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Temperature Effect on the Vapor Phase Fluorescence in Cyano-Substituted Anthracenes. Reconsideration of the S_1–T_n Energy Gap

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Abstract: For several cyano-substituted anthracenes, temperature effect on the fluorescence lifetime and yield has been examined in the gas phase over the 180–295 °C range in both isolated and thermalized molecule limit. In the isolated molecule limit, 9-cyano-10-ethylanthracene (CEA), 9-cyano-10-phenylanthracene (CPA), and 9,10-dicyanoanthracene (DCA) exhibit fluorescence whose yield and lifetime decrease significantly as the excitation energy increases. On the other hand, the fluorescence in 9-cyanoanthracene (CA) is rather insensitive to the excitation wavelength as far as the excitation remains within S_1. In accordance with this distinctly different behavior, temperature effect on the thermalized fluorescence is appreciable only for the first three compounds and practically no temperature effect has been observed for CA. Based on these results, the activation energies relevant to the intersystem crossing from S_1 to T_n are calculated to be 0, 1510 ± 80, 1750 ± 60, and 1210 ± 30 cm^{-1} for CA, CEA, CPA, and DCA, respectively. By contrast, the fluorescence lifetimes of CEA and DCA in solution (dodecane) remain nearly constant (ca. 13 ns) from room temperature to 192 °C. CA shows only a slight decrease in the lifetime varying from 15.2 ± 0.2 at 17 °C to 13.4 ± 0.1 ns at 167 °C. CPA alone exhibits a great change in dodecane as well as in the gas phase, but its extent is smaller in dodecane than that in the gas phase. The activation energies obtained in dodecane are 1100 ± 40 cm^{-1} for CPA and approximately zero for CEA and DCA, greatly contrasting with the results in the gas phase. A comparison of the results between the two phases has led us to the conclusion that the activation energies measured in solution for meso-substituted anthracenes cannot be taken as equal to the energy gaps between S_1 and T_n. Even the activation energies in the gas phase where the situation is much simpler do not correspond to the energy gaps but appear to give the upper limits of the energy gaps.

Photophysical processes of excited molecules are affected by various things such as solvent, temperature, pressure, chemical substitution, etc. Among these, the temperature effect has provided one of the best ways to probe the decay manifold of excitation energy. Since the excitation energy is usually lost via several processes each of which depends in a different way on temperature, a close examination of the temperature effect on the fluorescence is useful in differentiating one dissipative channel from others. In fact, temperature-dependent fluorescence quantum yield in meso-substituted anthracenes[1-3] or E-type delayed fluorescence[4] has fully revealed the temperature-dependent intersystem-crossing process (ISC) or reverse ISC. The activation energies associated with these temperature-dependent phenomena have been taken as equal to the energy gaps between the two electronic states involved in ISC.[1-3] Consequently, the energy gaps obtained thus have been used to locate the energy levels of excited states when spectroscopic data are not available. However, a careful examination of the systems studied so far shows that the activation energy in solution can seldom be ascribed to a single process, but represents an overall temperature-dependent processes. For instance, apart from their intrinsic temperature dependence, radiative processes are influenced by refractive index in such a manner that the temperature effect on the medium can never be neglected in a crucial discussion of the energy dissipation process.[5,6]

To avoid this complication, it is most desirable to study the temperature effect on fluorescence in the gas phase. Unfortunately, the gas-phase studies so far have mainly been concerned with the photophysical processes of isolated (collision free) molecules, where thermodynamic consideration is invalidated. For this, no reliable data on the activation energies of photophysical processes are available in the gas phase[7,8] and in consequence no attempt has ever been made to compare the activation energy between the two phases. It is surprising to find such a lack of comparative work when we recall that the true meaning of activation energies in solution does not become clear until they are compared with the corresponding ones in the gas phase.

