Photoelectron Ejection from Tetraaminoethylenes in Aromatic Hydrocarbons. Role of the Molecular "Rydberg" State in Excited Charge-Transfer States and Long-Range Electron-Transfer Processes

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Abstract: Absorption and fluorescence spectra and photocurrents for tetraaminoethylenes in aromatic hydrocarbons have been studied. The first absorption bands of these systems are assigned to the transition corresponding to the photoelectron ejection from the solute molecules into the solvents. From the studies on the solvent and temperature dependences of the absorption and fluorescence spectra, it has been demonstrated that the ejected electrons spend a large part of their time in vacant spaces between the solvent molecules in the case of saturated hydrocarbon solvents, but that they become localized more and more within the solvent molecules by changing the solvent to benzene and 1-methylnaphthalene. The concept of the "Rydberg" configuration is introduced to describe the electronic distribution in the vacant spaces. It is pointed out that, for general electron donor-acceptor systems dissolved in some solvents, the mixing between the charge-transfer and "Rydberg" configurations still remains significant even at a relatively long distance between the donor and acceptor, showing the possibility of the long-range intermolecular interactions. The mechanism of the long-range electron transfer between the donor and acceptor in the excited state ($D^{*}\cdots A \rightarrow D^{+}\cdots A^{-}$) is discussed on the basis of this new idea

Photoelectron ejection from molecules into organic media has been studied by some authors either from photocurrent measurements or spectroscopic monitoring of the photoionized products. Recently, we have observed absorption spectra assigned to transitions from the ground state to the "Rydberg" and ionized states of solute molecules in organic solvents.[1-4] Fluorescence spectra which were assigned to be originating from the "Rydberg" states in solvents were also observed.[2-5] One important consequence of these studies is that these low-lying "Rydberg" states just after excitation in saturated hydrocarbons or ethers are destabilized relative to those in the vapor phase, as shown by the blue-shift of the "Rydberg" absorption bands. The qualitative interpretation made before[2-4] is that the "Rydberg" electrons in the solvents are subject to repulsive potentials by the solvent molecules, which are larger than the stabilization due to their electronic polarization.

It is well known that aromatic hydrocarbons can be electron acceptors. It is then expected that the absorption and fluorescence spectra assigned to the "Rydberg" transition may be largely altered by changing the solvent from saturated hydrocarbons to aromatic ones. Preliminary studies on the "Rydberg" state in benzene were already reported.[2] In the present paper, the results of detailed studies will be presented. Based on these studies, it is also discussed that the "Rydberg" state of electron donors plays an important role in the charge-transfer-type interactions between electron donors and acceptors.

Experimental Section

The preparation and handling of tetrakis(dimethylamino)ethylene (TMAE) and 1,1′,3,3′-tetramethyl-2,2′-biimidazolidinylidene (TMBI) were described previously.[1] A Wako spectrograde toluene was used after drying with Na-K alloy. Isopropylbenzene (cumene) and 1-methylnaphthalene were dried with Na wire and distilled twice through a Widmer column under reduced pressure. Absorption spectra of weakly transmitting solutions at 77 K were measured with a Shimadzu MPS-50L spectrophotometer by using thin cells. The details of other procedures were described elsewhere.[1,2,4]

Results

Absorption and fluorescence spectra of TMAE in various solvents are shown in Figure 1. Those in the gas phase and saturated hydrocarbons were already reported,[2] but are included in Figure 1 because they are important as reference data. The absorption spectra of TMAE in benzene[2] and cumene and that of TMBI in benzene at room temperature are almost the same in shape and position as that of TMAE in toluene, shown in Figure 1B. The absorption edge of TMAE in cumene is blue-shifted at low temperature like that in the toluene solution.

The fluorescence spectrum of TMAE in benzene at room temperature was reported to have a relatively broad peak at about 24 kK (1 kK = 10^3 cm^{-1}).[2] The position and shape of the fluorescence spectrum of TMBI in benzene are almost the same as those of TMAE. The fluorescence spectrum of TMAE in toluene at room temperature, however, shows two peaks at 24.3 and 19.4 kK, as shown in Figure 1B. The fluorescence spectra of TMAE in the mixtures of benzene and *n*-pentane in the range of volume ratio from 1:1 to 1:2 also show two peaks at 23.8 and 20.4 kK. The relative intensity of these two peaks, both in toluene and in the mixed solvents, depends on the excitation wavelength and temperature. The fluorescence spectrum of TMAE in cumene shows only one peak at 19.4 kK. By decreasing the temperature, the fluorescence bands at 19.4 kK in toluene and cumene are blue-shifted to 20.4 and 21.4 kK at 77 K, respectively, like the fluorescence spectra in saturated hydrocarbons, while the band at 24.3 kK in toluene does not shift so much and disappears below −100 °C, the freezing point of toluene. No detectable fluorescence is observed for TMAE in 1-methylnaphthalene.

