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Energetics of Intramolecular Photoassociation in 3-Phenyl-1-(dimethylamino)propane in the Vapor Phase

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Abstract: The photophysical properties of 3-phenyl-1-(dimethylamino)propane (I) are reported in the vapor phase under collision-free conditions. The absorption spectrum is interpreted as the sum of noninteracting phenyl and amino chromophores. Excitation at 265 nm (near the O–O band of the phenyl chromophore) produces a relatively broad, structureless emission (λ_{max} = 300 nm) which is assigned as fluorescence from the intramolecular exciplex in I. The lifetime and quantum yield are 28 ns and 0.08, respectively. The formation rate constant of the exciplex is estimated to be $\gtrsim 3 \times 10^9$ s^{-1}, considerably faster than that of the excimer in the analogous diamine. The band position is in very good agreement with the extrapolation of solution-phase data. Excitation at high energies (238 and 228 nm), producing the locally excited amino chromophore, results in weak emission at 289 nm which closely resembles that of an *N*,*N*-dimethylalkylamine; quantum yields are 0.008 and 0.003 m, respectively. Multicomponent fluorescence decay curves are observed which imply that feedback from the nascent exciplex produced via amino excitation takes place. The effects of collisional relaxation by using 2-methylbutane are also described. Pressures between ca. 200 and 400 torr are required to produce exciplex emission with λ_{exc} = 238 and 228 nm. At these higher pressures, the fluorescence decay of the exciplex is independent of excitation wavelength between 265 and 228 nm. The fluorescence excitation spectrum of the exciplex shows a fall off below ca. 250 nm under isolated conditions; with the addition of ca. 400 torr of buffer gas partial restoration of excitation spectrum vis-à-vis the absorption spectrum is observed.

Photophysical studies of bichromophoric molecules have captured the attention of many investigators for several years.[1] The particular appeal of such molecules is that the selective deposition of electronic-excitation energy can be accomplished in (at least) one of the chromophores. The interaction between the pendant groups can then be studied kinetically, spectroscopically, chemically, etc. If the two chromophores being borne by the molecular framework are noninteractive in the electronic ground state (as evidenced, e.g., by the electronic absorption or photoelectron spectrum), specific interactions may nevertheless take place between these groups consequent to photoexcitation of one. In some cases such interactions are not observed, or are seen in very low efficiency, in the respective *inter*molecular systems. Examples of such intramolecular specificity are provided by 1,3-disubstituted propanes in which photoassociation, namely excimer (or exciplex) formation and emission, can be studied, but where *inter*molecular excimer (or exciplex) emission may be significantly less efficient. For example, excimer emission is readily observed in both 1,3-diphenylpropane[2] and 1,3-bis(dimethylamino)propane[3] in dilute solution, while such emission is discernable only in neat toluene[4] and is not observed in highly concentrated *N*,*N*-dimethylethylamine[5] at ambient temperature.

Similarly, while the fluorescence spectrum of the heterobichromophoric molecule, 3-phenyl-1-(dimethylamino)propane (I), is dominated by the intramolecular exciplex in solution,[6] the intermolecular exciplex between appropriate alkylbenzene and trialkylamine molecules is not observed in nonpolar solution at ambient temperature.[7] DeSchryver and co-workers have reported extensive studies of the photokinetics and spectroscopy of I and related compounds.[6,8] They have demonstrated that at ambient temperatures, exciplex emission and emission efficiencies of I are large enough so that virtually only exciplex emission is observed in isopentane. Furthermore, this emission is seen irrespective of whether the phenyl or amino chromophore is initially excited. On the basis of the solvent dielectric strength dependence of the exciplex emission maximum, a dipole moment of 14.5 D was attributed to the intramolecular exciplex of I.[6]

Lichtin et al. have reported multiphoton ionization studies of I in the vapor phase, comparing the fragmentation patterns as well as ionization efficiencies of I with those of toluene and trimethylamine.[9] They concluded that rapid intramolecular energy transfer occurs subsequent to preparing the locally excited (LE) state of either chromophore.

While a few studies of intramolecular vapor-phase exciplex emission have been reported, the systems all possessed the anthracene moiety as the electron-acceptor species.[10-14] Moreover, these systems all possessed donor groups which have LE states considerably higher in energy than anthracene (e.g., naphthyl, pentamethylbenzene, and *N*,*N*-dimethylanilino function) and which cannot be selectively photoexcited. As a result, photoexcitation was confined to the anthracene chromophore in these studies.

In this paper, the photophysical and spectroscopic properties of I are reported in the isolated vapor phase. Because of the absorption characteristics of the two chromophores in I, significant separability in initial photoexcitation of the phenyl or amino group is possible. Also, since each chromophore is emissive, the nature of energy relaxation subsequent to the photoproduction of either LE state can be probed. In addition, the behavior of the system can be examined between the limits of collisional isolation and complete collision-induced vibrational-energy relaxation.

Another important aspect of the linked phenylamino compound is that efficient intermolecular energy transfer between photoexcited amine and benzene has been shown to take place in

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(10) M. Ito, T. Kotani, and Y. Hanashima, *Chem. Phys. Lett.*, **1980**, *75*, 307.

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(13) M. Ito, Y. Hanashima, N. Wada, and I. Hanazaki, *Bull. Chem. Soc. Jpn.*, **1983**, *56*, 1944.

