Photoelectron Ejection and Fluorescence from Molecular "Rydberg" States in Polar Solvents

Yoshihiro NAKATO, Akihiro NAKANE,* and Hiroshi TSUBOMURA

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

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Absorption and fluorescence spectra and photo-current yield curves of tetraaminoethylenes are studied. The UV absorption of these compounds is mostly attributable to the transitions from the ground state to the "vertical" Rydberg-like and ionized states. Their spectral shapes in ether and in pentane are nearly coincident with each other, showing that these states just after excitation are little affected by the solvent polarity. Based on this result and the results of photo-current measurements, the spontaneous formation of free, solvated electrons from the "vertical" Rydberg-like states in polar solvents has been verified. It is also found that the maximum wave numbers, the lifetimes and the yields of the fluorescence from the lowest "relaxed" Rydberg-like state depend strongly on solvent polarity, temperature and rigidity. These results are explained by taking account of the competition between electron ejection and relaxation processes and of the presence of a non-fluorescent, solvated cation-electron pair. The photo-electron ejection from other organic molecules in polar solvents reported before is shown to be explained by the same scheme as presented here.

So far, several different mechanisms on the electron ejection from organic molecules into polar solvents under illumination in the near ultraviolet region have been proposed, as reviewed previously.[1,2] This rather conflicting situation seems to arise mainly from the change of the ionization threshold with solvent polarity, causing varied degree of solvation for the ejected electron and parent cation.

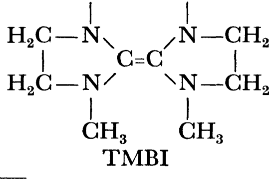
The solvated cation-electron pair was proposed by some authors as a long-lived intermediate state caused by excitation in order to explain the appearance of the absorption spectra assigned to the cation not contributing to the photo-current.[1,3-5] Such a state is of great interest, but more experimental knowledge seems necessary for defining it clearly.

Recently, we reported the absorption spectra of some molecules assigned to transitions to Rydberg-like and ionized states in organic solvents.[2,6,7] From the measurements of photo-currents and absorption spectra, it was suggested that a spontaneous formation of the solvated electron from the Rydberg-like states occurred in polar solvents, competing with the relaxation to the lower excited states.[2] It was also found that the energy and yield of the fluorescence, conceivably originating from the lowest Rydberg-like state, decreased with increasing solvent polarity.[2,8]

In the present paper, we will report the results of our detailed studies on the photo-electron ejection and the Rydberg-like states of tetraaminoethylenes in polar solvents.

Experimental

The preparation and handling of tetrakis(dimethylamino)-ethylene (TMAE), and 1,1′,3,3′-tetramethyl-2,2′-bi-imidazolidinylidene (TMBI), were described previously.[6]



TMBI

Purification of solvents was made in a similar way as described elsewhere.[2,6] These solvents, especially the polar ones, were carefully dried with Na-K alloy in evacuated ampoules.

Absorption spectra were measured with a Cary Model 15 spectrophotometer. Fluorescence and its excitation spectra were measured with an Aminco-Bowman spectrophotofluorimeter, which was calibrated at Prof. Mataga's laboratory to obtain the correct fluorescence quantum spectrum by use of a standard lamp. The spectral distribution of the excitation light intensity of this apparatus was also obtained by the actinometry using the fluorescence of a concentrated Rhodamin B solution. Steady-state photo-currents were measured by using a quartz cell equipped with two parallel electrodes.[2] The temperatures of the sample solutions were controlled by putting the cell in a quartz Dewar containing isopentane cooled with nitrogen gas. The fluorescence lifetime was measured with a nitrogen gas laser (λ 337.1 nm) as an exciting light source, having the duration of about 5 ns and a repetition frequency of *ca.* 50 Hz. The fluorescence decay was recorded by a photomultiplier, a sampling oscilloscope and an X-Y recorder.

Results

The absorption spectra of TMBI observed in pentane and diethyl ether are shown in Fig. 1. The absorption spectra, the photo-current yield curves and the fluorescence excitation spectra of TMAE in ether and hydrocarbons are shown in Fig. 2. The photo-

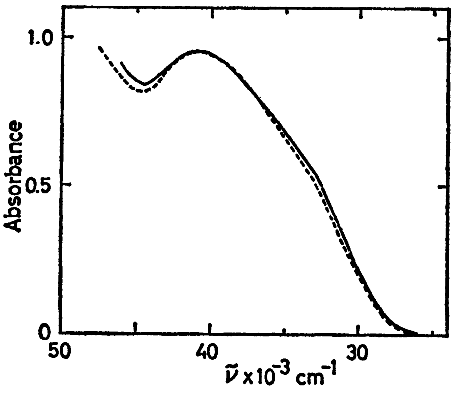


Fig. 1. The absorption spectra of TMBI in ether (----) and in pentane (——).