The photocurrent threshold of TMAE in benzene at room temperature was reported to lie at 29.4 kK.[2] The photocurrent yield of TMAE in 1-methylnaphthalene was found to be much lower than that in benzene and the threshold could not be determined definitely, though it was likely to be near 25 kK.

Discussion

As reported in previous papers,[1,2,4] the absorption band of TMAE in the gas phase, appearing as a shoulder at about 29 kK (Figure 1A) is assigned to the transition from the ground state to the Rydberg state, based on its solvent- and temperature-dependent behaviors. The lowest (π-π^*)-type absorption band has the peak at 38.5 kK and a tail down to about 30 kK, being insensitive to the environments except only slight red-shift by change from the gas phase to the solution phase.

The onset of the absorption spectrum in toluene is blue-shifted by decreasing the temperature (Figure 1B). This is

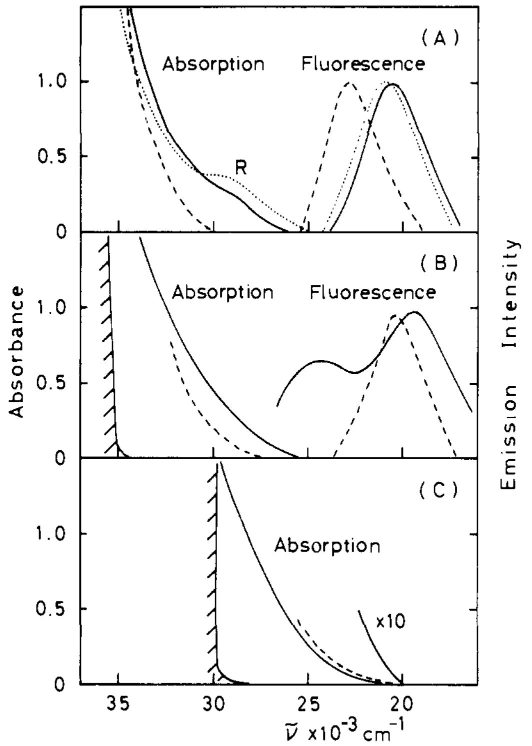

Figure 1. Absorption and fluorescence spectra of TMAE: (A)····· in the gas phase; — and - - - - in MP at room temperature and 77 K, respectively, where MP is a mixed solvent of methylcyclohexane and isopentane in a volume ratio of 1:1; (B) in toluene, — at room temperature and - - - - at 77 K; (C) in 1-methylnaphthalene, — at room temperature and - - - - at 77 K. The absorption band designated by R in (A) is the Rydberg band. The hatched parts in (B) and (C) show the solvent absorption. The change in solvent volume with temperature is corrected.

interpreted to show that the ejected electrons are subject to repulsive potentials by the toluene molecules and not captured by them, like the electrons in saturated hydrocarbons.[2-4] It is to be noted, however, that the blue-shift in toluene is smaller than that in saturated hydrocarbons, as seen from Figures 1A and B. The room temperature absorption spectrum in toluene also shows a slight increase in absorbance in the region below about 29 kK compared with the spectrum in MP, as pointed out previously in a TMAE-benzene system.[2] One could therefore assume the presence of the contact charge-transfer state between TMAE and toluene in the energy region higher than 28 kK. Such a state is thought to remain unchanged or be rather stabilized by lowering the temperature. The similarity of the shape and position of the absorption spectra for TMAE in benzene, toluene, and cumene shows that the "vertical" excited states in these solvents are of almost the same character.

The fluorescence spectra of TMAE in benzene and toluene are quite different from each other and also from those in saturated hydrocarbons. It was reported before[2] that the fluorescence spectrum of TMAE in saturated hydrocarbons appearing at 20.5 kK was assigned, from its blue-shift with lowering temperature, to be originating from the molecules in the "Rydberg" state situated in the cavity formed in the solvent, while the one in benzene appearing at about 24 kK was assigned to be from the charge-transfer state between TMAE and benzene. Based on these results, the fluorescence spectra of TMAE in benzene, toluene, and cumene can be explained by assuming the following competitive relaxation processes (eq I and II), where R_{FC} is the solute molecule in the vertical (or Franck-Condon) "Rydberg" state, R_C the one in the "Rydberg" state situated in the cavity formed in the solvent, CT the excited charge-transfer state between the solute and solvent molecule(s), G the molecules in the ground state, and $\tilde{\nu}_{CT}$ and $\tilde{\nu}_R$ are 24 and 19.4 kK at room temperature, respectively. The present experimental results are then explained as follows: Process I is predominant in benzene, processes I and II are competing in toluene, and process II is predominant in cumene. This sequence is well understood by taking account of the destabilization of the charge-transfer state by steric repulsion of alkyl groups. The two fluorescence bands observed in the mixed solvents of benzene and n-pentane can also be explained as due to the competition between processes I and II.

