly, a hybrid Nd^{3+}/glass oscillator, Nd^{3+}/YAG amplifier laser generated ~5-ps, 3-cm^{-1} pulses at 1061 nm. After passing through two KDP crystals, a single 355-nm pulse is formed which is used for excitation. The fluorescence kinetices in specific wavelength ranges are obtained by an Imacon 675 Photochron II streak camera. The time width of the excitation pulse is first deconvoluted before analyzing the transient behavior. Ten or more shots are averaged to produce a single experimental trace. HBT was purchased from Frinton Laboratories and recrystallized twice from methylcyclohexane with minimum boiling ethanol.

Results

A. Emission Spectra. The 490-nm fluorescence observed after excitation of the enol ground state of HBT has been previously assigned to emission originating from a cis-keto excited $^1\pi$–π^* state.[5] Emission from HBT excited by a 361-nm pulse in a 4 K Ar matrix is shown in Figure 1. This spectrum shows greater vibronic structure than does the equivalent SA spectrum. As in SA, there are two principal bands indicating a short progression in some ≃1400-cm^{-1} mode. In "rigid" HBT, however, we observe that the first band is resolved into a five- or six-member progression in some low-frequency ~270-cm^{-1} mode. This observation indicates that the transition is accompanied by a large change in geometry along a low-frequency normal mode. In general, this spectrum exhibits a rather sharp blue edge which implies that we observed an allowed Franck–Condon transition with respect to the normal modes which participate in the enol–keto isomerization. This observation implies that the fluorescence terminates in a stable keto local minimum in the electronic ground state. Richey and Becker have made a similar observation with respect to SA fluorescence.[6]

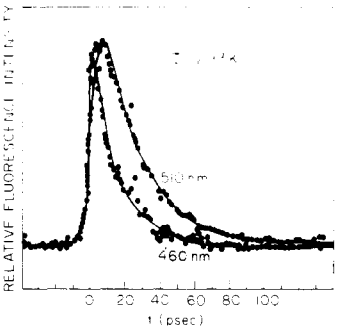


Figure 2. Time- and wavelength-resolved emission traces (355-nm excitation) of HBT (~10^{-4} M) in diethyl ether at 510 ± 5 and 460 ± 5 nm. The solid line computer fits are described in the text.

Table I. Lifetime Dependence of Long-Lived Emission Component on Viscosity

solvent	lifetime, ps	viscosity, cP
ether	23	0.23
isopentane	84	0.223
methylcyclohexane	145	0.729
1:1 isopentane/methylcyclohexane	110	

B. 293–200 K Fluorescence Kinetics. At 293 K in diethyl ether solution, HBT exhibits the wavelength-dependent fluorescence kinetics shown in Figure 2. In the region of 505–515 nm, a single transient occurs with a pulse limited rise time $\tau_r < 5$ ps and a decay time $\tau_f = 23 \pm 3$ ps. Between 455 and 465 nm, however, two fluorescing transients are observed. The strongest fraction of the emission intensity is pulse limited with respect to both rise time and fall time. There is, however, a weaker emission with a τ_f = 23 ps. The lifetime τ_f was found to be sensitive to solvent at room temperature, varying, as shown in Table I, by a factor of about 5 from ether to methylcyclohexane. It was also determined that τ_f increases by about a factor of 2 from isopentane to the more viscous methylcyclohexane.

The room temperature emission decay characteristics differ somewhat from those of SA, in that the solvent dependence of τ_f was less pronounced in SA. In addition, in SA we did not observe a pulse limited transient superimposed upon the τ_f decay.

We have observed the temperature dependence from 200 to 293 K of the total fluorescence decay in isopentane. As shown in Figure 3, the decay time increases rapidly and becomes nonexponential below room temperature. In all four panels of Figure 3, the time-resolved fluorescence can be fit by a sum of two exponentials. For purposes of comparison, Figure 4 shows the single exponential decay of anthracene fluorescence obtained by the streak camera under identical conditions.