(14) P. M. Felker, J. A. Syage, W. R. Lambert, and A. H. Zewail, *Chem. Phys. Lett.*, **1982**, *92*, 1.

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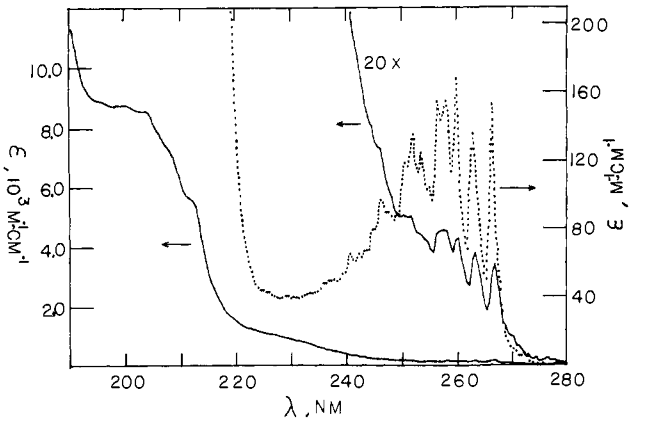

Figure 1. Absorption spectra of I (—), left-hand axis, and ethylbenzene (•••), right-hand axis, in the vapor phase at 296 K.

nonpolar solution by Halpern and Wryzykowska.[15] They also showed that moderately efficient energy transfer between electronically excited benzene and amine also occurs. In I, where, because of the favorable geometrical constraint of the two chromophores, the exciplex becomes a kinetically important species in electronic relaxation, the question of intramolecular electronic energy transfer in relation to exciplex formation thus becomes relevant.

Results and Discussion

The vapor-phase absorption spectrum of I, shown in Figure 1, can be interpreted as the sum of the absorption spectra of the individual chromophores. The same conclusion was reached regarding the absorption in nonpolar solution by Van der Auweraer et al.[6] In the vapor phase, the O–O band of the ^1L_b transition of the alkylbenzene group appears at 266.8 nm, close to the analogous O–O band of ethylbenzene (266.5 nm) whose absorption spectrum is also indicated in Figure 1. The additional diffuseness observed in the vibronic bands of I relative to ethylbenzene (especially in the higher members) is due both to the increase in the number of vibrational modes arising from the $(CH_3)_2N(CH_2)_3$ substituent and to the onset of the (unstructured) $3s \leftarrow n_N$ absorption of the amino chromophore. The latter is especially noticeable at wavelengths below ca. 250 nm.

The shoulder at 230 nm is a feature which is characteristic of the absorption spectra of trimethylamine (and, in fact, *N*,*N*-dimethylalkylamines as well) and is associated with the Franck–Condon maximum of the $3s \leftarrow n_N$ transition in the amine. Is should be noted that at this wavelength, the absorption of ethylbenzene shows a minimum ($\epsilon_{230} = 37$ M^{-1} cm^{-1}); the measured ϵ_{230} for I, 1.0×10^3 M^{-1} cm^{-1}, is comparable with that of an amine prototype, *N*,*N*-dimethyloctylamine (1.3×10^3 M^{-1} cm^{-1}). It can thus be presumed that at 230 nm, optical excitation results primarily in the LE state of the amino chromophore in I. Finally, it should be noted from Figure 1 that the shoulder observed at ca. 214 nm in I represents the maximum of the $3p \leftarrow n_N$ transition(s) of the amino group (seen at 202 nm in *N*,*N*-dimethyloctylamine vapor); the apparent shift to 241 nm in I is probably due to the sharply rising absorption of the phenyl chromophore in that region.

Phenyl Excitation. Figure 2 illustrates the fluorescence spectra of I at a (vapor) temperature of 295 K and a vapor pressure of 0.18 torr. For $\lambda_{exc} = 265$ nm (about 250 cm^{-1} above the O–O band), the spectrum is relatively broad and structureless having λ_{max} at ca. 300 nm. This spectrum is quite unlike that of ethylbenzene and *N*,*N*-dimethyloctylamine. The fluorescence spectrum of the former is structured having a maximum at 280 nm. Moreover, the fluorescence intensity of ethylbenzene at 300 nm is only ca. 0.32 of the maximum intensity at 280 nm. The fluorescence of I ($\lambda_{exc} = 265$ nm) is thus attributed to emission from the intramolecular exciplex between the amino and phenyl groups. Because of the very low ε value of the amino chromophore at 265 nm,[16] excitation at this wavelength primarily produces LE alkylbenzene in I. Fluorescence from *N*,*N*-dimethyloctylamine with $\lambda_{exc} = 265$ nm under conditions in which the amine pressure is comparable with that of I is significantly weaker than the exciplex emission seen in I. Thus any direct excitation of the amino chromophore in I at 265 nm either results in LE amine emission hidden by the exciplex or in the formation of the exciplex.

