TABLE I: Catalog of Possible and Forbidden Solvated Electron States As Determined by Threshold Photoconductivity Spectra[a]

	l'	
l	possible angular momenta	forbidden angular momenta
0	1	none
1	0, 2	1
2	3	0, 1, 2
3	4	0, 1, 2, 3
⋮	⋮	⋮
l	$l + 1$	0, 1, 2, ..., l

[a] The integer l appears in eq 2.26. The ground-state solvated electron orbital angular momentum quantum number is l', and the quantum number for the z component of the orbital angular momentum is m'. For $l = 0$, the selection rule requires the existence of a state with $l' = 1$, $m' = 0$ or ± 1. For $l = 1$, the existence of a state with $l' = 1$, $m' = 0$ and/or $l' = 2$, $m' = 0$ or ± 1 is required. The state with $l' = 1$, $m' = 0$ or ± 1 is forbidden. For $l \geq 2$, the existence of a state with $l' = l + 1$, $m' = 0$ or ± 1 is required. States with $l' \leq l$ and $m' = 0$ or ± 1 are forbidden.

results from the experimental point of view. Consider the case where the photocurrent cross section has been experimentally determined to obey eq 2.26 with a value of $l \geq 2$. We may conclude that $\mathbf{K}(0) = \mathbf{K}(1) = ... = \mathbf{K}(l-1) = 0$ and $\mathbf{K}(l) \neq 0$. Find the relevant value of l in the first column of the table. From the second column, one may conclude that solvated electron wave functions with $l' = l + 1$, $m' = 0$ or ± 1 exist. Wave functions with $l' \leq l$, $m' = 0$ or ± 1 are forbidden; otherwise, the cross section in the threshold region would depend upon a smaller value of l than the one found. The forbidden values of l are given in the third column of the table. On the basis of the threshold behavior of the cross section alone, however, nothing can be concluded concerning the existence of states with $l' \geq (l + 2)$. These angular momentum states contribute powers of k in eq 2.19 which are higher than the one which determines the threshold behavior.

Discussion and Conclusions

The photocurrent I is proportional to the cross section σ. If eq 1.1 and 2.26 are to be proportional, we see that l must have the value unity. Because B was not determined in the experiments,[3] it is not possible to compare it with the factors multiplying $E(E - E_{\text{th}})^{(2l+1)/2}$ in eq 2.26.

Nevertheless, because $l = 1$, we conclude on the basis of Table I that the ground state of the solvated electron in the amine and alcohol glasses must have s character ($l' = 0$) or d character ($l' = 2$) or a linear combination of both. Due to Table I, moreover, if d character is involved, $m' = 0$ or ± 1. In the case of d character, we cannot conclude anything one way or the other concerning the existence of substates $m' = \pm 2$. The existence of p character ($l' = 1$) is forbidden, as indicated in the Table.

Our conclusion that l' can be zero is consistent with the frequently made assumption that the ground state of the solvated electron is a pure s state.[10] Inasmuch as glasses are isotropic, it may be that the Hamiltonian of the solvated electron is spherically symmetric. In that case, the orbital angular momentum operator would commute with the Hamiltonian, and the angular momentum and energy would have simultaneous eigenfunctions. A pure s-energy eigenstate would then be possible.

Our derivation of the selection rules is similar to that of Geltman, who treated the cross section for electron photodetachment from negative ions of diatomic molecules.[11] Geltman's result was subsequently extended to cover molecular negative ions of any symmetry by Reed et al.[12]

Finally, it is to be noted that eq 2.26 is an absolute formula for the photocurrent cross section. It is accurate to the extent that an electron in the conduction band of the glass can be represented by the function $\exp(i\mathbf{k}\cdot\mathbf{r})$.

---

(10) T. Shida, S. Iwata, and T. Watanake, *J. Phys. Chem.*, **76**, 3683 (1972).
(11) S. Geltman, *Phys. Rev.*, **112**, 176 (1958).
(12) K. J. Reed, A. H. Zimmerman, H. C. Anderson, and J. I. Brauman, *J. Chem. Phys.*, **64**, 1368 (1976).