In an aprotic solvent like isopentane, HBT is in an intramolecularly hydrogen bonded conformation.[5] Therefore, in such

(2) A. Baca, R. Rossetti, and L. E. Brus, *J. Chem. Phys.*, **70**, 5575 (1979).
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(4) P. F. Barbara, L. E. Brus, and P. M. Rentzepis, *Chem. Phys. Lett.*, **69**, 447 (1980).
(5) R. Nakagaki, T. Kobayashi, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **51**, 1671 (1978).
(6) W. F. Richey and R. S. Becker, *J. Chem. Phys.*, **49**, 2092 (1968).

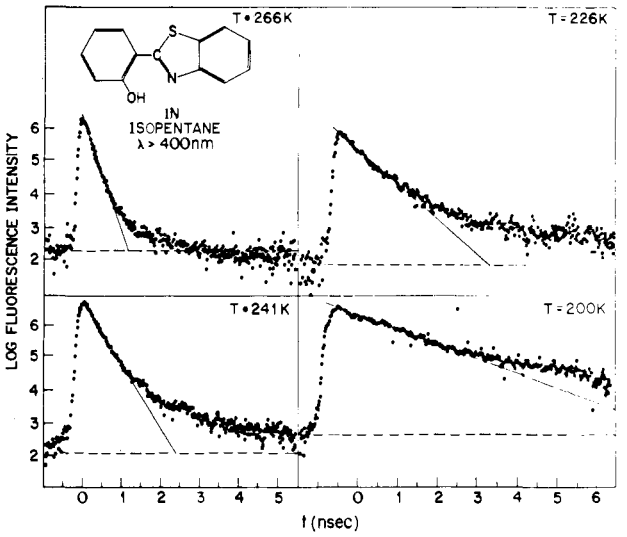

Figure 3. Time-resolved emission traces (355-nm excitation) of HBT ($\sim 10^{-4}$ M) in isopentane. The temperatures (±2 °C) were determined by a chromel–alumel thermocouple inserted in the sample near the region of excitation.

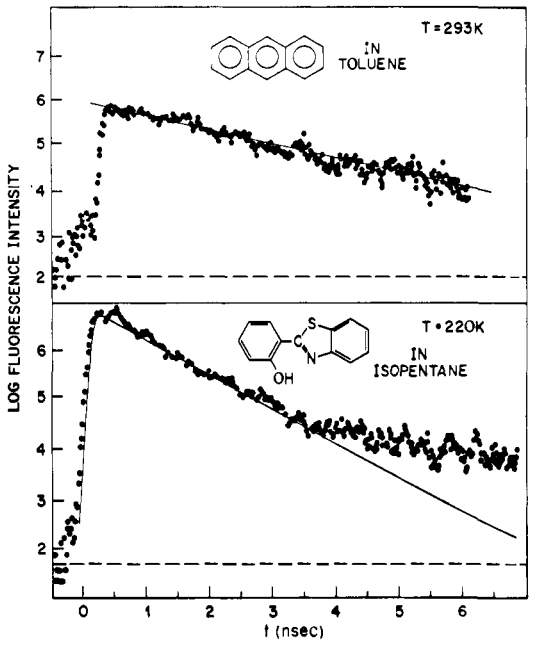

Figure 4. A comparison of the time-resolved fluorescence curve (355-nm excitation) of a dilute solution of anthracene with that of HBT ($\sim 10^{-4}$ M) in isopentane (220 K). A biexponential decay is clearly visible for HBT.

solvents only this conformation of the molecule is excited by 355-nm light. This fact simplifies the kinetic analysis, because different conformers can have different excited-state kinetics.[7] The fluorescence data indicate that there are two (or possibly more) different cis-keto species fluorescing in the excited state on the time scale of hundreds of picoseconds. Without further independent evidence it is not possible to state whether these two species decay independently or are sequential transients. Since the fluorescent lifetime is on the order of 5 ns, we can conclude that the dominant decay mechanism is by one or more radiationless processes.

The decay curves of the above processes were fitted to the sum of two exponentials labeled I (faster) and II (slower), and the lifetimes obtained from these plots follow the Arrhenius behavior demonstrated in Figure 5. The Arrhenius activation parameters appear in Table II for both triacetin and isopentane solvents.