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* Present Address: Toray Industries Inc., Plastic Application Technology Dept., 9-1 Ooe-cho, Minato-ku, Nagoya 455-91, Japan.

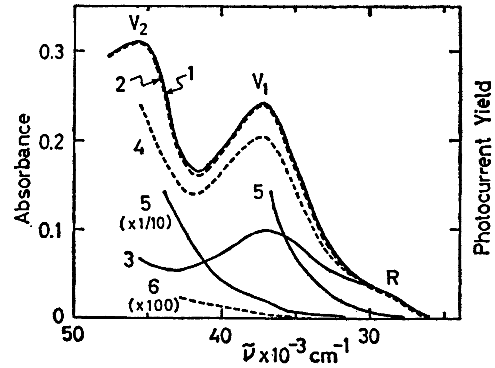

Fig. 2. The absorption spectra, the photo-current yield curves and the fluorescence excitation spectra of TMAE. Curve 1: The absorption spectrum in ether. Curve 2: That in pentane. Curve 3: The fluorescence excitation spectrum in ether. Curve 4: That in 3-methylpentane. Curve 5: The photocurrent yield curve in ether. Curve 6: That in pentane. The fluorescence excitation spectra both in ether and in 3-methylpentane are adjusted so as to make their strengths agree with those of the corresponding absorption spectra in the lower energy region.

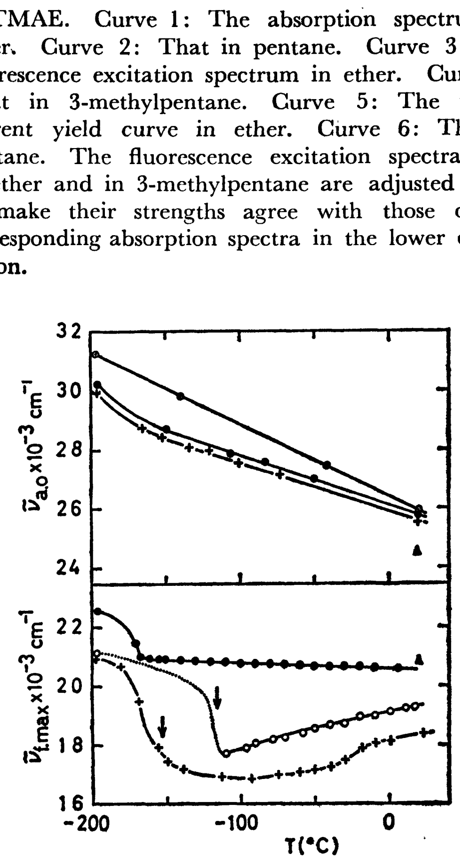

Fig. 3. The temperature dependence of the onset of the absorption band ($\tilde{\nu}_{ao}$) and the fluorescence maximum ($\tilde{\nu}_{f,max}$) of TMAE: (●) in 3-methylpentane, (○) ether, (+) 2-methyltetrahydrofuran (2-MTHF), (▲) the gas phase. The temperature dependence of the wave number of the absorption onset of TMBI in 3-methylpentane (⊙) is also included.[7] Arrows show the solidifying point of the solvent (the melting point in the case of ether and the temperature at which the dielectric constant abruptly changes in the case of 2-MTHF[13b]). Dotted lines are drawn by conjecture so that the temperature dependences of $\tilde{\nu}_{f,max}$, τ_f and ϕ_f^{rel} in Figs. 3 and 4 will be in harmony with each other in each solvent.