Picosecond and Nanosecond Laser Photolyses of *p*-(Dimethylamino)phenyl Azide in Solution

Takayoshi Kobayashi,* Hiroyuki Ohtani,[†]

Department of Physics, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Kaoru Suzuki,

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

and Tsuguo Yamaoka

Department of Image Science and Technology, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba-shi, Chiba 260, Japan *(Received: August 6, 1984)*

Photodissociation of *p*-(dimethylamino)phenyl azide (DMAPA) in toluene at room temperature takes a place from the excited singlet state of azide within 6 ps. A transient absorption spectrum of a precursor of the relevant nitrene, *p*-(dimethylamino)phenylnitrene (DMAPN), was measured, and the formation time of DMAPN in the ground triplet state was determined to be 120^{+58}_{-26} ps.

Introduction

Photochemical or thermal decomposition of azides produces highly reactive intermediates, nitrenes[1] the ground state of which is triplet. Nitrenes are reactive because of electron deficiency of the nitrogen atom. Reactions are, for example, dimerization, insertion, and hydrogen abstraction.[1] The chemistry of azides and nitrenes attracts attention because of the interest both in application and in fundamental research. Reactions of nitrenes are being applied to materials for photoimaging and microlithographic processes.[2] From the viewpoint of fundamental research, azides

---

[†] Hamamatsu Photonics, Ichino-cho, Hamamatsu-shi, Shizuoka 435, Japan.

(1) (a) Lwowski, W. "Nitrenes"; Interscience: New York, 1970; pp 99–162. (b) Reiser, A.; Wagner, H. M. In "Photochemistry of the Azido Group"; Patai, S., Ed.; Interscience: New York, 1971; pp 441–501.

0022-3654/85/2089-0776$01.50/0

are good model compounds for the study of primary processes in photodissociations. Thermal reaction of nitrenes can also be studied with nanosecond or picosecond resoltuion with the aid of nanosecond or picosecond laser "photolysis", since nitrenes are easily formed by the photodissociation of relevant azides in the picosecond or nanosecond time scale (vide infra). In spite of the above-mentioned interest and importance, photochemical primary processes of azides or nitrenes in the picosecond regime have never been studied.

In the present paper we have studied the mechanism of the photodissociation of *p*-(dimethylamino)phenyl azide (DMAPA) in toluene with nanosecond (Q-switched Nd:YAG and N_2 lasers), picosecond (mode-locked ruby laser), and subpicosecond (passively mode-locked dye laser) spectroscopy apparatus. Dissociation of the azide in the excited singlet state to the relevant nitrene, *p*-(dimethylamino)phenylnitrene (DMAPN), was found to take place within 6 ps. The formation of DMAPN in the ground triplet state proceeds via a singlet precursor (DMAPN in the excited singlet state or a relevant tautomer) with a time constant of 120^{+58}_{-26} ps.

Experimental Section

Laser Photolysis. Excitation light sources for nanosecond photolysis were a N_2 laser (337 nm, 10-ns fwhm, Molectron UV 24) and a third harmonic of a Q-switched Nd:YAG laser (355 nm, 5-ns fwhm, Quanta-Ray DCR-1A). A probe light source was a Xe flash lamp (300 W, 500 μs, Varian Xenon Illuminator, VIX 300F). Output signals of a photomultiplier (Hamamatsu, R666S) coupled with either a Shimadzu Bausch & Lomb monochromator (f = 17 cm with a 1350 grooves/mm grating) or Ritsu MC 10N monochromator (f = 10 cm with a 600 grooves/mm grating) were digitized by a transient recorder (Iwatsu, DM901), and stored in floppy diskettes after being accumulated in a microcomputer (NEC, PC8001).

Excitation light sources for picosecond and subpicosecond photolyses were a second harmonic of a mode-locked ruby laser (347 nm, 30-ps fwhm) and a second harmonic of a passively mode-locked rhodamine 6G laser pumped by a CW Ar^+ laser (305 nm, 0.5-ps fwhm), respectively. The picosecond and subpicosecond spectroscopy apparatus have been reported elsewhere.[3,4]

The sample of DMAPA in methylcyclohexane rigid matrix (77 K) was exposed to a Xe lamp (450 W) for about 5 min. The azide sample decomposed almost completely to the relevant nitrene. The absorption spectrum of the nitrene at 77 K was measured with a spectrometer (Cary 14).