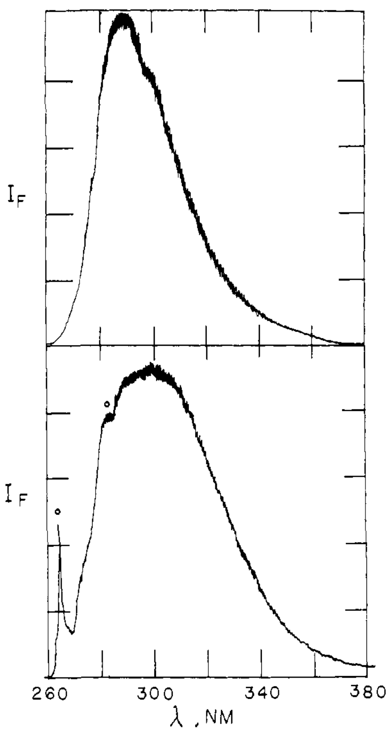

Figure 2. Emission spectra of I vapor at 296 K. The upper spectrum is obtained with $\lambda_{exc} = 228$ nm and the lower with $\lambda_{exc} = 265$ nm. For the lower spectrum, the circles indicate scattered light.

Because of the presence of scattered light, emission from the LE phenyl chromophore cannot be identified with certainty (see Figure 2). Nevertheless, one can conclude that if alkylbenzene fluorescence is present, its contribution to the total emission spectrum is small. Likewise, in solution (e.g., *n*-hexane or isopentane), emission from the phenyl chromophore at ambient temperature is very weak, if present at all, in relation to that of the intramolecular exciplex.[6,8]

With the addition of 2-methylbutane as a collisional relaxer, the emission spectrum of the exciplex shifts from $\lambda_{max} = 300$ to 310 nm (at 415 torr). There is also a concomitant narrowing of the exciplex emission. The spectral width of the exciplex was determined as

$$\tilde{\nu}_{hwhm} = \tilde{\nu}_{max} - \tilde{\nu}_{1/2}$$

where $\tilde{\nu}_{1/2}$ is the wavenumber position at half-maximum intensity as measured at *lower* energy. This approach was necessary because of the presence of scattered light and possibly alkylbenzene emission on the high-energy side of the exciplex emission spectrum (see Figure 2). $\tilde{\nu}_{hwhm}$ values for I are 3000 and 2400 cm^{-1} with 0 and 415 torr of added 2-methylbutane, respectively. These values compare with $\tilde{\nu}_{hwhm} = 2410$ cm^{-1} measured for I in *n*-hexane solution at 296 K.

It is interesting to consider whether the exciplex emission maximum observed in the collisionally relaxed vapor agrees with that predicted by the solvent polarity dependence in solution. Van der Auweraer et al.[6] have shown that $\tilde{\nu}_{max}$ for the exciplex in I is linear with the solvent polarity parameter, $(f - 1/2f')$, viz.

$$\tilde{\nu}_{max} = \tilde{\nu}_0 - \frac{2\mu^2(f - 1/2f')}{hca^3} \qquad (1)$$

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(15) A. M. Halpern and K. Wryzykowska, *Chem. Phys. Lett.*, **1981**, *22*, 82.

(16) For *N*,*N*-dimethylethylamine, ε(265) is ca. 0.5 M^{-1} cm^{-1}.

where $\tilde{\nu}_{max}$ is the observed exciplex maximum, $\tilde{\nu}_0$ is the "hypothetical" gas-phase emission frequency, and μ^2 and a are respectively the dipole moment of and the charge separation in the solvated exciplex. $f = (\epsilon - 1)/(2\epsilon + 1)$ and $f' = (n^2 - 1)/(2n^2 + 1)$, ϵ and n being the dielectric constant and refractive index of the solvent, respectively. Their data provided a value of μ = 14.5 D for an assumed a = 5 Å. The extrapolated value of $\tilde{\nu}_{max}$ to $(f - 1/2f') = 0$, i.e., $\tilde{\nu}_0$, as determined from their data[6] is ca. 32 200 cm^{-1} and compares very favorably with that now observed for I in the vapor, 32 300 cm^{-1}.

The above observations regarding the exciplex emission maximum and band width imply that the (D--a)* separation in the exciplex as well as the shape of the repulsive potential of ground state D--A in the vicinity of the separation are similar in the gas-phase and nonpolar solution; they also lend credence to the idea that the exciplex is bound primarily through an electrostatic mechanism.

In other instances where either intramolecular or intermolecular exciplex emission has been reported in the vapor phase, it has been observed that the exciplex emission maximum is blue shifted relative to the condensed phase.[10,17-21] In fact, Abbott et al. assumed the validity of eq 1 and deduced a value for μ for the intermolecular exciplex between 1,4-dicyanonaphthalene and 2,5-dimethyl-2,4-hexadiene by using the vapor-phase and solution values of $\tilde{\nu}_{max}$.[18] However, regarding the intermolecular 9,10-dicyanoanthracene–1,2-dimethoxybenzene exciplex, Hirayama and Phillips[19] observed a great discrepancy between $\tilde{\nu}_{max}$ measured in the vapor phase and $\tilde{\nu}_0$ implied in eq 1 (based on solution data of Eriksen and Foote[22]). Hirayama and Phillips argued that for this system, the solvent might induce structural changes in the exciplex, thus rendering eq 1 invalid.