With this in mind, in the present paper the temperature effects on the fluorescence lifetime and yield are studied in detail on four cyano-substituted anthracenes in the gas phase, viz., 9-cyanoanthracene (CA), 9-cyano-10-ethylanthracene (CEA), 9-cyano-10-phenylanthracene (CPA), and 9,10-dicyanoanthracene (DCA). The results obtained are compared with those in solution. A great discrepancy between the results in the two phases becomes apparent, leading us to the conclusion that the activation energies obtained in solution cannot be taken as equal to the energy gaps between the lowest excited singlet state S_1 and the excited triplet state T_n to which ISC is believed to occur predominantly.

Experimental Section

The four cyanoanthracenes were synthesized according to the literature[9,10] and purified by recrystallization and then by sublimation in vacuo. Dodecane of a guaranteed grade was purified by passing it twice through a column packed with silica gel (200 mesh). Spectroscopic *n*-hexane from Merk was used as received.

In order to obtain a sufficient vapor pressure, a sample in a sealed suprasil cell was heated in a furnace. Two types of furnaces were employed as follows: one was made of two separate brass blocks for heating muffled with insulating material, being very similar to that employed by Ware and Cunningham,[11] and this was mainly used to record the absorption spectra on a Hitachi 124 spectrophotometer; the other consisted of a transparent Dewar vessel in which small blocks for heating a sealed sample cell were placed (its details will be given elsewhere).[12] This was

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Table I. A Comparison of the Spectroscopic Data between the Gas Phase and Solution

	absorption (0–0 band), cm^{-1}		fluorescence (0–0 band), cm^{-1}	
compd	gas phase	in CH[a]	gas phase	in CH[a]
CA	25 950	24 970	25 920	24 790
CEA	25 540	24 570	24 910	24 180
CPA	25 510	24 600	25 380	23 670
DCA	24 940	23 900	24 810	23 700

[a] CH stands for cyclohexane.

used to record the fluorescence spectra on a Shimadzu RF502 spectrofluorophotometer and to measure the fluorescence lifetimes with a Hitachi MPF4 spectrofluorophotometer equipped with a flash lamp of a 10 ns pulse width and sampling devices. In both cases, the lower and the upper part of the cell could be heated separately by two independently controlled heating elements. In a similar manner, the solution samples were heated up close to the boiling point of dodecane (214 °C). Dodecane was used as a solvent because its viscosity does not change significantly as temperature increases. The concentrations of the samples (ca. 10^{-5} M) were determined spectroscopically in the same way as before[13] and the pressures of *n*-hexane were calculated from the volumes of the cells and the weights of *n*-hexane added.

The fluorescence lifetimes were calculated with a computer by using the least-squares method from the decay curves displayed on a recorder. The gas-phase lifetimes of DCA (10.6 ns, at 204 °C in the thermalized molecule limit) and 9-methylanthracene (6.4 ns, at 170 °C in the thermalized molecule limit) calculated thus compare favorably with those previously obtained by the time-correlated single-photon counting technique.[5,12] This proves that the present procedure for lifetime calculation is reliable provided that the lifetime is longer than 5 ns. Below 5 ns, it becomes less reliable since the effect of the pulse width of the exciting light cannot be neglected even at the later part of the fluorescence decay curves. All the compounds remained stable at high temperatures and thus neither pyrolysis nor photolysis was responsible for the shortening of the fluorescence lifetime in the gas phase. The relative fluorescence quantum yields were determined from the areas of the corrected fluorescence spectra by the cut and weigh method.

Results

Absorption and Fluorescence Spectra in the Gas Phase. In Table I, the absorption and fluorescence 0–0 bands observed for the four cyanoanthracenes in the gas phase and in cyclohexane are compared. For both fluorescence and absorption, a large blue shift of the order of 1000 cm^{-1} is noticed when going from cyclohexane to the gas phase. No comparable data are available in the gas phase, but Nicol et al.[14] calculated the gas phase 0–0 absorption band of CA to be 26 571 ± 76 cm^{-1} by extrapolating their solution data to the gas phase. The extrapolated value is further blue shifted by 620 cm^{-1} compared with the present experimental value. The large blue shifts found for the compounds in Table I are due to the fact that the electronic transition involved is an allowed transition between ^1L_a and ^1A.[15]

The absorption spectra in the gas phase are insensitive to temperature and the spectral shapes and absorbances change only slightly as the temperature increases, indicating that the thermal perturbation on the electronic transition is very small.