$$\begin{tikzcd} & \mathrm{CT} \arrow[r, "hc\tilde{\nu}_{\mathrm{CT}}"] & \mathrm{G} & \text{(I)} \\ \mathrm{R}_{\mathrm{FC}} \arrow[ur, dashed] \arrow[dr, dashed] & & & \\ & \mathrm{R}_{\mathrm{C}} \arrow[r, "hc\tilde{\nu}_{\mathrm{R}}"] & \mathrm{G} & \text{(II)} \end{tikzcd}$$

The absorption spectrum of TMAE in 1-methylnaphthalene is largely red-shifted compared with those in other solutions. This spectrum does not blue-shift with decreasing temperature and is somewhat intensified. It was reported[6] that n-pentane solutions of TMAE and anthracene, pyrene, or perylene showed the absorption spectra starting at about 600-650 nm, which were assigned to the contact charge-transfer transition. The shift of the absorption edge by change from 1-methylnaphthalene in the present work to pyrene, anthracene, and perylene is nearly parallel to the shift of their electron affinity.[7] From these results, the absorption spectrum of TMAE in 1-methylnaphthalene can be assigned to the transition to the contact charge-transfer state between TMAE and the surrounding 1-methylnaphthalene molecule(s).

The "Rydberg" Configuration and Its Role in the Charge-Transfer State and the Electron-Transfer Process. We will here discuss the above-mentioned results in somewhat more detail based on the molecular orbital theory and investigate the relation between the "Rydberg" state and the charge-(or electron-) transfer phenomena in solution. As has been mentioned above, the wave function for the lowest excited singlet state of TMAE in saturated hydrocarbons extends far into the surrounding solvents. We assume that such a state can be represented simply by the "Rydberg" configuration, $\Phi(\mathrm{R})$, as follows:

$$^1\Psi \sim {}^1\Phi(\mathrm{R}) = \sqrt{1/2}\{\Phi(\phi_{\mathrm{R}}\bar{\chi}_1) - \Phi(\bar{\phi}_{\mathrm{R}}\chi_1)\} \qquad (1)$$

where $\Phi(\phi_{\mathrm{R}}\bar{\chi}_1)$ and $\Phi(\bar{\phi}_{\mathrm{R}}\chi_1)$ are Slater determinants given by

$$\Phi(\phi_{\mathrm{R}}\bar{\chi}_1) \sim |\phi_{\mathrm{R}}\bar{\chi}_1\chi_2\bar{\chi}_2\chi_3 \cdots\cdots \theta_1\bar{\theta}_1\theta_2 \cdots\cdots| \qquad (2)$$

$$\Phi(\bar{\phi}_{\mathrm{R}}\chi_1) \sim |\bar{\phi}_{\mathrm{R}}\chi_1\chi_2\bar{\chi}_2\chi_3 \cdots\cdots \theta_1\bar{\theta}_1\theta_2 \cdots\cdots| \qquad (2')$$

The functions χ_1, χ_2, ··· refer to the occupied molecular orbitals of TMAE, χ_1 being the highest one, the functions θ_1, θ_2, ··· refer to those of the solvent molecules surrounding TMAE, and the function ϕ_{R} refers to the Rydberg-like orbital putting the center at TMAE and extending far into the solvent around it. In the first approximation, ϕ_{R} can be taken to be the function like the lowest Rydberg orbital of TMAE in the gas phase, but orthogonalized to all other filled orbitals of the solvent molecules and somewhat expanded in size due to the electronic polarization of them. An unbarred orbital contains an electron of α spin, and a barred orbital one of β spin. The wave functions for the corresponding triplet state can be written as follows:

$$^3\Psi \sim {}^3\Phi(\mathrm{R}) = \sqrt{1/2}\{\Phi(\phi_{\mathrm{R}}\bar{\chi}_1) + \Phi(\bar{\phi}_{\mathrm{R}}\chi_1)\}, \quad \Phi(\phi_{\mathrm{R}}\chi_1), \text{ or } \Phi(\bar{\phi}_{\mathrm{R}}\bar{\chi}_1) \qquad (3)$$

It is to be noted that the energy difference between the singlet and triplet states is thought to be very small, owing to the large spatial extent of the orbital ϕ_{R} relative to χ_1 and, therefore, the small exchange energy between them. Unfortunately, both

TMAE and TMBI showed no detectable phosphorescence according to our experiments.

In an advanced treatment, the excited state may be represented by a linear combination of the above-mentioned "Rydberg" configuration and the charge-transfer configuration, similar to the case of unsaturated hydrocarbon solvents discussed later. However, the contribution of the charge-transfer configuration will be small in this case, since its energy is expected to be much higher than that of the "Rydberg" configuration.

According to the studies on the excess electron in rare gas matrices,[8,9] the requirement of orthogonality imposed on the "Rydberg" orbital, which causes the rapid oscillation of the orbital amplitude within the solvent molecules, leads to a large increase in the orbital energy. This means that the solvent molecule acts effectively as a short-range repulsive potential for the outer electron. On the other hand, the "Rydberg" orbital is expanded in size and the electron in it is stabilized in energy due to the long-range electronic polarization of the solvent. The situation is probably the same in the case of saturated hydrocarbons. The observed blue-shift of the lowest "Rydberg" absorption band is understood as due to the sum of these two effects, the solvent repulsion being larger in magnitude than the stabilization by the electronic polarization. These considerations lead to a conclusion that the function ϕ_R in saturated hydrocarbons should have relatively large amplitude in the vacant spaces between the solvent molecules.