The observation that the emission spectrum of I is dominated by the intramolecular exciplex, even when the absorbing chromophore (alkylbenzene) is excited near the O–O band (vide supra), requires some comment. It may be thought that since the formation of the exciplex is an activated process, in which a conformational transition takes place from an uncoupled state (e.g., trans,trans or trans,gauche) to a folded configuration (gauche$^{\pm}$, gauche$^{\mp}$), the initial production of the LE state of the alkylbenzene chromophore near its zero-point level may cause the entire molecule to lack sufficient energy to initiate the process. This complication has, in fact, been recently observed by Felker et al.,[14] who reported that 3-(4-(dimethylamino)phenyl)-1-(9-anthryl)-propane (II) when excited at the O–O band of the (lowest) anthracene transition in a jet-cooled beam, exhibited only LE anthracene fluorescence. Exciplex emission was observed only if sufficient excess energy was deposited in the anthracene chromophore. It should be pointed out that in their experiment, the entire molecule is vibrationally (and presumably rotationally) cooled consequent to the free expansion in the jet. Felker et al., in fact, have estimated that for a thermally equilibrated molecule at 300 K, the vapor-phase intramolecular exciplex formation rate constant in II would be ca. 1.6 × 10^9 s^{-1}. Interestingly, this is faster than the exciplex formation rate constant of II of 7 × 10^8 s^{-1} reported by Wang et al. in cyclohexane solution.[23]

In the study reported here, I is excited at ca. 250 cm^{-1} above the O–O band of the alkylbenzene transition. In addition, the molecule is under static cell conditions at 296 K. It is therefore not surprising in light of the above discussion that the dynamics of intramolecular exciplex formation are fast relative to the intrinsic decay rate of the LE state of the alkylbenzene chromophore.[24] Moreover, one can conclude that rapid intramolecular energy flow occurs between the $(CH_3)_2N(CH_2)_3$ residue (most of which is thermally equilibrated at 300 K) and the spectroscopically cooled phenyl group.

The fluorescence decay of I (with λ_{exc} = 267 nm), analyzed at 300 nm, can be adequately represented as a single exponential component having a lifetime of 28 ns. There is no apparent component having a negative amplitude which would correspond to the "feed in" of the exciplex emission. When analyzed at 340 nm,[25] however, a decay curve represented as

$$I_f(t) = \exp(-t/28) - 1.0 \exp(t/0.3) \qquad (t \text{ in ns})$$

provided a satisfactory χ^2 value (1.3). An approximately equally good fit could be obtained for a single-component analysis (28 ns), but only with the inclusion of an abnormally large positive convolution shift. While the negative component cannot be characterized with certainty (i.e., better than 0.3-ns resolution), a lower limit for the intramolecular exciplex formation rate constant, k_{EM}, of ca. 3 × 10^9 s^{-1} can be established. The above observations also pertain to a similar study of I in the presence of ca. 400 torr of 2-methylbutane.

Van der Auweraer et al.[8] showed that in isopentane solution at low temperatures (e.g., 140 K) the fluorescence spectra of I could be "resolved" into LE alkylbenzene and exciplex components. On the basis of a detailed photokinetic analysis of this system, it has been postulated that exciplex formation could ensue from two different ground-state conformations. These differ in terms of the magnitude of the activation barriers and entropies involved in intramolecular exciplex formation; hence, they are called "fast" and "slow" starting conformations. Van der Auweraer et al.[8] reported frequency factors and activation energies for these formation rate constants, k_f and k_s, as 6 × 10^{11}; 7.5 × 10^9 (s^{-1}) and 12.8; 11.0 (kJ/mol), respectively. Using these data, one can obtain probable lower limits for the exciplex formation rate constants in the vapor phase. Presumably, the activation energies for folding together of the pendant groups to form the exciplex from the "slow" and "fast" starting conformations will be lower in the vapor phase relative to isopentane solution owing to the absence of neighboring solvent molecules. Such analysis for 296 K yields k_f = 3.3 × 10^9 s^{-1} and k_s = 8.6 × 10^7 s^{-1}.

While the very close agreement of the observed lower limit of the "build-in" rate constant for excimer emission in the vapor phase of ca. 3 × 10^9 s^{-1} with k_f may be fortuitous, it at least rationalizes the very fast exciplex formation rate constant of I in the vapor phase at 296 K. According to the kinetic scheme presented by Van der Auweraer et al., the actual formation rate of the exciplex would depend, of course, on the relative populations of "slow" and "fast" starting conformers.

A rather interesting comparison can be made between the vapor-phase exciplex-formation rate constant in I with that in the analogous diamine, 1,3-bis(dimethylamino)propane (III). For the latter compound, efficient excimer emission is observed at ambient temperature both in the vapor phase and in solution.[3,26] Ito et al. reported the results of a photokinetic study of III in the isolated vapor phase.[26] By applying the standard monomer-excited kinetic scheme,[27] they were able to assign a value of 2.8 × 10^8 s^{-1} to the intramolecular excimer formation rate constant, k_{EM}. This is more than an order of magnitude smaller than the analogous rate constant in I, ca. 3 × 10^9 s^{-1}.

If one assumes that the intrinsic dynamics (i.e., near O–O excitation) of intramolecular excimer (or exciplex) formation in I and III are governed by the requisite conformational transition statistics and barriers of the trimethylene linkage, it is puzzling that the two bichromophoric molecules differ so widely in their photoassociation rate constants.[28] One factor to consider is that

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[17] J. Prochorow, S. Okajima, and E. C. Lim, *Chem. Phys. Lett.*, **1979**, *66*, 590.

[18] G. D. Abbott, D. V. O'Connor, and D. Phillips, *J. Chem. Soc., Faraday Trans. 1*, **1981**, *77*, 1381.