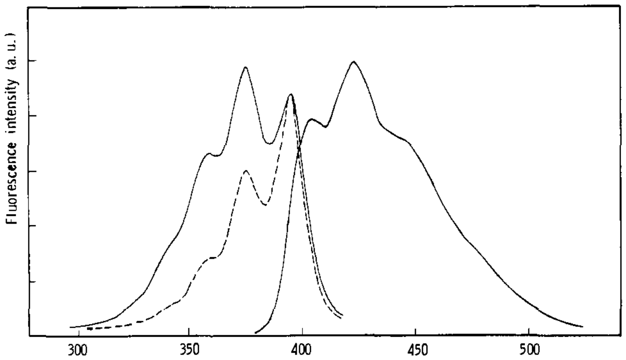

Figure 1. Fluorescence and excitation spectra of CPA (ca. 5 × 10^{-6} M) in the gas phase at 203 °C: (—) thermalized molecule limit (*n*-hexane, 2160 torr), (---) isolated molecule limit (CPA, ca. 0.15 torr). In the isolated molecule limit, the fluorescence spectrum varies only slightly with the excitation wavelength. The excitation spectra (band pass, 1.5 nm) observed at 424 nm are normalized at the 0–0 band. A large drop in the intensity at the shorter wavelength seen in the broken line indicates the existence of excess-energy-dependent decay processes.

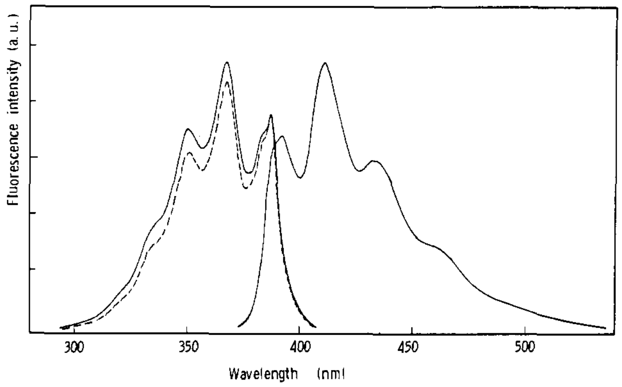

Figure 2. Fluorescence and excitation spectra of CA (ca. 7 × 10^{-6} M) in the gas phase at 179 °C: (—) thermalized molecule limit (*n*-hexane, 1380 torr), (---) isolated molecule limit (CA, ca. 0.2 torr). The excitation spectra (band pass, 1.5 nm) were monitored at 412 nm. Even in the isolated molecule limit, we see the fluorescence quantum yield does not vary substantially with the excitation energy.

Figure 1 shows the fluorescence and excitation spectra of CPA in the gas phase. In the presence of *n*-hexane (2160 torr) added as a relaxer, i.e., in the limit of the thermalized molecule,[16] the fluorescence spectrum does not change with the excitation wavelength and the excitation spectrum given by the solid line is exactly the same as the absorption spectrum in the gas phase. On the other hand, without *n*-hexane, i.e., in the isolated molecule limit (CPA, ca. 0.15 torr),[16] the excitation spectrum given by the broken line differs significantly from that obtained in the thermalized molecule limit. The emission intensity which is normalized to the intensity at the 0–0 band excitation decreases rapidly with an increase in the excitation energy, indicating that the fluorescence quantum yield of the isolated CPA also decreases rapidly when the excitation energy is increased. Analogous behavior was noted for CEA and DCA. The excitation spectra in the two limits for the latter are given in Figure 3 in ref 17. In accordance with this behavior, the fluorescence lifetime of isolated DCA decreases monotonously from 11.4 to 6.2 ns as the excess energy increases from 0 to 4410 cm^{-1}.[12,18]