Materials. DMAPA was synthesized by the following method. (*N*,*N*-Dimethylamino)-*p*-phenylenediamine was dissolved in an aqueous solution of 10% HCl. Diazotization of the amine was performed by adding saturated $NaNO_2$ aqueous solution to the solution. After the diazotization NaN_3 was added and the DMAPA was precipitated. The precipitate was filtrated, washed with water, dried, and recrystallized from ethyl ether solution. Toluene (Kodak or Dojin, spectroscopic grade) was used as solvent without further purification. Reagent grade phenol (Tokyo Kasei) was purified by distillation. Methylcyclohexane (Wako Jun-yaku, spectroscopic grade) was used after distillation. The azide samples were prepared with concentrations of 0.5–1 in absorbance units (1-mm light path) at the excitation wavelength for laser photolysis, and unless otherwise stated the concentrations were kept the same.

Results and Discussion

The absorption spectra of the transient species at room temperature and of the photoproduct at 77 K of DMAPA are shown in Figure 1. The open circles in the figure show the time-resolved spectrum just after excitation of the azide in toluene solution by 10-ns N_2 laser pulse at room temperature. The solid curve in the figure shows the absorption spectrum of the photoproduct in methylcyclohexane matrix at 77 K. Both spectra show an intense characteristic band with a peak at 470 nm. The spectrum resembles that of T_1 (the lowest excited triplet state) $\leftarrow T_0$ (the ground triplet state) in *p*-aminophenylnitrene formed by the photodissociation of the relevant azide.[5] The transient spectrum shown in Figure 1 (open circles) is converted to the other spectrum within 180 μs. The final spectrum has an absorption maximum around 400 nm. The increase in absorbance (430–480 nm) follows second-order kinetics. These results indicate that the transient spectrum in Figure 1 (open circles) is due to the $T_1 \leftarrow T_0$ transition in DMAPN and that the second-order process corresponds to the dimerization of DMAPN to 4,4′-bis(*N*,*N*-dimethylamino)azobenzene.[6] The broader spectrum at room temperature than at 77 K is due to the population of vibrationally excited states. The spectra shown in Figure 1 were not assigned to intermediates in the chain reaction proposed by Waddell and Go[7] because of the following two reasons: (i) The reaction of nitrene with azide does not take place in a rigid matrix. (ii) The formation of azobenzenes does not follow second-order but first-order kinetics in the chain

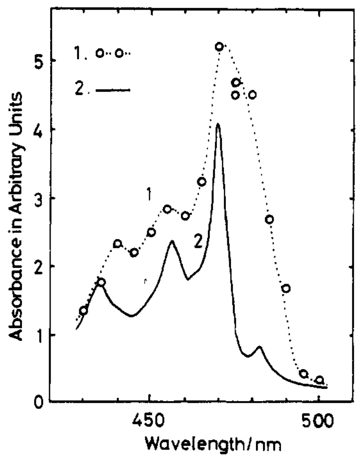

Figure 1. Absorption spectra of triplet *p*-(dimethylamino)phenylnitrene. Open circles (curve 1) show the absorption spectrum in toluene 10 ns after 337-nm excitation (10-ns fwhm) at room temperature. A solid line (curve 2) shows the absorption spectrum in methylcyclohexane matrix at 77 K.

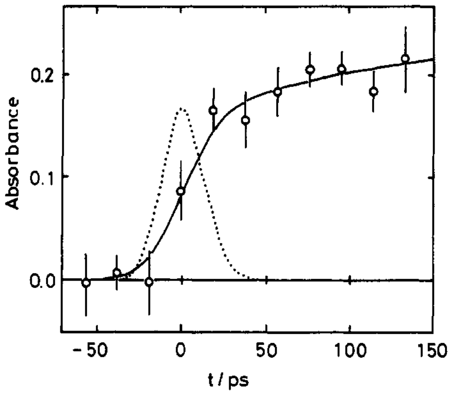

Figure 2. Time dependence of transient absorption at 465 nm following 347-nm excitation (30-ps fwhm) of *p*-(dimethylamino)phenyl azide in toluene at room temperature. The buildup of the transient absorption shows an initial fast process and a following slow process. The calculated curve (—) was obtained by summing two growing curves with best-fitted time constants of 0 and 120 ps. Excitation (···) and probe pulse shapes were taken to be Gaussian (30-ps fwhm) for the convolution calculation.