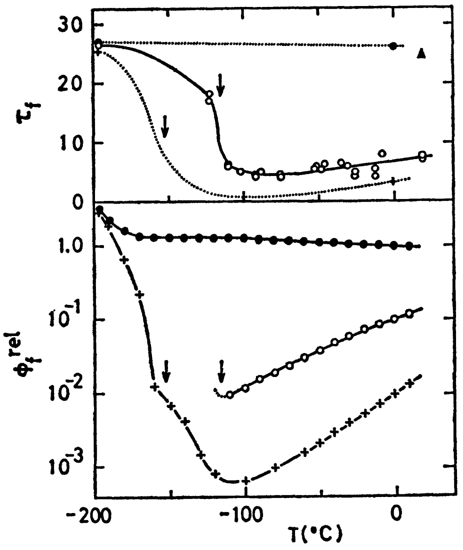

Fig. 4. The temperature dependence of the fluorescence lifetime (τ_f, in ns) and the relative fluorescence yield (ϕ_f^{rel}) of TMAE: (●) in 3-methylpentane, (○) ether, (+) 2-methyltetrahydrofuran, (▲) the gas phase. The wave number of excitation light is 30.3 kK for measurements of ϕ_f^{rel}, and 29.7 kK for τ_f. ϕ_f^{rel} is corrected for the change of the absorption intensity at 30.3 kK with temperature. The meanings of arrows and dotted lines are the same as those in Fig. 3.

current yield in the present work means $(\varepsilon \cdot i)/(I_0 - I)$ in a relative scale,[9] where ε, i and $(I_0 - I)$ are the molar extinction coefficient, the steady-state photo-current and the light intensity absorbed by the sample solution, respectively.[10] The absolute photo-ionization yield in ether is about 0.9×10^{-5} electrons per absorbed photon at 29.4 kK ($\times 10^3$ cm^{-1}) and that in pentane is about 1.6×10^{-7} at 40 kK.

Figure 3 shows the solvent and temperature dependences of the onset of the absorption spectrum and the fluorescence maximum of TMAE, and Fig. 4 shows those of the fluorescence lifetime and the relative yield. The absorption bands in polar solvents do not change much from those in nonpolar solvents. Both are gradually blue-shifted with decreasing temperature, while the fluorescence wave numbers, lifetimes and yields in polar solvents are quite different from those in nonpolar solvents. They show monotone decrease down to about −100 °C and abrupt increase below that due to solidification of these solvents.

The fluorescence of TMAE was quenched by atmospheric oxygen. When air was introduced into evacuated sample cells, the fluorescence intensity decreased instantaneously but the absorption intensity remained nearly the same at least for about ten minutes. The rate constant of the quenching reaction, calculated from the fluorescence lifetime, 7 ns, and an oxygen concentration, 4×10^{-3} M, is 1.9×10^{10} M^{-1} s^{-1}, the same order of magnitude as that for a diffusion-limited reaction.

Discussion

As reported previously,[6,7] the absorption spectrum of TMBI in the wave number region lower than 45 kK is assigned to the transitions to the Rydberg-like and ionized states. The transition to the lowest (π-π^*)-

type excited state of TMBI appears as the steeply rising absorption beginning at 45 kK. The close agreement of the spectra in pentane and ether (Fig. 1) shows that the Rydberg-like and ionized states just after the vertical excitations are little affected by the solvent polarity. This fact can also be regarded as a proof of the existence of "dry" electrons in polar solvents, first proposed by Hamill.[11)]

In the absorption spectra of TMAE (Fig. 2), only the transitions to the lower Rydberg-like states appear as a shoulder (denoted by R in Fig. 2) and those to the higher Rydberg-like states and to the ionized state are hidden by the strong (π-π^*)-type absorption bands (denoted by V_1 and V_2).[2,6)] However, the overall absorption spectrum in ether is identical with that in pentane.

Quite contrary, the photo-current yield curve and the fluorescence excitation spectrum in ether are much different from those in hydrocarbons (Fig. 2). Based on the above argument, this can be attributed to the relaxation processes from the vertical or Franck-Condon states, leading to different solvation states with solvent polarity.

Various relaxation processes expected for the ether solution are given in Fig. 5, including the ones already proposed and discussed in some detail in a previous paper.[2)] Since the "vertical" ionization threshold in ether should be equal to that in pentane (~34 kK) as seen from the close agreement of the absorption spectra, the steeply rising photo-current in the region higher than 34 kK observed in ether (Fig. 2) is assigned to the direct photoionization, and the photo-current in the lower energy region is assigned to process (2), the spontaneous formation of the solvated electrons from the "vertical" Rydberg states. The amount of charge carriers observed in ether at −65 °C is found to be twice as large as that at room temperature. This can be explained in view of the increase of the dielectric constant of ether (6.7 at −65 °C and 4.5 at room temperature). It is therefore expected that the ionization process (2) becomes more efficient in more polar solvents.