By contrast, the relative fluorescence yield in the isolated CA (ca. 0.2 torr) does not change significantly with the excitation wavelength and the excitation spectrum obtained is close to that in the thermalized molecule limit as is shown in Figure 2. Again, this result is consistent with the excitation energy independent fluorescence lifetime of isolated CA reported by the present author and Phillips.[13]

Temperature Effect on τ_f and Relative Fluorescence Yield. Figure 3 shows how the fluorescence lifetimes of DCA and CEA depend on temperature in the thermalized molecule limit. In both cases, τ_f decreases appreciably as the temperature increases and is approximately halved at around 280 °C.

The short fluorescence lifetime of CPA in the gas phase made it impossible to examine the temperature effect on τ_f. Therefore,

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[18] See Figure 2 in ref 12 which clearly shows 700 torr of *n*-hexane thermalizes well the excess-energy-dependent behavior of DCA seen when excited in the isolated molecule limit (ca. 0.3 torr).

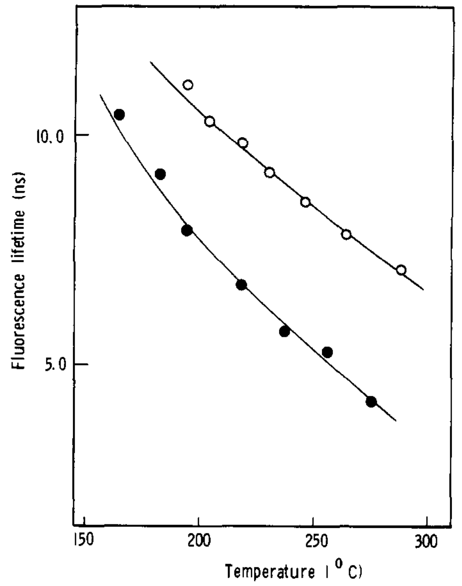

Figure 3. Temperature effect on the fluorescence lifetimes of CEA and DCA in the thermalized molecule limit: (●) CEA (*n*-hexane, 5.1 × 10^{-2} M), (○) DCA (*n*-hexane, 4.2 × 10^{-2} M).

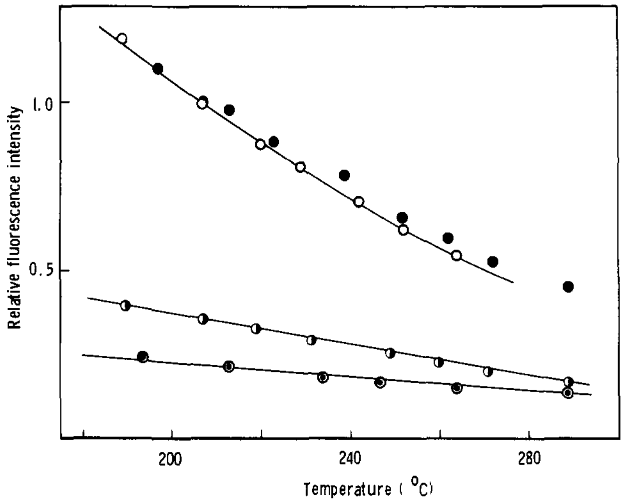

Figure 4. Temperature effect on the relative fluorescence yield of CPA: (○) thermalized molecule limit (*n*-hexane, 7.3 × 10^{-2} M) with the excitation at 355 nm, (●, ◑, ⊙) isolated molecule limit (CPA, ca. 0.2 torr) with the excitation at 392, 355, and 340 nm, respectively. The band pass is 5 nm in any case. In the isolated molecule limit, temperature effect on the relative fluorescence yield was examined at three different excitation wavelengths. At the 0–0 band excitation, the temperature effect is very similar to that observed in the thermalized molecule limit as is indicated by full and open circles. With increasing excitation energy, the temperature effect becomes less prominent.