[19] S. Hirayama and D. Phillips, *J. Phys. Chem.*, **1981**, *85*, 643.

[20] U. Lachmann, Ph.D. Dissertation, Georg August University, Göttingen, 1978.

[21] Y. Hanashima and M. Ito, *Bull. Chem. Soc. Jpn.*, **1981**, *54*, 3271.

[22] J. Eriksen and C. S. Foote, *J. Phys. Chem.*, **1978**, *82*, 2659.

[23] Y. Wang, M. Crawford, and K. B. Eisenthal, *J. Phys. Chem.*, **1980**, *84*, 2696.

[24] $1/\tau$ for ethylbenzene has been measured to be 1.58 × 10^7 s^{-1} at 0.5 torr and for O–O excitation, 267 nm.

[25] At this wavelength, emission from the phenyl chromophore is negligible.

[26] M. Ito, Y. Hanashima, and I. Hanazaki, *J. Phys. Chem.*, **1983**, *87*, 569.

[27] J. B. Birks "Photophysics of Aromatic Molecules", Wiley-Interscience, London, 1970.

for I, rapid intramolecular electron transfer between $N(CH_3)_2$ and Ph* may preceed the conformational transition to form the exciplex. If this were to occur, the conformational transition required for exciplex formation would be accelerated due to the electrostatic attraction between the (partially charged) pendant groups. Such a process has been described for a mechanism of intramolecular exciplex formation in polar solution; in nonpolar solution, however, exciplex formation is postulated as being rate determined by conformational dynamics rather than electron- (or charge) transfer dynamics.[29] It would seem therefore unlikely that in the vapor phase, exciplex formation would be accelerated in this way relative to excimer formation where preexcimer charge transfer is probably less important. Another factor to consider is the possibility that excimer and exciplex formation in the 1,3-disubstituted propanes is a complex kinetic process involving different starting conformers. Thus, while Van der Auweraer et al. considered this in their analysis of I in solution,[8] Ito et al. assumed a simpler kinetic scheme with respect to III in the vapor.[26] In addition, k_{EM} reported by Ito et al. was extracted by an analysis of the fast component obtained from the fluorescence decay of amine monomer; Ito et al. indicated that the rise time of excimer emission was very fast, and they attributed this to overlapping monomer and excimer emission. In the work reported in this paper, k_{EM} is inferred from the fast negative component observed in the exciplex decay; the separate fluorescence decay of the LE alkylbenzene chromophore could not be distinctly observed. Therefore the apparent discrepancy may be due, in part, to different experimental approaches and assumed kinetic models. The formation rate constant obtained by Ito et al. may, in fact, reflect the dynamics of both "fast" and "slow" starting conformers and thus appear to be smaller than k_{EM} which, as determined in this work, may be more sensitive to "fast" conformers. Further studies of the excimer formation rates and their activation parameters in III both in the vapor and in solution are needed to clarify this point.

Amine Excitation As was pointed out earlier, photoexcitation of I at shorter wavelengths than ca. 250 nm results in appreciable LE amino chromophore production. The emission spectrum of I (under isolated conditions) was determined at three additional wavelengths: 249, 238, and 228 nm.[30] When I is excited at either 238 or 228 nm, the spectrum assigned as exciplex emission is not observed; instead, the emission spectrum shown in Figure 2 for $\lambda_{exc} = 228$ is obtained. This spectrum closely resembles that of an amine prototype, *N,N*-dimethyloctylamine (as measured under isolated conditions), both with respect to the position of λ_{max} and the presence of the shoulder at ca. 300 nm. For this reason, it is assigned as fluorescence from the LE amino chromophore. For $\lambda_{exc} = 249$ nm, a spectrum intermediate between those shown in Figure 2 is observed.

Fluorescence decay curves spanning ca. 4 decades of intensity of these emission spectra (analyzed at 287 nm) were observed to be nonexponential; for $\lambda_{exc} = 283$ and 228 nm, three-component reiterative reconvolution fits were found to provide significantly smaller χ^2 values than for two-component fits. For example, at 238 nm, the decay curve thus obtained ($\chi^2 = 1.7$) is

$$I(t) = \exp(-t/2.0) + 0.18\exp(-t/6.4) + 0.013\exp(-t/40) \quad (t \text{ in ns})$$

and for $\lambda_{exc} = 228$ nm ($\chi^2 = 1.3$) it is

$$I(t) = \exp(-t/0.96) + 0.014\exp(-t/9.7) + 0.001\exp(-t/40) \quad (t \text{ in ns})$$

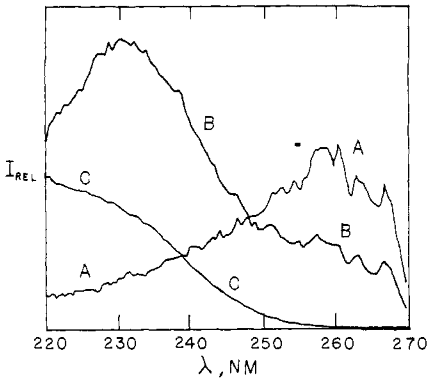

Figure 3. Corrected excitation spectra of I vapor monitored at 300 nm at 296 K. Spectrum A, no added 2-MB; spectrum B, in the presence of 415 torr of 2-MB; spectrum C, corrected excitation spectrum of *N,N*-dimethyloctylamine vapor at 296 K monitored at 287 nm, no added 2-MB; the pressure is 0.20 torr. Each spectrum is separately and arbitrarily scaled.