We next consider the lowest excited state of TMAE in 1-methylnaphthalene. We assume that it is represented by a linear combination of the charge-transfer configurations, $\Phi_{CT}(D^+N_i^-)$, and the "Rydberg" configuration, $\Phi(R)$, as follows:

$$\Psi \sim \sum_i a_i \Phi_{CT}(D^+N_i^-) + b\Phi(R) \qquad (4)$$

where D denotes a TMAE molecule, and N_i the ith member of the 1-methylnaphthalene molecules surrounding TMAE.[10] The function $\Phi(R)$ is described like eq 1 or 3, provided that the solvent in this case is 1-methylnaphthalene. The function $\Phi_{CT}(D^+N_i^-)$ is also described in a similar way as eq 1 or 3, provided that the function ϕ_R in eq 1-3 is replaced by the lowest vacant orbital of N_i. The contribution of $\Phi_{CT}(D^+N_i^-)$ gives the electronic distribution within the N_i molecule, while that of $\Phi(R)$ gives the electronic distribution even in the vacant spaces between the 1-methylnaphthalene molecules.

As mentioned in the foregoing section, the energy of the lowest excited state of TMAE in 1-methylnaphthalene agrees well with the value expected from the assignment that it is the contact charge-transfer state. This suggests that $|a| \gg |b|$ in eq 4, $|a|$ being the largest coefficient of the $|a_i|$'s. On the other hand, it is to be noted that almost no overlap is expected between the π orbital of the C=C group or the lone-pair orbitals on the N atoms of TMAE and the π orbitals of 1-methylnaphthalene, owing to the crowding of many methyl groups around the $N_2C{=}CN_2$ skeleton (e.g., the distance between the $N_2C{=}CN_2$ and naphthalene planes is about 0.5 nm).[11] In such a situation, the probability of the optical transition between the ground-state and the charge-transfer configurations will be negligibly small. Therefore, the absorption intensity in this case must originate entirely from the part of the "Rydberg" configuration, $\Phi(R)$, in eq 4.

Studies on the absorption intensity[3] and the fluorescence lifetime[4] show that the probability of the Rydberg transition is not so much changed by the distortion of the "Rydberg" orbital due to the solvent. We can then assume that the probability of the optical transition between the ground state and the "Rydberg" configuration for TMAE in 1-methylnaphthalene is of the same order of magnitude as that in other solvents, e.g., saturated hydrocarbons. Based on these considerations, the extent of configurational mixing, b^2, can be roughly estimated to be about 0.1 by taking the molar extinction coefficient of the lowest "Rydberg" band in saturated hydrocarbons to be about 1000 M^{-1} cm^{-1} [3] and that of the absorption band of TMAE in 1-methylnaphthalene at around 24 kK to be about 100 M^{-1} cm^{-1}.[12] This result is in agreement with the above-mentioned conclusion that $|a| \gg |b|$, showing that the ejected electrons are mostly localized within the 1-methylnaphthalene molecule(s) in this case, in contrast to those in the saturated hydrocarbon solvents.

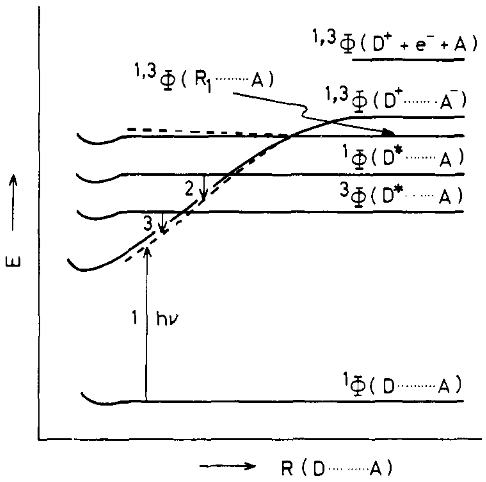

Figure 2. Schematic representation of energy levels of various electronic configurations for an electron donor (D)–acceptor (A) pair dissolved in some solvents (saturated hydrocarbons) as functions of the distance R between D and A. The higher "Rydberg" and acceptor-excited configurations are not shown for simplicity. The effect of the configurational mixing through the overlap between the π or σ orbitals of D and A is also not shown. The energy difference between the singlet and triplet states is taken to be negligibly small both for the "Rydberg" configuration and for the charge-transfer configuration. The spatial distribution of the solvent molecules around D and A for the "Rydberg" and charge-transfer configurations is taken to be the same as the equilibrium distribution for the ground or locally excited configuration at any distance R, which corresponds to the distribution for the "vertical" state in processes 1, 2, or 3.