instead of τ_f, the relative fluorescence yield was measured against temperature at several excitation wavelengths. The results are illustrated in Figure 4. In the gas phase, the change in absorbance by raising temperature is negligibly small and the refractive index practically remains unity. Thus, the relative fluorescence intensity is directly proportional to the fluorescence quantum yield before any correction for absorbance and *n*. In the presence of *n*-hexane (7.3 × 10^{-2} M), the temperature dependence of the relative fluorescence yield is independent of the excitation wavelength and is close to the trend observed when isolated CPA is excited at the 0–0 band (392 nm) as is indicated by full and open circles in Figure 4. In the absence of *n*-hexane, however, the temperature effect on the relative fluorescence yield is dependent to a substantial extent on the excitation wavelength and becomes less prominent with increasing excitation energy. This is easily understood if the excess excitation energy is partially redistributed among various vibrational modes before the collision with other molecules.[16,19] Thermal energy becomes less important as the excess energy increases from 0 to 3900 cm^{-1} and hence the energy-redistributed state predominantly determines τ_f and ϕ_f. Similar phenomena were also observed for DCA and CEA.

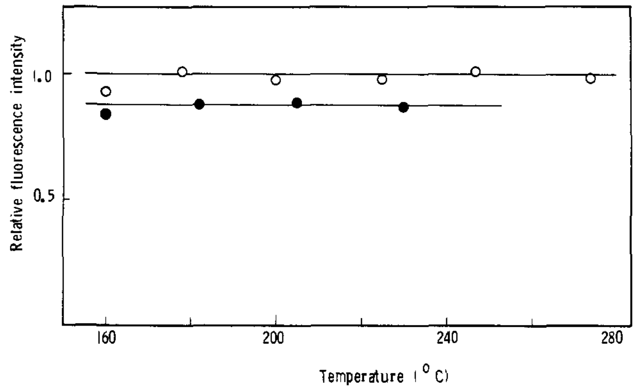

Figure 5. Temperature effect on the relative fluorescence yield of CA in the isolated and thermalized molecule limits: (○) thermalized molecule limit (*n*-hexane, 4.9 × 10^{-2} M), (●) isolated molecule limit (CA, ca. 0.2 torr). The excitation wavelength was 366 nm (band pass, 5 nm) in both cases. Contrary to CEA, CPA, and DCA, the relative fluorescence yield of CA is insensitive to temperature in both limits. The values in the isolated molecule limit are shown below those in the thermalized molecule limit for clarity. Slight drops in the yield at the lowest temperatures are due to the incomplete vaporization of the sample.

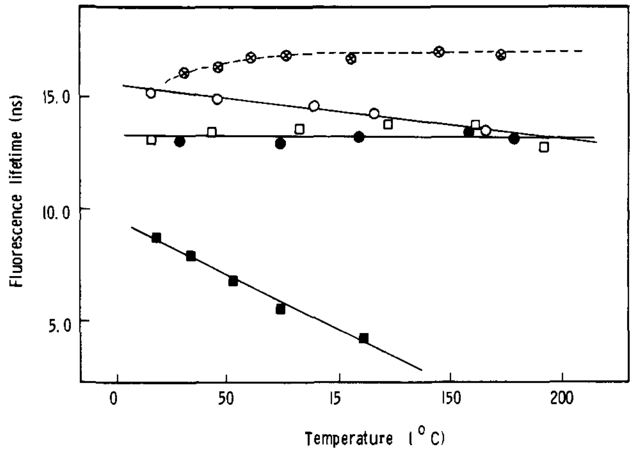

Figure 6. Temperature effect on the fluorescence lifetimes of CA, CEA, CPA, and DCA in dodecane. The concentrations are in the range 0.8–1.0 × 10^{-5} M. The temperature effect on the fluorescence intensity corrected for concentration change but not for refractive index *n* is also shown for DCA: (○) CA, (□) CEA, (●) DCA, (■) CPA, and ⊗ DCA in fluorescence intensity.