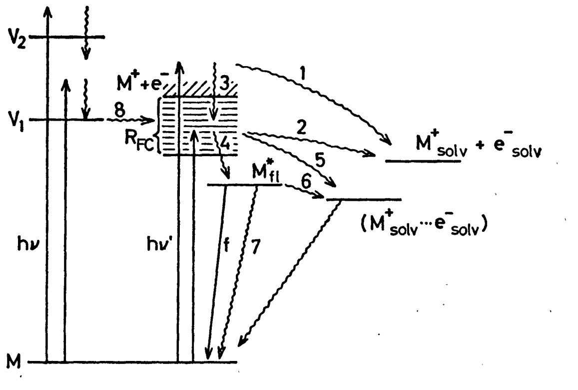

Fig. 5. The levels and processes showing photo-excitation and relaxation of TMAE in polar solvents such as ether. M: The ground state TMAE. V_1 and V_2: The (π-π^*)-type excited states of TMAE, each corresponding to the absorption bands denoted by V_1 and V_2 in Fig. 2. R_{FC}: The vertical (or Franck-Condon), Rydberg-like states. $M^+ + e^-$: The Franck-Condon, ionized state. M^*_{fl}: The fluorescent state (the solvated Rydberg state). $M^+_{solv} + e^-_{solv}$: The solvated cation and electron, free from each other. $(M^+_{solv} \cdots e^-_{solv})$: The non-fluorescent, solvated cation-electron pair. In nonpolar solvents, the state of free cation and electron contributing to photo-currents lies at almost the same energy as the Franck-Condon, ionized state. The solvated states such as $M^+_{solv} + e^-_{solv}$ and $(M^+_{solv} \cdots e^-_{solv})$ as well as the solvation processes (1), (2), (5), and (6) are of course absent in non-polar solvents and the fluorescent state is the Rydberg state situated in the solvent cavity.

The shape of the fluorescence excitation spectrum in ether in the lower energy region nearly coincides with that of the Rydberg absorption band (R), while the shape of the photo-current yield curve in ether does not (Fig. 2). These results show that the ionization process *via* the fluorescent state ($R_{FC} \rightsquigarrow M^*_{fl} \rightsquigarrow M^+_{solv} + e^-_{solv}$) is not a main process, or in other words, process (2) competes, as shown in Fig. 5, with other relaxation processes (4) and (5), which will be discussed later.

The fluorescence excitation spectrum in ether extends into the region of the photo-current action spectrum, indicating the presence of processes (3) and (4), the relaxation from the vertical, ionized and Rydberg states to the fluorescent state in ether as well as in nonpolar solvents. Its shape in the higher energy region is rather different from the absorption spectrum, though the fluorescence excitation spectrum in 3-methylpentane is much more similar to the absorption spectrum. These results indicate that processes (2) and (5) exist and process (1) is more probable in ether.

These fluorescence excitation spectra show peaks corresponding to those of the absorption spectra (V_1),[12)] suggesting the existence of non-radiative transition from the V_1-state to the Rydberg-like state (process (8)). One might thus expect that an auto-ionization from the V_1-state would occur in ether. The photo-current yield curve, however, shows very slight swelling at about 37 kK (Fig. 2). This fact can be explained by assuming that the molecules excited to the vibrationally excited V_1-state first relax to its lowest vibrational level lying near 30 kK, as shown in Fig. 5, and next pass into the Rydberg-like state, for which the photo-current yield is much smaller than for the case where the molecules are excited directly to the Rydberg-like or ionized states of the same energy as the vibrationally excited V_1-state.

The present results obtained in an extended temperature range (Fig. 3) are in good harmony with the structures of Rydberg states in solution discussed before,[2,8)] and confirm them. Namely, the gradual blue-shifts of the lowest Rydberg absorption bands with lowering the temperature are attributed to the elevation of the solvent density surrounding the solute molecules increasing the repulsive interaction between the Rydberg electron and the solvents in the vertical Rydberg state. The relative constancy of the position of the fluorescence maximum with temperature in the case of fluid, 3-methylpentane solutions is ascribed to the presence of the relaxation from the vertical to the fluorescent state, leading to the expansion of the solvent cavity so as to lower the Rydberg electron-solvent repulsive interaction. The red-shifts of the fluorescence maxima in fluid, polar solvents with decreasing temperature are also ascribed to the relaxation process leading to the solvated Rydberg state, going further by the increasing dielectric polarization at low temperature.[13] The blue-shifts of the fluorescence maxima on solidification of the solvents, both polar and nonpolar, are attributed to the restriction of such relaxations in rigid solutions.