---

(2) (a) Tsunoda, T.; Takayama, M., Paper presented in part at the PIRA (The Research Association for the Paper and Board, Printing and Publishing Industry, England) International Conference, London, April 1975. (b) Tsunoda, T.; Yamaoka, T.; Takayama, M. *Nippon Kagaku Kaishi* **1975**, 2074–9. (c) Koseki, K.; Yamaoka, T. *Ibid.* **1983**, 1708–14.

(3) Kobayashi, T.; Nagakura, S. *Chem. Phys. Lett.* **1976**, *43*, 429–34.

(4) (a) Ippen, E. P.; Shank, C. V. In "Picosecond Phenomena"; Shank, C. V., Ippen, E. P., Shapiro, S. L., Eds.; Springer-Verlag: West Berlin, 1978; pp 103–7. (b) Ippen, E. P.; Shank, C. V. In "Ultrashort Light Pulses"; Shapiro, S. L., Ed.; Springer-Verlag: West Berlin, 1978; pp 83–122.

(5) Smirnov, V. A.; Brichkin, S. B. *Chem. Phys. Lett.* **1982**, *87*, 548–51.

(6) Absorption maxima of 4-(*N*,*N*-dimethylamino)azobenzene have been reported to be 415 nm (for trans) and 458 and 365 nm (for cis). Fischer, E.; Frei, Y. *J. Chem. Phys.* **1957**, *27*, 328–30.

(7) Waddell, W. H.; Go, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 5804–5.

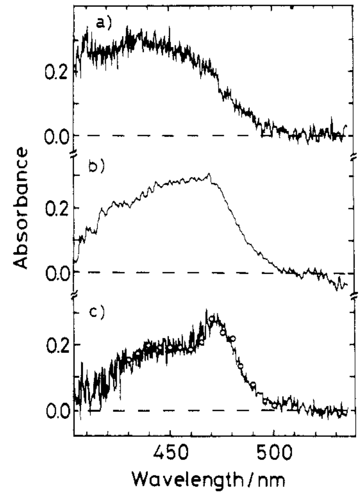

Figure 3. Transient absorption spectra of *p*-(dimethylamino)phenyl azide in toluene following 305-nm excitation (0.5-ps fwhm) at different delay times: (a) 6 ps, (b) 25 ps, and (c) 100 ps, respectively. Open circles show the spectral dependence of the sum of the absorbance of 25-ps spectrum with 61% weight and 10-ns spectrum with 39% weight.

reaction. The ground triplet nitrene is formed within the resolution time of the nanosecond spectroscopy apparatus (10 ns) at room temperature.

Figure 2 shows the time dependence of the transient absorption intensity of DMAPA in toluene excited by the 30-ps (fwhm) pulse at 347 nm at room temperature. Monitoring wavelength (465 nm) corresponds to the characteristic absorption band of the ground triplet nitrene. Errors (δA) shown in Figure 2 were obtained from the equation

$$\delta A = [\sum_{i=1}^{n}\{A(t)_i - A(t)\}^2/(N-1)]^{1/2}$$

The time profile of the transient absorption cannot be simulated with an exponentially growing curve calculated with any single time constant. The curve seems to be composed of an initial fast process with a time constant shorter than the ruby laser resolution time (30 ps) and a following slow process. The time constant for the slow process is 120^{+58}_{-26} ps.