CA, on the other hand, behaves quite differently. Instead of τ_f which is very short (see Table II), Figure 5 shows the temperature dependency of the relative fluorescence yield in both limits of the isolated and thermalized molecule. Over a wide temperature range the relative yield remains constant in both cases. For clarity, the relative yield for the isolated molecule is shown below that for the thermalized molecule limit, but its value has no significance. This temperature-insensitive behavior is consistent with the excitation-energy-independent τ_f of isolated CA reported by Hirayama and Phillips[13] and can also be expected from the excitation spectrum of the fluorescence in isolated CA shown in Figure 2. It appears that in the absence of the data on the excess energy dependence of τ_f in the isolated molecule limit, the excitation spectrum can reveal important features of the excess-energy dependence of τ_f.

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(19) From their study of the vapor-phase fluorescence of POPOP by picosecond laser, Kopainsky and Kaiser[20] have shown that the excess excitation energy is rapidly redistributed among the vibrational manifold within the lifetime of the excited state. See also ref 8.

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Table II. Fluorescence Lifetime (ns)[a]

compd	gas phase	in dodecane (room temp)
CA	3.8[b]	15.2
CEA	10.5 (164 °C)	13.1
CPA	<3.5 (190 °C)	8.7
DCA	11.1 (194 °C)	13.0

[a] Standard deviations are in the range 0.1-0.3 ns. [b] Taken from ref 13.

Summarizing the results so far, two cases are apparent: (i) For CPA, CEA, and DCA, the fluorescence lifetimes and yields decrease rapidly with increasing temperature. (ii) For CA, the fluorescence yield (and presumably the fluorescence lifetime as well) remains constant with increasing temperature. The category to which other molecules belong can easily be deduced from a comparison of the vapor-phase excitation spectrum between the two limits.

Temperature Effect in Solution. Figure 6 shows the temperature dependence of the fluorescence lifetimes of the four cyano-substituted anthracenes observed in deaerated dodecane. It is surprising to find that DCA and CEA do not show any decrease in τ_f as temperature increases, exhibiting a remarkable contrast to the gas-phase results. For DCA the fluorescence intensity change corrected for a change in concentration but not for refractive index n is also given in Figure 6. It is apparent that the fluorescence intensity will not decrease (presumably will remain constant or decrease slightly) after a proper correction for n^2.[21] The fluorescence lifetime of CA, on the other hand, decreases a little as temperature increases, again contrasting to its behavior in the gas phase. CPA shows a significant decrease in τ_f in dodecane as well, but this tendency is less prominent compared with that in the gas phase.

Table II compares the typical fluorescence lifetimes in solution and in the gas phase for the four compounds studied here. A great shortening of τ_f is noticed for CA and CPA in going to the gas phase. High temperatures may be responsible for this shortening in CPA, but not for that in CA, since the latter shows little temperature effect on the fluorescence yield in the gas phase at least within the temperature range studied.

Activation Energy. The reciprocals of the fluorescence lifetime and the relative fluorescence quantum yield are given by eq 1 and 2, respectively,

$$1/\tau_f = k_r + k_{nr} \qquad (1)$$

$$1/\phi_f \propto 1/I_f = C(1 + k_{nr}/k_r) \qquad (2)$$

where k_r and k_{nr} are radiative and nonradiative rate constants and I_f and ϕ_f are fluorescence intensity and quantum yield, respectively. C is a constant to be determined experimentally. If we confine ourselves to the discussion on the thermalized molecule limit in the gas phase, k_r can reasonably be assumed to be temperature independent or at least its dependence, if any, is negligible in the following discussion. In fact, the absorption spectra in the gas phase show only a minute change over the temperature range studied, indicating the electronic transition probability is independent of temperature.