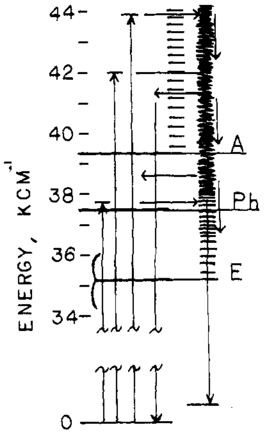

Figure 4. Energy-level diagram of I. The energy axis represents transition energy from the electronic ground state. The zero-point levels of the lowest excited states of the LE amino and alkylbenzene chromophores are denoted as A and Ph. E represents the exciplex ground state for which the estimate limits are shown. The three upward arrows indicate transitions effected by 265-, 238-, and 228-nm light, respectively. Other arrows symbolize coupling to the exciplex manifold, vibrational relaxation, feed-back to LE states, and emission.

The individual time constants obtained in these analyses are obviously a complicated function of the rate constants contained by an appropriate photokinetic scheme and are not considered at this time. An important observation to make is that for both decay curves, the fraction of the fastest component represented in the total decay curve is large, i.e., ca. 0.71 and 0.65, respectively, for the examples cited above. Thus, since at these excitation wavelengths the amino chromophore is the principal light absorber, one can associate the fastest (dominant) component with the LE amine which is quenched by the phenyl group.

It is important to point out that the fluorescence lifetime of N,N-dimethyloctylamine was found to be essentially constant (48 ns) between $\lambda_{exc} = 250$ and 230 nm in the isolated vapor phase. In addition, the fluorescence excitation spectrum of this amine, shown in Figure 3, follows its absorption spectrum over the common wavelength range studied. Thus one can conclude that, under collision-free conditions, the amino chromophore retains its high intrinsic emissivity.[31-33]

The failure to observe exciplex emission at these excitation wavelengths implies that if in fact the exciplex is formed via the LE amino chromophore, the nascent exciplex does not undergo efficient intramolecular vibrational relaxation, and thus decays via rapid dissociation into the LE amino and/or alkylbenzene

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(28) In the vapor phase, one can ignore the effects of solvent drag on the relative mobility of the pendant groups; therefore, the phenyl ring should be relatively more mobile in comparison with the case in solution.

(29) See, e.g., T. Okada, M. Migita, N. Mataga, Y. Sakata, and S. Misumi, *J. Am. Chem. Soc.*, **1981**, *103*, 4715 and references cited therein.

(30) These correspond to the useful emission lines of a medium-pressure Hg lamp.

(31) The fluorescence quantum efficiency of *N,N*-dimethyloctylamine was taken to be 1.0.

(32) Y. Matsumi and K. Obi, *Chem. Phys.*, **1980**, *49*, 87.

(33) C. G. Cureton, D. V. O'Connor, and D. Phillips, *Chem. Phys. Lett.*, **1980**, *73*, 231.

chromophores or, in addition, undergo es nonradiative decay. The energy-level diagram shown in Figure 4 illustrates these points. In this diagram, the O–O levels of the two chromophores are indicated, as is the estimated position of the intramolecular exciplex of I.[34] The levels populated at the three wavelengths used are also depicted. Vibrational levels for the exciplex and the LE states are schematically represented, as are vibrational relaxation, LE feedback, nonradiative, and radiative decay channels.

Relative to 265-nm excitation, consequent to which exciplex formation and emission are observed (vide supra), excitation at 238 and 228 nm deposits 4280 and 6120 cm^{-1} of additional internal energy, respectively. This is a significant amount of energy which may not be removed from the critical reactive modes of the exciplex on a time scale of nanoseconds. A decrease in the emission efficiency of exciplexes and excimers has been reported to accompany increasing excitation energy for several systems in the vapor phase.[3,11,12,35]

The *total* amount of excess vibrational energy possessed by the nascent exciplex consequent to 238- or 228-nm excitation is, of course, the relevant quantity to consider, and this requires knowledge of the exciplex binding energy. This measurement has not been reported, but Lichtin et al. indicate an estimated binding energy for I of 0.2–0.4 eV.[9] This, then, would indicate a *total* excess energy content of 6.6–8.3 kcm^{-1} and 7.9–9.5 kcm^{-1} for 238- and 228-nm, excitation, respectively. Similar considerations apply to the excess energy dependence of the LE state of the alkylbenzene chromophore under these conditions.

The quantum efficiency of the (amine-like) emission produced by 238- and 228-nm excitation was measured to be 0.0077 and 0.026, respectively. Since these efficiencies, if interpreted in terms of the *irreversible* quenching of the LE amino chromophore by the phenyl group, imply lifetimes of ca. 0.38 and 0.13 ns, respectively, the fact that the fast components of the decay curves are longer than these values (i.e., 2.0 and 0.96 ns) implies that some feedback from either LE alkylbenzene and/or exciplex is important.