The lowest excited state of TMAE in benzene or toluene can also be described similarly to eq 4. As is mentioned before, the "vertical" excited state in these systems is of Rydberg character, i.e., $|b| > |a_i|$. It is to be noted, however, that the energies of the "Rydberg" and charge-transfer configurations lie relatively close to each other in this case. Also, they seem to change with the relative structure of the solute and solvent molecules largely, in different ways.[2] These situations will make the magnitude of the coefficients a_i and b very sensitive to the structure of the surrounding solvent, which may be the reason why the two fluorescence spectra of different characters are observed. We can then conclude that benzene or toluene is situated just between the two typical solvents, saturated hydrocarbon and 1-methylnaphthalene, as to whether the ejected electrons are localized within the solvent molecules or not.

Now, let us generally consider an electron donor (D)–acceptor (A) pair dissolved in some solvents (saturated hydrocarbons), based on the above discussion. Energy levels for various electronic configurations are shown schematically in Figure 2 as functions of the distance R between D and A. As usual, the wave functions for these electronic configurations, except the "Rydberg" ones, can be written as a product of eigenfunctions for the separate donor, acceptor, and solvent molecules, provided that the exchange of electrons between these molecules is allowed for. One might assume that the wave function for the "Rydberg" configuration, $\Phi(R_n \cdots A)$, is also described as a simple product of the eigenfunction for D in the

nth "Rydberg" state, which is written as eq 1 or 3, and that for A in the ground state. It is preferable, however, that the "Rydberg" orbital contained in $\Phi(\mathrm{R}_n\cdots\mathrm{A})$ is taken to be orthogonalized not only to the filled orbitals of the solvent molecules, but also to those of the acceptor molecule, being slightly different from the "Rydberg" orbital for D in the solvent in the absence of A.

The energy for the "Rydberg" configuration, $\Phi(\mathrm{R}_n\cdots\mathrm{A})$, at a very long distance R between D and A can be taken to be equal to that for the nth "Rydberg" state of D in the solvent in the absence of A. It is empirically known that the lowest Rydberg state for most of the large organic molecules in the gas phase lies at about 2.5 eV lower energy than the gas-phase ionization potential.[1,4,13,14] It has also been known that the lowest "Rydberg" state of the molecules in organic solvents at room temperature lies at about 0.2–0.3 eV higher energy than the lowest Rydberg state in the gas phase.[1-4] Besides, the higher "Rydberg" states in solution are estimated to lie relatively close to the lowest "Rydberg" state in energy from the relatively small energy difference between the lowest "Rydberg" and ionized (conductive) states in solution, about 0.5–1.0 eV.[2-4] It is assumed in the present work that the energy of the "Rydberg" configuration, $\Phi(\mathrm{R}_n\cdots\mathrm{A})$, is hardly changed by decreasing the distance R until the overlap between the π or σ orbitals of D and A begins to occur (Figure 2). Since A approaches to D by changing places with the solvent molecules around D one by one, this will be true if the shift of the energy of the "Rydberg" orbital due to its orthogonalization to the filled orbitals of the electron acceptor molecule is not so much different from that due to the orthogonalization to the filled orbitals of the solvent molecule.

The above-mentioned wave functions for the various electronic configurations will be eigenfunctions for the system when D and A are far apart, but they become mixed with each other when D and A come close together. It must be emphasized here that, as is shown by broken lines in Figure 2, the mixing between the "Rydberg" and charge-transfer configurations begins to occur from a relatively long distance R at which the overlap between the π or σ orbitals of D and A is still negligibly small and, therefore, the functions for other configurations remain a good approximation to the eigenfunctions. This type of mixing is very interesting, showing the occurrence of long-range intermolecular interaction, though almost no attention has been given so far to this point.

The resultant charge-transfer state, $\Psi_{\mathrm{CT}}(\mathrm{D}^+\cdots\mathrm{A}^-)$, can be expressed as follows:

$$\Psi_{\mathrm{CT}}(\mathrm{D}^+\cdots\mathrm{A}^-) = a\Phi_{\mathrm{CT}}(\mathrm{D}^+\cdots\mathrm{A}^-) + \sum_n b_n\Phi(\mathrm{R}_n\cdots\mathrm{A}) \quad (5)$$

where the coefficient b_n is given by perturbation theory as

$$\begin{aligned} b_n/a &= (H_{\mathrm{R}_n,\mathrm{CT}} - S_{\mathrm{R}_n,\mathrm{CT}}E_{\mathrm{CT}})/(E_{\mathrm{CT}} - E_{\mathrm{R}_n}) \\ H_{\mathrm{R}_n,\mathrm{CT}} &= \langle\Phi(\mathrm{R}_n\cdots\mathrm{A})|H|\Phi_{\mathrm{CT}}(\mathrm{D}^+\cdots\mathrm{A}^-)\rangle \\ S_{\mathrm{R}_n,\mathrm{CT}} &= \langle\Phi(\mathrm{R}_n\cdots\mathrm{A})|\Phi_{\mathrm{CT}}(\mathrm{D}^+\cdots\mathrm{A}^-)\rangle \quad (6) \end{aligned}$$