(7) P. J. Wagner and C. P. Chen, *J. Am. Chem. Soc.*, **98**, 239 (1976).

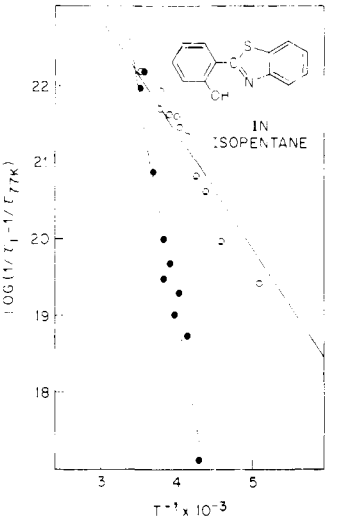

Figure 5. An Arrhenius plot for radiationless processes I and II. The temperature-dependent lifetime for process I was calculated from a linear fit of the logarithm of the fluorescence intensity vs. time in the region of 0 ps to $\sim 1.0\tau_{1/2}$, while the lifetime for process II was calculated from the region $1.5\tau_{1/2}$ to $2.5\tau_{1/2}$. At low temperature, <50 K, identical lifetimes (~ 5 ns) were observed in both time regions.

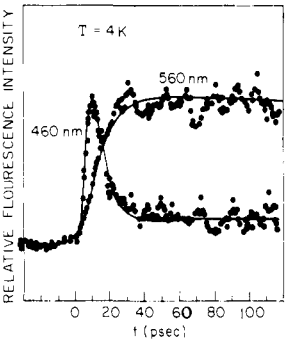

Figure 6. Time- and wavelength- (±5 nm) resolved fluorescence curves (355-nm excitation) for HBT in a frozen ether solution ($\sim 10^{-5}$ M).

Table II. Arrhenius Parameters for the Short-Lived (I) and Long-Lived (II) Excited State Species of HBT

solvent	E_A, kcal/mol[1]	A	transient
isopentane	4.0 ± 0.3	6.6×10^{12}	I
isopentane	11.4 ± 1.5	6.1×10^{17}	II
triacetin	14.5 ± 3	$\sim 10^{20}$	I
triacetin	13.5 ± 3	$\sim 10^{20}$	II

C. $T < 200$ K Bimodal Transient Kinetics. Below ~ 100 K the two decay lifetimes become long and merge into a single exponential decay with a time constant of $\simeq 5$ ns. In this range the contribution of the high-temperature radiationless transition to the emission process is negligible. However, at low temperature a different transient behavior was observed during the first few picoseconds of the fluorescence. Figure 6 shows the wavelength-resolved behavior for HBT in ether. The 560–600-nm emission appears with a rise time of 7 ± 2 ps followed by a nanosecond decay. The 460 ± 5 nm fluorescence reveals a bimodal behavior: a short-lived component A with pulse-limited rise time, $\tau_r < 5$ ps and $\tau_f = 7 \pm 2$ ps, and a long component B exhibiting τ_f in the nanosecond region. Detection of the rise time on the B component is hindered by the decay of A because, as made evident in Figure 6, the prompt fluorescence is dominated by component A at 460 nm, while only B appears in the range 560–600 nm. We find that at intermediate wavelengths the emission kinetics are composed of the sum of components A and B with their relative intensities varying with wavelength. These results are unchanged when the phenolic proton is replaced with a deuteron.

These observations are very similar to our previous SA data.[1] In that paper, it was shown that A and B represent sequential

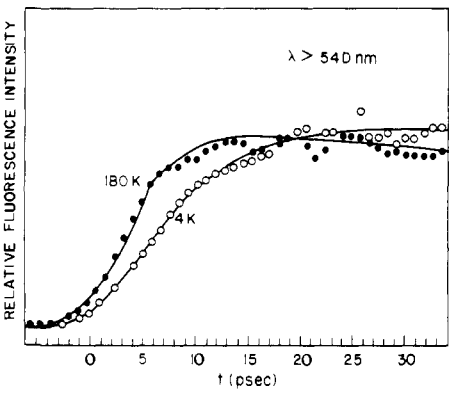

Figure 7. Time- and wavelength- (540–600 nm) resolved fluorescence curves for a frozen solution ($\sim 10^{-5}$ M) of HBT in ether at 180 and 4 K. The computer-generated curves are described in the text.