The fluorescence lifetimes (τ_f) decrease greatly with increasing polarity and with decreasing temperature in polar solvents, but are restored to nearly the same level in the rigid solvents at 77 K as that in 3-methylpentane at room temperature, irrespective of whether they are polar or non-polar (Fig. 4). The Rydberg orbital in the fluorescent state in rigid solutions at 77 K must be largely distorted due to the repulsive interaction between the Rydberg electron and the surrounding solvent molecules as seen from the blue-shifts of the fluorescence maxima, while that in hydrocarbons at room temperature must be almost the same as that in the vapor phase, since the molecules in the Rydberg state are situated within the solvent cavity. These considerations lead to the conclusion that the fluorescence lifetime is hardly affected by distortion of the Rydberg orbital due to the surrounding solvent molecules.

We therefore tentatively assume that a non-fluorescent, solvated cation-electron pair, $(M^+_{solv}\cdots e^-_{solv})$, exists as an intermediate state attained by processes (5) and (6) in the case of polar solvents, as shown schematically in Fig. 5. The lifetime in polar solvents is then expressed by $\tau_f=1/(k_f+k_7+k_6)$, where k_f and k_7 are the rate constants of radiative and non-radiative processes from the fluorescent to the ground state, and k_6 is that of process (6). Since k_f and probably k_7 are nearly independent of the distortion of the Rydberg orbital and, therefore, of the solvent polarity, as discussed above, the decrease of τ_f with solvent polarity is mainly attributed to the increase of k_6.

The fluorescnce yield, ϕ_f, decreases with the solvent polarity much more than the fluorescence lifetime, τ_f, as seen from Fig. 4. The fluorescence yield in polar solvents is expressed by $\phi_f=k_4\cdot(k_4+k_5+k_2)^{-1}\cdot\tau_f\cdot k_f$. Based on the same reason as above, the decrease of (ϕ_f^{rel}/τ_f) with the solvent polarity must also be attributed to the increase of (k_2+k_5). Since the absolute value of k_2 is very small, as seen from the small absolute photo-current yield ($\sim 10^{-5}$ at 30.3 kK in ether), the decrease of (ϕ_f^{rel}/τ_f) is mostly attributed to the increase of k_5. Thus, we can conclude that a large part of molecules excited to the Rydberg-like states near 30 kK in ether pass directly or *via* the fluorescent state into the solvated cation-electron pairs and only a small fraction turns to the free charge carriers or fluoresces. With increasing solvent polarity, process (2) will become more important.

The Photo-ionization of Other Organic Molecules in Polar Solvents. The ionization thresholds of organic molecules in nonpolar solvents are found to be 1.1—1.8 eV lower than the gas-phase ionization potentials, depending on the molecular size of solute and the molecular sphericity of solvent.[7,14–16] According to the scheme of the photo-electron ejection proposed in the present work, the ionization threshold in a polar solvent is expected to be further lowered, down to the lowest vertical Rydberg-like state.

The ionization threshold of *N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine (TMPD) in hexane is measured to be about 5.0 eV,[15,16] 1.2 eV lower than the gas-phase ionization potential, 6.20 eV.[17] Richard and Thomas showed that TMPD was photo-ionized in water by illumination even at a photon energy of 3.57 eV.[4] The similar conclusion was also derived from an analysis of the fluorescence lifetimes and yields for TMPD in water–ethanol mixed solvents.[18] The lowest Rydberg states of aniline and its alkyl derivatives were reported to lie in the range 4.7—4.2 eV, being parallel to the sequence of decreasing ionization potentials.[19] Thus, the additional lowering of the ionization threshold of TMPD observed in polar solvents can be explained by the electron ejection from the lowest Rydberg-like state.

The ionization thresholds of aromatic hydrocarbons such as anthracene, pyrene and perylene in boric acid glass at room temperature were reported to be about 2.2—2.5 eV lower than the gas-phase ionization potentials.[20] These results can also be regarded as showing the electron ejection *via* the Rydberg-like state in polar solvents.[21]

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