One can then see that the dependence of b_n on the distance R is mainly determined by the spatial extent of the "Rydberg" orbital for D in solution. Unfortunately, we have no detailed knowledge on it at present. Qualitatively speaking, however, the radius of the "Rydberg" orbital at the radial density maximum, $r_{\max}$, for the lowest "Rydberg" state in solution may be estimated to be fairly larger than the corresponding value in the gas phase, 0.29 nm,[1] from a large decrease in the energy difference between the lowest "Rydberg" and ionized states on change from the gas phase to the solution phase.[3] Then, it is certain that even the spatial extent of the "Rydberg" orbital for the lowest "Rydberg" state is very much larger than that of π or σ orbitals. Accordingly, the magnitude of the coefficient, $|b_1|$, is thought to be significant even at a relatively long distance R between D and A, unless the lowest "Rydberg" configuration lies at much higher energy than the charge-transfer configuration.[15] From these considerations, we can conclude that absorption or emission bands assigned to the long-range charge- (or electron-) transfer transition between D and A may be observed in some appropriate systems[16] (process 1 in Figure 2).

Recent experiments[17-21] have suggested the possibility of the electron transfer from aromatic molecules in the lowest (π–π^*)-type excited state (D*) to some electron acceptors (A), which are separated from D* at somewhat longer distances than those for the contact pairs.

$$\mathrm{D}^*\cdots\mathrm{A} \rightarrow \mathrm{D}^+\cdots\mathrm{A}^-$$

Such long-range electron transfer has so far been explained in terms of electron tunneling through the potential barrier, which is usually pictured in somewhat arbitrary manners under one-electron approximation. Also, we should notice the fact that the absorption band assigned to the transition to the *lowest* (π–π^*)-type excited state of TMBI in the gas phase appears at slightly higher energy than the ionization potential.[1,3] This band has a relatively sharp peak and is quite insensitive to the environments, in contrast to the absorption bands of Rydberg character.[3] The similar result is obtained for TMAE.[1,2,4] These results show that the *lowest* (π–π^*)-type excited state exists in the ionization continuum (i.e., above the potential barrier) as a discrete level, probably having a definite lifetime.[22] The existence of such a state seems to contradict the simple tunneling model because the transmission coefficient will become one for that state. The tunneling model may be regarded as giving the rate of the electron transfer only relatively with respect to the change of the height and width of the potential barrier.

Based on the preceding discussion, we can calculate the electron-transfer rate by an alternative model. Since the interaction between D* and A at a long distance R is very weak, the above process can be regarded as the radiationless transition between two stationary states; the locally excited state, $\Psi_{\mathrm{LE}}(\mathrm{D}^*\cdots\mathrm{A})$, and the electron-transfer state, $\Psi_{\mathrm{ET}}(\mathrm{D}^+\cdots\mathrm{A}^-)$, (processes 2 and 3 in Figure 2). The electron-transfer rate, k, can then be given by[23,24]

$$k = (2\pi/\hbar)\,|\langle\Psi_{\mathrm{ET}}|H|\Psi_{\mathrm{LE}}\rangle|^2\rho \quad (7)$$

$$\sim (2\pi/\hbar)\left(\sum_k \hbar^2\beta_{\mathrm{el}}{}^k F^k\right)^2\rho \quad (8)$$

where ρ is the effective level density of the electron-transfer state, $\beta_{\mathrm{el}}{}^k$ the electronic term of the vibronic coupling matrix element, and F^k the Franck–Condon factor. Taking $\Psi_{\mathrm{ET}}(\mathrm{D}^+\cdots\mathrm{A}^-)$ to be expressed similarly to eq 5 and $\Psi_{\mathrm{LE}}(\mathrm{D}^*\cdots\mathrm{A})$ to be identical with $\Phi_{\mathrm{LE}}(\mathrm{D}^*\cdots\mathrm{A})$, the locally excited configuration, the $\beta_{\mathrm{el}}{}^k$ can be represented as

$$\beta_{\mathrm{el}}{}^k = \sum_n b_n\langle\Phi(\mathrm{R}_n\cdots\mathrm{A})| \times (\partial U/\partial Q_k)_0|\Phi_{\mathrm{LE}}(\mathrm{D}^*\cdots\mathrm{A})\rangle/\Delta E^0 \quad (9)$$

because the matrix element $\langle\Phi_{\mathrm{CT}}(\mathrm{D}^+\cdots\mathrm{A}^-)|(\partial U/\partial Q_k)_0\cdot|\Phi_{\mathrm{LE}}(\mathrm{D}^*\cdots\mathrm{A})\rangle$ is negligibly small in the present case, where U is the total electronic potential energy, Q_k the kth normal coordinate, and ΔE^0 the difference in the electronic energy between the locally excited and electron-transfer states.