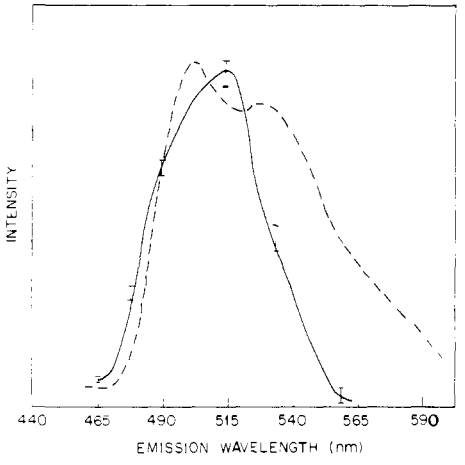

Figure 8. A time-unresolved fluorescence spectrum of a frozen solution ($\sim 10^{-5}$ M) of HBT in ether at 4 K (----); fluorescence spectrum of component A derived from the low-temperature time- and wavelength-resolved fluorescence as described in the text (–).

excited transient species produced by excitation of isolated enol monomers. The dynamical process A ⇝ B was concluded to represent vibrational or conformational relaxation in the $^1\pi$–π^* excited singlet state. Our present data show that the dynamics are essentially the same for HBT, which has a similar enol → keto chromophore, yet one C_1–C_7 bond which contributes to torsion. In HBT the interconversion in ether solvent occurs within 7 ± 2 ps, while in SA the interconversion occurs within 9 ± 2 ps.

Figure 7 shows the temperature dependence of the B component rise time at wavelengths longer than 540 nm. The τ_r = 7 ± 2 ps value observed at 4 K is clearly different than the pulse-limited τ_r < 5 ps value measured at 180 K.

The 4 K emission spectrum of the A component compared with that of the B component is presented in Figure 8. The B component is a time-averaged emission spectrum recorded in a HBT–diethyl ether matrix. This spectrum is dominated by the B component because of the very long (nanosecond) lifetime as compared with that of the A component. The spectrum of A is obtained by using the relative initial intensities from the time-resolved data, such as in Figure 6, for the intensity of A emission at a specific wavelength compared with B emission. From the data it is evident that the A spectrum is *narrower* and concentrated to shorter wavelengths than the B spectrum.

The rate of conversion of A to B, determined by the fall time of the A component, has been measured in various 4 K frozen solvents. The time constants measured in various solvents follow: diethyl ether, 7 ± 2 ps; isopentane, 8 ± 3 ps; decalin, 15 ± 4 ps; nonadecane, 15 ± 4 ps; triacetin, 15 ± 4 ps; glycerol, 31 ± 5 ps. In the first four examples, the decay time increases slightly with increasing room temperature viscosity for these aprotic solvents. We recognize that extrapolating the room temperature viscosity to frozen 4 K solutions is ambiguous. The viscosity, however, is expected to give some idea of the relative hardness of the solution at 4 K. Glycerol in fact gives the longest lifetime and has the highest viscosity. However, the interpretation of the glycerol experiment is more complex because of the possible hydrogen bonding between the solvent and HBT. It may be that the variation of lifetime with solvent in these experiments is controlled by factors other than viscosity.

We have investigated another derivative of SA, salicyliden-2-aminonaphthalene. The measured A to B conversion time of this molecule in ether at 4 K was 8 ± 2 ps. The dynamic process we describe here appears to be dependent upon the chromophore which experiences the keto–enol conversion and rather insensitive to the nature of the remainder of the molecule.