When k_{nr} is rewritten as $k^0_{nr} \exp(-E/RT)$, the Arrhenius plot of $(1/\tau_f - k_r)$ or $(1/I_f - C)$ gives an activation energy E. In either case the value of k_r or C was treated as an adjustable parameter. In Table III are listed those activation energies calculated by means of the least-squares method. The value of k_r adopted for DCA and CEA is 3.3×10^7 s^{-1} which is of the correct order of magnitude for their radiative rate constants in the gas phase. In the case of CPA, the values of C (including those in the isolated molecule limit) were estimated by assuming the fluorescence quantum yield of the thermalized CPA is 0.1 at 190 °C. CPA has the largest activation energy among the four compounds and the apparent activation energy in the isolated molecule limit becomes smaller as the excitation energy increases. The activation energies in this limit have no direct thermodynamic significance because the molecule is not in thermal equilibrium, but it is worth mentioning that such values could never be obtained in solution.

Table III. A Comparison of the Activation Energies (cm^{-1}) between the Gas Phase and Solution

compd	gas phase[a]	in dodecane
CA	≃0	strongly dependent on τ^0 (see Table IV)
CEA	1510 ± 80	≃0
CPA	1750 ± 60	1100 ± 40
isolated molecule limit	1270 ± 60 (355 nm) 850 ± 50 (340 nm)	
DCA	1210 ± 30	≃0
MA[b]	110 ± 20	740[c]

[a] Measured under thermalized conditions otherwise stated (see text). [b] 9-Methylanthracene. [c] Taken from ref 3.

Since no temperature effect was found for DCA and CEA in dodecane, the apparent activation energies are zero. The activation energy of CA in dodecane will be discussed in the next section.

Discussion

For the meso-substituted anthracenes, the energy dissipation following the excitation to S_1 is believed to be dominated by two processes, viz., $S_1 \rightarrow S_0$ radiative and $S_1 \rightsquigarrow T_n$ (usually $n = 2$ or 3) nonradiative processes.[1-3,22] The latter process alone is regarded as being dependent on temperature and the activation energy relevant to this process is taken as equal to the energy gap between S_1 and T_n. Many authors have tried to confirm this concept or used it to locate the T_n levels of some meso-substituted anthracenes.[3,23-25] Apart from a few exceptions such as 9-*tert*-butylanthracene and 9-methoxyanthracene,[3] this appears to hold true. However, it has not been discussed in detail why the activation energy relevant to ISC can be taken as equal to the energy gap between the electronic states involved in ISC. For isolated molecules in the gas phase, it is well documented that both radiative and nonradiative rate constants depend on the excess energy,[16,26-28] that is, each vibrational state in S_1 has different k_r and k_{nr}. Taking this into account, the observed k_{nr} should be given by averaging the energy dependent $k_{nr}(\epsilon)$ over a Boltzmann distribution as in eq 3.[27,29,30] For simplicity, a factor for the state

$$k_{nr} = \int_0^\infty k_{nr}(\epsilon) \exp(-\epsilon/RT)\, d\epsilon \qquad (3)$$

density is included in $k_{nr}(\epsilon)$. It is very difficult to predict the exact form of $k_{nr}(\epsilon)$ in such large molecules as anthracenes. However, if k_{nr} in eq 3 is to be expressed in the form of $k^0_{nr} \exp(-E/RT)$ with temperature-independent k^0_{nr}, a trivial form of $k_{nr}(\epsilon)$ is a step function expressed as $k_{nr}(\epsilon) = 0$ when $0 < \epsilon < E$, while $k_{nr}(\epsilon)$ = constant when $\epsilon \geq E$. From the gas-phase studies so far[16,26] it is evident that such a step function is not justifiable. Depending on the form of $k_{nr}(\epsilon)$, k_{nr} is endowed with a different activation energy which may be temperature dependent, so it cannot be said that the activation energy associated with ISC gives the energy gap between S_1 and T_n. If the activation energy should correspond to the energy gap, the great discrepancy found between the two phases cannot be reconciled. Compared with the energy of S_1

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Table IV. Parameter Dependence of the Activation Energy of CA in Dodecane

τ^0,[a] ns	ϕ_f	$-E$, cm^{-1}
16.95	0.891	471
16.67	0.906	525
16.39	0.921	594
16.13	0.936	685
15.87	0.951	814
15.63	0.966	1015

[a] Natural radiative lifetime.