For simplicity, let us here omit all the b_n's for $n \neq 1$ in eq 5 or 9. The rate k can then be expressed in the form $k = b_1{}^2k_1$, where k_1 is given by

$$k_1 = (2\pi/\hbar)(\sum\hbar^2\langle\Phi(\mathrm{R}_1\cdots\mathrm{A})| \times (\partial U/\partial Q_k)_0|\Phi_{\mathrm{LE}}(\mathrm{D}^*\cdots\mathrm{A})\rangle F^k)^2\,\rho/(\Delta E^0)^2 \quad (10)$$

As mentioned before, the "Rydberg" orbital contained in $\Phi(R_n \cdots A)$ is very similar to that for the "Rydberg" state of D in the solvent in the absence of A. It can then be safely assumed that the matrix element of $(\partial U/\partial Q_k)_0$ between $\Phi(R_1 \cdots A)$ and $\Phi_{LE}(D^* \cdots A)$ in eq 10 is nearly equal to that between the lowest "Rydberg" and (π–π^*)-type excited states for D in the solvent in the absence of A. It might also be assumed that the latter is of the same order of magnitude as the corresponding matrix element for D in the gas phase by taking account of the fact that the lifetime of the fluorescence from the lowest "Rydberg" state is not so much altered by change from the gas phase to the solution phase.[4] We can then see that the value of k_1 can be estimated empirically based on the probability of the intramolecular radiationless transition from the Rydberg state to the (π–π^*)-type excited state of D, together with the considerations on the difference in F^k, ρ and ΔE^0 between the electron-transfer and intramolecular radiationless transitions.

To get a rough estimate for the rate k, we assume tentatively in the present work that the value of k_1 is of the order of 10^{12}–10^{13} s^{-1}, based on the probability of the intramolecular radiationless transition calculated from the line widths of the Rydberg bands of aromatic hydrocarbons.[25] Then, when $b_1{}^2$ is 10^{-4}, we obtain $k \sim 10^8$–10^9 s^{-1}, the same order of magnitude as the decay rate of the singlet excited state of D. Based on the result for TMAE in 1-methylnaphthalene, it does not seem unreasonable to assume this order of magnitude for $b_1{}^2$ at a relatively longer distance R between D and A than that for the contact pair, if the energy separation between the "Rydberg" and charge-transfer configurations is not too large.[15] It is to be noted that the electron transfer from the donor in the triplet excited state (process 3 in Figure 2) may occur at a longer distance R than that from the donor in the singlet excited state (process 2 in Figure 2) if it is energetically allowed because the triplet state has a very long lifetime.

As mentioned above, the coefficient $|b_n|$ becomes larger as the energy of the "Rydberg" configuration gets closer to that of the electron-transfer configuration. On the other hand, the terms $\beta_{el}{}^k$ and F^k becomes larger as the energy of the locally excited state gets closer to that of the "vertical" electron-transfer state (whose nuclear configuration is the same as the equilibrium nuclear configuration in the locally excited state). Then, we can see that the electron transfer can occur at a longer distance between D and A as the donor becomes stronger and has the lowest Rydberg state closer to the lowest (π–π^*)-type excited state. Aromatic amines such as TMPD and *N,N*-dimethylaniline are typical examples as such donors.[15] One might point out that the "vertical" electron-transfer state becomes energetically far lower than the locally excited state, if the acceptor is very strong. It should be noted, however, that the energy of the electron-transfer state becomes considerably higher as the distance between D and A gets larger. Also, another electron-transfer state in which the acceptor anion is excited may get energetically closer to the locally excited state.

The rate of electron transfer may be affected by the solvent polarity. Let us first consider the potential energy curves for the locally excited and electron-transfer states as functions of the structure of orientation of the solvent molecules. It is sure that the equilibrium structure of orientation in the locally excited state is quite different from that in the electron-transfer state in polar solvents. Since the potential energy generally changes steeply with the nuclear coordinates at nonequilibrium positions, we can expect that the potential energy for the electron-transfer state is largely altered even by the small change of the structure of orientation due to the thermal fluctuation near the equilibrium position in the locally excited state. Now, we redraw the above-mentioned potential energy curves as functions of the intramolecular normal coordinates of D and A. The effect of the difference in the structure of orientation of the solvent molecules can be represented by upward or downward shifts of the potential energy curves in this case. As can be seen from the above discussion, the shift of the potential energy curve for the electron-transfer state ranges over a wide region of energy in polar solvents, though that for the locally excited state is only of the order of kT. Since the terms $\beta_{el}{}^k$ and F^k depend strongly on the relative position of the potential energy curves, we can conclude that the rate k changes largely with the solvent polarity.