Discussion

Our experimental results reveal that the excited-state relaxation of HBT in solution occurs on three different time scales. The slowest processes occur on the time scale of $\sim 10^2$ ps at temperatures of 200–293 K in fluid solutions. We have shown that these relaxation processes are strongly dependent upon solvent and temperature, and have negligible quantum yields at $T < 100$ K. The second time scale involves the A ⇝ B conversion, which we were able to time resolve as 7 ± 2 ps in ether at 4 K. At higher temperatures this process becomes pulse limited, i.e., <5 ps. The fastest process is attributed to the intramolecular proton transfer producing the cis-keto tautomer from the Franck–Condon enol tautomer. In both HBT and SA, this tautomerization occurs within 5 ps at $T \geq 4$ K in a number of solvents.

The cis-keto excited state formed by proton transfer probably has substantial vibrational excitation in the bonds involved in the tautomerization. It also may not be torsionally relaxed. Our lack of any knowledge concerning the shape of the torsional potential energy surface in the excited state of HBT prevents us from proposing a quantitative mechanism for this decay process and assignments for the slower relaxation processes. Nevertheless, we can propose a reasonable physical interpretation of our observations.

It is well known that excited state large amplitude torsional motion in substituted stilbenes and similar sterically hindered molecules is strongly dependent upon solvent viscosity and temperature.[8-10] In the $^1\pi$–π^* excited states of these molecules, the equilibrium torsional angles can be substantially rotated from their positions in ground electronic states. In such cases, excited state torsional relaxation induces a pronounced red shift of the emission as relaxation proceeds. The fluorescence quantum yield is often strongly dependent on the angle, and thus the relaxed excited state has a different quantum yield, and lifetime, than the vertical Franck–Condon excited state. In low-temperature frozen solutions, these experiments show that, as expected, such large-amplitude motions are entirely suppressed.

Our 200–293 K, 10^2–10^3-ps radiationless decay lifetimes show Arrhenius parameters that are strongly dependent upon solvent. Therefore we propose that these decay processes involve angular motion about the C_1–C_7 bond in the excited state. The Arrhenius parameters in some sense must measure a temperature-dependent local viscosity; however, they do not provide any measure of the height of an intramolecular barrier for internal rearrangement.

This idea is supported by the very high preexponential factors calculated and presented in Table II. As the temperature continues to increase, the rates must reach a plateau and not continue to increase as predicted by the Arrhenius equation. It does not seem possible to extract information from our kinetic data concerning the shape of the intramolecular potential energy surface. We believe that, since the room temperature fluorescence is not strongly Stokes shifted from the low-temperature fluorescence, the equilibrium angle must be about the same in the excited- and

(8) G. Fischer, G. Seger, K. A. Muszkat, and E. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1969 (1975).
(9) J. Kordas and M. A. El-Bayoumi, *J. Am. Chem. Soc.*, **96**, 3043 (1974).
(10) H. H. Klingenberg, E. Lippert, and W. Rapp, *Chem. Phys. Lett.*, **18**, 417 (1973).

ground-state cis-keto forms. Our kinetic data do imply, however, that there must be a strong variation in radiationless transition rate with angle in the excited state of HBT.

In various frozen environments at 4 K, this large angle torsional motion is negligible on the time scale of the $^1\pi-\pi^*$ excited state fluorescence. Nevertheless, one might envision a small amplitude C_1-C_7 torsional relaxation into some sort of local minimum on the potential-energy surface. It is known, for example, that some torsional relaxation occurs in the excited state of biphenyl isolated in solid neon and argon at 4.2 K.[2] In this regard it is useful to compare our SA and HBT data for the A $\rightsquigarrow$ B transient. As previously discussed, the data are remarkably similar with only small spectral shifts and changes in rates. Theoretically we might expect the torsional potential energy surfaces and moments of inertia to be different in the two cases, as SA has three, presumably coupled, torsional motions while HBT has only one well-defined torsion of C_1-C_7. The similarity of the HBT and SA results, and the very weak "viscosity" dependence for HBT observed in Table I, seems to support the idea that torsional relaxation does not principally influence the A $\rightsquigarrow$ B transient behavior at 4 K.