In order to examine the decrease in exciplex emission efficiency with increasing excess vibrational energy directly, the excitation spectrum of I (monitored at 300 nm) was determine under isolated conditions. This (corrected) spectrum is shown in Figure 3. The abrupt decline in the fluorescence intensity at excitation wavelengths below ca. 250 nm, when compared with the increase in absorption (see Figure 1), indicates that a significant fall off in exciplex fluorescene efficiency occurs at these higher excitation energies. This rationalizes the interpretation that one observed LE amine fluorescence under conditions in which the exciplex and LE alkylbenzene emission efficiencies fall below that of the LE amine chromophore. Thus for λ_{exc} = 238 nm, the quantum yield of exciplex fluorescence is <0.0077; at 228 nm it is <0.026. The exciplex fluorescence quantum efficiency, measured for λ_{exc} = 265 nm, was found to be 0.08; thus it decreases by more than an order of magnitude when λ_{exc} is decreased to 238 nm.

Buffer Gas Addition. Finally, the investigation of collisional relaxation on the photophysics of I is reported. 2-Methylbutane (2-MB) was used as the buffer gas. At the highest pressure studied, 415 torr, the corrected fluorescence excitation spectrum, shown in Figure 3, can be seen to demonstrate a restoration of intensity to the level expected from the absorption spectrum down to ca. 230 nm. Apparently, vibrational relaxation within the exciplex manifold is, at 415 torr of pressure, efficient for $\lambda_{exc} >$ 230 nm, and thus fluorescence enhancement of the exciplex results. The decrease in intensity below ca. 230 nm is real and is not attributable to a fall off in the intrinsic efficiency of LE amine fluorescence (see Figure 3). At a total pressure of 415 torr, this implies that the lifetime of the initially excited state of the amino chromophore, presumably intramolecularly quenched by the phenyl group, is ~0.2 ns.

The fluorescence decay curves obtained at λ_{exc} = 265, 238, and 228 nm were measured at intermediate 2-MB pressures, as were the fluorescence spectra. As expected, the decay curves for λ_{exc} = 238 and 228 nm remained complex and were analyzed in terms of three exponential components. As the 2-MB pressure increased, the amplitudes of the intermediate and long component increased, eventually, eventually resulting in single-exponential decay at these excitation wavelenghts. The lifetime of I at ca. 400 torr of 2-MB was 23 ns. At intermediate pressures, the decay curves were not easily resolved into unique sets of components and for this reason, in addition to the fact that a kinetic model deals with the photokinetics of I, these data are not presented further.

The emission spectra of 1 at the three excitation wavelengths used were also determined as a function of 2-MB pressure. As expected, the "amine-like" spectrum produced at λ_{exc} = 238 and 228 nm gradually shifted and broadened, converging to the exciplex spectrum. The transformation of the 228-nm produced spectrum occurred at higher pressures relative to that obtained for λ_{exc} = 238 nm. In both cases, there was a concomitant increase in emission intensity. Although one would expect to observe fluoresence enhancement of the exciplex for λ_{exc} = 265 nm at higher buffer gas pressures, this effect was not explicitly documented for experimental reasons. It can be condluded, however, that if fluorescence enhancement does occur under these conditions, it is relatively slight.

Summary

In the linked phenylamino compound, I, the exciplex between the pendant groups becomes a kinetically important species in electronic relaxation in contrast with the *inter*molecular system in which exciplex emission is not observed in nonpolar solution, but in which reversible electronic energy transfer occurs. The exciplex emission in I dominates even in the isolated vapor phase when excitation is near the O–O band of the phenyl chromophore. Apparently, enough residual internal energy is retained by the molecule under static cell conditions to induce the rapid conformational transition to the appropriate exciplex geometry. The fact that this rate is significantly larger than that for intramolecular excimer formation in the analogous diamine indicates that the former process is probably accelerated by the electrostatic attraction between the pendant groups after photoexcitation.

The very high intrinsic emissivity of the amino chromophore results in amine fluorescence being observable despite very strong quenching by the phenyl group. The inability of the exciplex, when formed via this route, to undergo efficient intramolecular vibrational relaxation results in feedback to the amino manifold. Finally, the failure to observe appreciable collisionally induced fluorescence enhancement of the exciplex when I is excited near the O–O band of the phenyl chromophore indicates that rapid intramolecular vibrational energy redistribution takes place in the isolated molecule thus removing (part of) the formation energy from the critical mode(s) of the exciplex.

Experimental Section

3-Phenyl-1(dimethylamino)propane (I) was prepared from 3-phenylpropylamine (Aldrich). Thirteen and one-half grams of this material was slowly added to 21 mL of 91% formic acid contained in a cooled 250-mL flask. Twenty five milliliters of 37% formaldehyde were then added, the temperature being kept below 295 K. After CO$_2$ evolution ceased, the mixture was heated to reflux for ca. 10 h. The mixture was cooled and acidified; the product was then extracted with 2-methylbutane from a basic solution. After solvent removal, I was dried and vacuum distilled. ^{1}H and ^{13}C NMR confirmed the structure of I, and a gas chromatogram indicated a purity level of 99.9%. The vapor pressure of I was determined between 273 and 300 K with use of a capacitance manometer (MKS Baratron Type 77). It is 0.22 torr at 298 K, and the heat of vaporization is ca. 6.0 kcal/mol.

Fluorescence spectra were obtained by using a 200-W Hg(Xe) source; radiation was isolated by using a 0.25-m Jarrell Ash monochromator; the lines thus isolated (265, 249, 238, and 228 m) had a band pass of ca. 1.2 nm. The relative intensities of these lines were determined by using a rhodamine-B (ethylene glycol) quantum counter. Decay curves were measured by using a time-correlated photon-counting apparatus described previously. A 0.25-m Jarrell-Ash monochromator was used to isolate radiation from a pulsed D$_2$ flashlamp (0.5 atm) triggered at 30 kHz by an EG&G Hy-6 thyratron. The pulse characteristics were ca. 1.8 ns fwhm and 0.8 ns (1/e). The band pass of this radiation was 1.6 nm.