Parts a–c of Figure 3 show the transient absorption spectra 6, 25, and 100 ps after 305-nm excitation (0.5-ps fwhm pulse) of DMAPA at room temperature. The transient spectra at 6 and 25 ps are due to precursors of the ground triplet nitrene as will be discussed later. The transient spectrum at 100 ps can be attributed to the superposition of the 25-ps precursor and the ground triplet nitrene. A simulated spectrum (open circles in Figure 3c) composed of a spectrum at 25 ps (61%, Figure 3b) and that of the triplet nitrene (39%, Figure 1) is essentially identical with that experimentally obtained at 100 ps (Figure 3c). Therefore, the spectrum shown in Figure 3b is attributed to a precursor of the ground triplet nitrene. The conversion from the precursor to the ground triplet nitrene occurs with a time constant of about 120 ps which was determined with the picosecond apparatus (see Figure 2). By use of the time constant (120 ps) and the above fraction of the precursor (61%) and the triplet nitrene population, the ratio of the absorption cross section of the precursor at 465 nm to that of the triplet nitrene was obtained to be 0.48 ± 0.12.

The quantum yield of the formation of nitrene in the ground triplet state from the relevant azide was measured to be unity in direct excitation while the yield was very low in the triplet sensitizer excitation experiment.[8] Therefore, the dissociation of DMAPA mainly occurs in its excited singlet state. The quantum yield of nitrene formation from 4,4′-diazidobenzophenone has been reported to be 1.0.[9] This implies that the dissociation rate is much larger than that of the intersystem crossing which is about 10^{11} s^{-1} for the parent molecules, benzophenone.[10] Therefore, the dissociation time constant is estimated to be much shorter than 10 ps. A possible formation pathway of DMAPN in the ground triplet state ($^3N(T_0)$) is described as

$$^1A^* \xrightarrow[-N_2]{<6\text{ ps}} {}^1N^*(S_n) \xrightarrow{<25\text{ ps}} P \xrightarrow{120\text{ ps}} {}^3N(T_0)$$

$^1A^*$ and $^1N^*(S_n)$ are DMAPA in the dissociative excited singlet state and DMAPN in the higher excited singlet state, respectively. There are three candidates for the precursor of $^3N(T_0)$, which is designated as P in the above-mentioned possible formation pathway. They are DMAPN in the lowest excited triplet state ($^3N^*(T_1)$) and in the lowest excited singlet state ($^1N^*(S_1)$) and a singlet valence tautomer such as relevant azepine or azirine.[11]

Firstly, nitrene in the excited triplet state can be ruled out because of the following reason. The time constants of internal conversion from S_1 to S_0 are usually several hundred nanoseconds, except in special cases, for example intra-[12a] or intermolecular[12b] proton-transfer quenching.[12] They depend on energy separations between initial and final states. The time constant, 120 ps, is too short to be assigned to the internal conversion from $^3N^*(T_1)$ to $^3N(T_0)$, because the energy level of $^3N^*(T_1)$ is estimated to be 20 700 cm^{-1} (482 nm) from the absorption spectrum at 77 K (Figure 1). There is no forbidden excited triplet state in the lower energy region.[13] Therefore, P cannot be assigned to $^3N^*(T_1)$ but to a singlet species.

Secondly, if P is attributed to $^1N^*(S_1)$, then the time constant for the $S_1 \rightarrow T_0$ intersystem crossing in DMAPN is 120 ps. This is very close to the time constant for the $S_1 \rightarrow T_0$ intersystem crossing in diphenylcarbene which was reported to be 110 ps ((9.1 ± 1.0) × 10^9 s^{-1}).[14] The time constant for the $S_1 \rightarrow T_0$ intersystem crossing in 1-pyrenylnitrene was reported to be 22 ns.[15] The time constant is more than 2 orders of magnitude longer than that in DMAPN obtained in the present study. The large difference may be due to the difference in the electronic characters of the excited singlet and ground triplet states in the two nitrenes. The slow process of the formation of 1-pyrenylnitrene (22 ns) was interpreted in terms of the intersystem crossing between the lowest excited singlet and ground triplet states, the electronic configurations of which are the same character. The singlet precursor (P) of DMAPN in the ground triplet state seems to have a different electronic configuration from that of the ground triplet nitrene because the intersystem crossing between the same electronic configurations usually occurs in the nanosecond time regime. The rapid formation of $^3N(T_0)$ in DMAPN may be due to the intramolecular charge-transfer structure in $^1N^*(S_1)$ induced by the *p*-dimethylamino group. The charge-transfer structure of the precursor deactivates the reaction in the singlet state[16] and enhances the intersystem crossing.