in solution, the energy of S_1 in the gas phase always increases as is seen from large blue shifts given in Table I. If we assume that the T_n level is insensitive to environmental change,[2] the energy gap between S_1 and T_n which lies above S_1 should decrease in the gas phase. Consequently, the activation energy in the gas phase should be smaller than the corresponding one in solution by ca. 1000 cm^{-1}. Contrary to this expectation, the activation energies observed are much greater in the gas phase except for CA and 9-methylanthracene for which the trends observed are in the expected direction. The pressure of *n*-hexane may not be high enough to achieve a complete Boltzmann distribution in the excited state.[12,31] Still, the discrepancy is too great to be rationalized. It should be noticed here that the results in the gas phase are consistent in so far as that when isolated molecules show the excess energy dependence of τ_f, τ_f in the thermalized molecule limit becomes temperature dependent and the associated activation energy takes a value of considerable magnitude. Otherwise, ISC scarcely depends on temperature as is seen for CA.

In solution the situation is rather complicated. There are some difficulties in determining the activation energy associated with k_{nr}. The radiative rate constant k_r is a function of n and hence k_r in solution is not temperature independent any more[5] and decreases with increasing temperature. When ϕ_f is close to unity as is the case for CA,[32] DCA, and CEA,[33] τ_f is largely determined by k_r and hence the temperature effect on τ_f through k_r becomes important. Since the temperature effect on k_r and k_{nr} is in the opposite direction, the apparent activation energies calculated from τ_f by assuming k_r as a constant will become smaller than that associated with k_{nr}. Nevertheless, it would be much too fortuitous to expect that the decrease in k_r caused by a decrease in n is mostly compensated by an increase in k_{nr}, making τ_f invariant in solution over a wide temperature range as is seen for CEA and DCA. The simultaneous determination of τ_f and ϕ_f may resolve this problem, but in practice it is difficult to determine ϕ_f correctly when n varies significantly with temperature.

Even when a decrease in τ_f with temperature is observed, the accurate determination of the activation energy is rather difficult. Table IV shows how the activaiton energy varies with k_r or ϕ_f. As is seen from the continuing debate on the fluorescence quantum yield of 9,10-diphenylanthracene[34] the variation of the fluorescence quantum yield by a magnitude of 0.2 is quite likely. As a result, k_r could vary by a similar extent. From Table IV it is obvious that the activation energy critically depends on the parameter k_r and is very uncertain even if τ_f can be determined with a reasonable precision. To make the matter more complicated k_r is not constant with temperature any more.

Thus it is very dubious to relate the activation energy to the energy gap between S_1 and T_n for the meso-substituted anthracenes with high (presumably medium as well) fluorescence quantum yields. In the gas phase we are not bothered by the complexities met in solution and hence the activation energy is expected to reflect a certain molecular property and seems to give the upper limit of the energy gap to be realized in the gas phase.

In conclusion, therefore, it is essential to examine whether or not τ_f in the isolated molecule limit depends on the excess-excitation energy and whether τ_f in the thermalized molecule limit shows any temperature effect before giving any interpretation to the apparent activation energies obtained in solution. The concept of relating the activation energy to the energy gap is very widely used and appears to be accepted, but all the solution data on meso-substituted anthracene must be reexamined from this point of view.

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(31) Within the experimental error, the same thermalized fluorescence lifetime 10.6 ns was reproduced for DCA in the individual presence of a wide variety of buffer gases such as ethanol, furan, toluene, cyclohexene, and acetonitrile at 204 °C, indicating a nonspecific interaction in thermalizing the excited DCA (and presumably the other compounds studied here). The full details will be published elsewhere. Hirayama, S. *Chem. Phys. Lett.*, in press.

(32) Donck, E. V.; Barthels, M. R.; Antheunis, N.; Swinner, M. *Mol. Photochem.* **1977**, *8*, 121–132.

(33) Estimated from τ_f.

(34) Birch, D. J. S.; Imhof, R. E. *Chem. Phys. Lett.* **1975**, *32*, 56–58.