It must be emphasized that, according to the mechanism proposed here, the rate of electron transfer is negligibly small when the acceptor is in the excited state[26]

$$D \cdots A^* \rightarrow D^+ \cdots A^-$$

because the matrix element $\langle \Phi(R_n \cdots A)|H|(D \cdots A^*)\rangle$ is nearly zero for somewhat separate D and A. The electron transfer will then occur only through the overlap of their π or σ orbitals in this case.[24]

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Molecular Orbital Studies of Electron Donor–Acceptor Complexes. 3. Energy and Charge Decomposition Analyses for Several Strong Complexes: $OC-BH_3$, H_3N-BH_3, $CH_3H_2N-BH_3$, $(CH_3)_3N-BH_3$, and H_3N-BF_3

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Abstract: The interaction energies of five strong EDA complexes were analyzed in terms of electrostatic, exchange, polarization, and charge transfer components as functions of intermolecular separation and orientation. Decompositions of intermolecular forces and charge distributions were also performed. The $OC-BH_3$ complex is found to be a strong complex because of large charge-transfer and electrostatic energies. A deviation from the most favored C_{3v} approach results in a decrease in electrostatic stabilization, approach of the O end of CO to BH_3 is less desirable due to a decrease in charge-transfer energy, and the planar BH_3 forms a less stable complex than the pyramidal BH_3 as a result of increased exchange repulsion. The principal contribution to H_3N-BH_3 stabilization is the electrostatic interaction. The H_3N-BH_3 rotational barrier is due to exchange repulsion, while the small methyl substituent effect is due to a cancellation of the effects of polarization and exchange interactions.

I. Introduction

Numerous studies have been published on "electron donor-acceptor (EDA) complexes" concerning their structures, bonding characteristics, and spectroscopic, electric, and other physical properties.[1] A particularly interesting and difficult theoretical question concerns the origin of stabilization, i.e., the relative importance of electrostatic and charge transfer forces in the ground state of the complex. As is evident from Mulliken's characterization of these complexes as "charge-transfer complexes", earlier work was predicated on the belief that the stabilization was principally due to the charge transfer force.[2] Later Hanna et al.[3] argued that in benzene–halogen complexes the electrostatic interaction, in particular the quadrupole-induced dipole interaction, is the principal binding force. Mulliken and Person have proposed that the electrostatic forces are likely to dominate the binding only in weak EDA complexes.[4] Quantum chemical calculations should be able to provide insight for this important problem.

The energy and charge distribution decomposition analyses have been successfully used for the elucidation of the origin of hydrogen bonding in ground and excited states.[5-11] The method of Morokuma and co-workers[5-9] decomposes the interaction energy ΔE, utilizing clear definitions within the molecular orbital framework, into energy components—electrostatic (E_{ES}), exchange repulsion (E_{EX}), polarization (E_{PL}), charge transfer (E_{CT}), and the coupling term (E_{MIX}).

These interactions may be conceptually viewed in the following manner. ES is the classical interaction between the undistorted charge distributions on the monomers A and B, including dipole-dipole and all higher order terms. PL is the energy change resulting from the distortion of electron clouds of one monomer by the presence of the other and vice versa. EX is a direct consequence of the Pauli principle which dictates that electrons on the two molecules not occupy the same portion in space. CT is the interaction of occupied MO's of A with vacant MO's of B and vice versa and causes electron delocalization and charge transfer. MIX is the sum of various coupling terms between the above-mentioned components and is delivered as a difference between the total interaction energy ΔE and the sum of the above four terms.

It has been found that near the equilibrium geometry of most hydrogen bonded complexes the electrostatic and charge transfer (both attractive) energies and the exchange repulsion are the three major contributors of nearly comparable magnitude, one part of the attraction cancelling with the repulsion. It has also been recognized that the electrostatic interaction alone is often sufficient to predict the relative direction with which the proton donor and the acceptor approach each other.

Considering the fact that numerous ab initio studies have been carried out for hydrogen-bonded complexes,[5-9,12-13] it is surprising that only a handful of ab initio calculations have been published for EDA complexes.[9,14-22] The energy decomposition analysis has recently been applied to several weak n–π and π–π type EDA complexes, including $(CN)_2CO\cdots H_2O$, $(CN)_2C{=}C(CN)_2\cdots H_2O$, $H_2CO\cdots C_2H_4$, and $(CN)_2CO\cdots C_6H_6$. For the first two complexes, the electrostatic energy was found to be by far the most important contributor near the equilibrium geometries.[15] In the latter two, which are very weak complexes, the electrostatic, charge transfer, exchange repulsion, and dispersion energies are all of approximately equal importance.[16]

In order to gain additional insight into the nature and origin of bonding in EDA complexes, we have performed energy and charge distribution analyses for the ground state of the "strong" complexes, $OC\cdots BH_3$, $H_3N\cdots BH_3$, $(CH_3)H_2N\cdots BH_3$, $(CH_3)_3N\cdots BH_3$, and $H_3N\cdots BF_3$. Previous calculations for some of these systems include: Fujimoto, Kato, et al. ($OC-BH_3$ and H_3N-BH_3),[18] Armstrong, Perkins, et al. ($OC-BH_3$, H_3N-BH_3, and H_3N-BF_3),[20] Veillard (H_3N-BH_3),[21] and