Very recently we have observed that similar blue-shifted transients occur on the $\simeq$10-ps time scale in the lowest $^1\pi-\pi^*$ excited states of anthracene and tetracene in 4 K frozen solutions.[11] Like SA and HBT, these molecules have relaxed fluorescence spectra with relatively sharp blue edges. Unlike SA and HBT, however, excited-state anthracene and tetracene are planar aromatic compounds without known torsional normal modes. In these latter two molecules, we conclude that we have directly time resolved the excited state vibrational energy redistribution and/or relaxation into the environment.

In view of these arguments, we feel that the A $\rightsquigarrow$ B transient behavior in both HBT and SA appears to represent a direct measure of excited state vibrational energy redistribution and/or relaxation. As previously mentioned, the nascent cis-keto tautomer produced by proton transfer probably has appreciable excess vibrational energy in the bonds involved in the tautomerism. Unfortunately, there are no quantitative structural or thermodynamic data on the relative stability of the keto and enol tautomers. This initial distribution will evolve intramolecularly and ultimately relax into the local environment, as a function of time. These processes will affect the emission spectrum, and it may be that our ability to readily detect them in SA and HBT is related to the unusually sharp emission spectra (Figure 1).

These results, which should also be examined in molecules having better spectral resolution and firm excited state vibrational assignments, may have general implications in the field of picosecond molecular dynamics. In many important biological and chemical systems, the electronic spectra are so broad as to preclude any clear measurement of vibrational excitation based upon the shape of the electronic spectra. If a chemical reaction, isomerization, or electron or proton transfer occurs in an excited state, one does not normally know whether the process occurs from a vibrationally relaxed or "hot" initial state. We now have the first data which suggest that relaxation in large organic species occurs on the $\sim$10-ps scale in low-temperature aprotic solutions.[11] It is possible therefore that some processes which have time constants much faster than $\sim$10 ps might initially proceed from a vibrationally "hot" electronic state.

(11) P. F. Barbara, P. M. Rentzepis, and L. E. Brus, *J. Chem. Phys.*, in press.

(12) After submission of this manuscript, an interesting and rather indirect measurement of room temperature vibrational thermalization has been reported: K. J. Choi and M. R. Topp, *Chem. Phys. Lett.*, **69**, 441 (1980).

Ethylenediamine and Aminoacetonitrile Catalyzed Decarboxylation of Oxalacetate

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Abstract: Monoprotonated ethylenediamine (ENH^+) and aminoacetonitrile (AAN) are highly effective catalysts for the decarboxylation of oxalacetate (OA^{2-}) with the latter amine showing 50% faster rates. The mechanisms of the reactions are the same as that earlier proposed by Guthrie and Jordan[4] from studies on the decarboxylation of acetoacetate (AA^-): amine and keto acid react to form ketimine which either decarboxylates or is competitively converted to enamine. We find that a proton is required to effect decarboxylation, but it also promotes enamine formation, the more so the greater basicity of the parent amine. Owing to this side reaction, the more basic amines tend to show lower catalytic activity with respect to decarboxylation. A second effect also contributes to the high activity of AAN: even though the rate constants for imine formation appear to be roughly similar with AAN and ENH^+, proton catalysis has a much larger net influence on the AAN rate because changes in $[H^+]$ are not canceled by inverse changes in [amine]. 4-Ethyloxalacetate forms an adduct with ENH^+ that has a considerably greater enamine content and a higher stability than its OA^{2-} analogue. These differences in substrate behavior must be taken into account when esters are used as models for the parent keto acids in these reactions. Comparison of our results with those previously published for OA^{2-} decarboxylation catalyzed by a partially quaternized poly(ethylenimine) suggests that OA^{2-} is predominantly bound to the quaternary amine sites but decarboxylation likely proceeds via a Schiff-base mechanism.

Amine-catalyzed decarboxylation of β-keto acids has aroused interest for many years[1-5] not only because the reactions themselves display interesting chemistry, but also because they are involved in enzymic decarboxylation processes.[6-9] The catalytic mechanism has been established to proceed via Schiff-base formation with the active species either being the protonated imine[1b,10] or one which has a labile proton so situated that it can be transferred to the nitrogen atoms as CO_2 loss occurs.[2] The carboxylic acid

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