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[34] The binding energy of the exciplex is estimated to be between 0.2 and 0.4 eV; see ref 9.

Fluorescence was viewed through an interference filter (Corion), 300 nm for the exciplex and 287 nm for the amine fluorescence band-pass 12 nm). Because of the low optical density of the sample, and thus low fluorescence intensity, measurements were carried out by using a cylindrical cell, entirely constructed of Suprasil, 10 cm × 3.0 cm. This arrangement helped decrease the scattered light. Typical acquisition times were ca. 1-2 h. Fluorescence excitation spectra were obtained by using the time-correlated photon-counting apparatus in the multichannel scaling mode; in this way, it essentially functioned as a counting gated integrator. The excitation resolution was 1.6 nm. Because of the very low intensities encountered, three or four scans, each with a duration of 20 min, were obtained and cumulatively stored in the multichannel analyzer. Spectra were corrected by using a sodium salicylate screen as quantum counter. Absorption spectra were obtained by using a Varian 2300 spectrophotometer. The fluorescence standards used were toluene vapor (for the exciplex) and N,N-dimethyloctylamine (for the amine emission). The former was assigned an efficiency of 0.25 for 265-nm excitation at a pressure of 0.6 torr. This value was scaled from the value of 0.30 as reported by Burton and Noyes, Jr.,[35] for an ca. 14-torr pressure by the ratio of the measured lifetimes (i.e., 64.3 ns for 0.6 torr and 54.5 ns for 14.5 torr). The fluorescence quantum efficiency from *N,N*-dimethyloctylamine vapor (0.18 torr) was assigned a value of 1.0 between λ_{exc} = 250 and 230 nm.

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Quantitative Models of Gas-Phase Proton-Transfer Reactions Involving Alcohols, Ethers, and Their Thio Analogues. Correlation Analyses Based on Residual Electronegativity and Effective Polarizability

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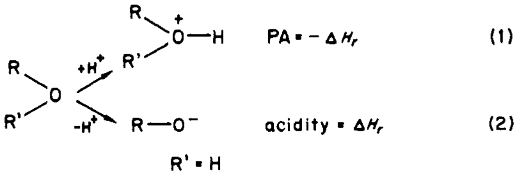
Abstract: The enthalpy of reaction for the gas-phase addition of a proton to an alcohol or ether (proton affinity) can be quantitatively modeled by a two-parameter expression. The two empirical parameters, residual electronegativity and effective polarizability, are both dependent on atomic composition, molecular structure, and reaction site and can be rapidly calculated by previously published procedures. Residual electronegativity reflects the electron-attracting ability of an atom in a particular molecular environment. Effective polarizability is related to conventional polarizability while allowing for attenuation of influence of more remote atoms and bonds. The same model applies to thiol and thioether proton affinity. Gas-phase acidity of alcohols is also described by these parameters, especially if allowance is made for the particularly high O-H bond-dissociation energy of water. The influence of polarizability is found to be less in determining the acidity values compared to proton affinity. It is concluded that the electronegativity and polarizability parameters offer novel access to quantitative reactivity data.

In discussing chemical reactivity, the organic chemist uses traditional concepts such as partial atomic charges, electronegativity, polarizability, hard and soft character, hyperconjugation, etc. However, these notions are frequently applied in a qualitative manner only. The synthesis and reaction design computer program EROS[1] is founded on just such descriptions of chemical reactivity, but in developing EROS, we are devising appropriate quantitative models for the above effects. In order to demonstrate their general applicability and suitability, we are first testing them against well-defined experimental data which have become available through recent developments in experimental technique. In particular, high-pressure mass spectrometry and ion cyclotron resonance spectroscopy have given accurate quantitative data on gas-phase reactions. Such data are of particular significance in that they have forced revision of some long-accepted concepts in chemical reactivity dealing as they do with isolated molecules uncorrupted by the influence of solvent.

Gas-phase protonation of alcohols is favored by alkyl groups in the order of increasing *positive* charge stabilization Me < Et < *i*-Pr < *t*-Bu.[2] This result is consistent with the traditional concept of such alkyl groups being electron releasing, as also implied by the aqueous-phase acidity of the alcohols (pK_a(MeOH) < pK_a(EtOH) < pK_a(*i*-PrOH) < pK_a(*t*-BuOH)). However, *gas*-phase studies of alcohol acidity show the opposite order to solution,[3] and they indicate that alkyl groups stabilize *negative* charge in the same sequence as they stabilize positive charge: Me < Et < *i*-Pr < *t*-Bu. This dichotomy was resolved by consideration of additional effects over and above the traditional inductive mechanism. Stabilization due to substituent polarizability was suggested by Brauman et al.[3] Thus, in any quantitative analysis of protonation reactions in the gas phase, we can expect to have to use multiparameter models and that measures of inductive effect alone will be insufficient. The two reaction types, protonation (eq 1) and deprotonation (eq 2), thus comprise fundamental test cases both in the context of our model development as well as in physical organic chemistry in general.



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