Finally, the relevant nitrene tautomers can also be considered to be the precursor of the ground triplet state nitrene. It is well-known that singlet valence tautomers of nitrenes (azirine or

---

[8] Yamaoka, T., unpublished results. The yield of azo compounds is unity in the flash photolysis of DMAPA in benzene. Triplet nitrene is efficiently formed.

[9] Reiser, A.; Marley, R. *Trans. Faraday Soc.* **1968**, *64*, 1806–15.

[10] Scott, G. W.; Anderson, Jr., R. W.; Hochstrasser, R. M.; Lutz, H. *Bull. Am. Phys. Soc.* **1975**, *20*, 46.

[11] (a) DeGraff, B. A.; Gillespie, D. W.; Sundberg, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 7491–6. (b) Chapman, O. L.; Le Roux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 282–5.

[12] (a) The time constant of $S_1 \rightarrow S_0$ relaxation of 2-hydroxybenzophenone in hexane is 35 ± 5 ps. Hou, S.-E.; Hetherington III, W. M.; Korenowski, G. M.; Eisenthal, K. B. *Chem. Phys. Lett.* **1979**, *68*, 282–4. (b) The time constant of $S_1 \rightarrow S_0$ internal conversion of Michler's ketone (4,4′-bis(*N*,*N*-dimethylamino)benzophenone) in ethanol is 19 ps. Ohtani, H.; Kobayashi, T.; Suzuki, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 43–7.

[13] Semiempirical MO calculations of phenyl azide have been reported: Shillady, D. D.; Trindle, C. *Theor. Chim. Acta* **1976**, *43*, 137–44.

[14] Sitzman, D. V.; Dupuy, C.; Wang, Y.; Eisenthal, K. B. In "Picosecond Phenomena"; Eisenthal, K. B., Hochstrasser, R. M., Kaiser, W., Laubereau, A., Eds.; Springer-Verlag: West Berlin, 1982; Vol. III, pp 168–73.

[15] Sumitani, M.; Yoshihara, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2995–8.

[16] McRobbie, I. M.; Meth-Cohn, O.; Suschitzky, H. *Tetrahedron Lett.* **1976**, *12*, 925–8, 929–32.

J. Phys. Chem. **1985**, *89*, 779-782 779

azepine) are formed in the photolyses of aryl azides.[11] 1-Pyrenylnitrene which has a large aromatic ring moiety may be more stable than the relevant tautomer, and it may be the reason why the tautomers could not be observed in 1-pyrenylnitrene.

In conclusion, the possible formation scheme of DMAPN is described as

$$^1\mathrm{A}^* \xrightarrow[-\mathrm{N}_2]{<6\text{ ps}} {}^1\mathrm{N}^*(\mathrm{S}_n) \xrightarrow{<25\text{ ps}}$$

$$^1\mathrm{N}^*(\mathrm{S}_1) \text{ or nitrene tautomer} \xrightarrow{120\text{ ps}} {}^3\mathrm{N}(\mathrm{T}_0)$$

In order to definitely conclude which of the two possible candidates, $^1N^*(S_1)$ and tautomer, is the major precursor of the ground triplet nitrene, it is necessary to perform further experiments such as time-resolved resonance Raman scattering.

Acknowledgment. T.K. expresses sincere gratitude to Dr. C. V. Shank for his hospitality during T.K.'s stay at Bell Labs, for his kindness to put the subpicosecond spectroscopic equipment at T.K.'s disposal, and for fruitful discussions. We are indebted to Dr. H. Uchiki for his help in the construction of nanosecond Nd:YAG laser spectroscopy apparatus. This work was partly supported by grants to T.K. from the Education Agency of Japan, the Kurata Foundation, and the Toray Science Foundation.

A Theoretical Study of Lone-Pair Orbitals in Chemical Interactions

Hiroshi Fujimoto,* Terumasa Yamasaki, Itaru Hataue, and Nobuaki Koga[1]

Division of Molecular Engineering, Kyoto University, Kyoto 606, Japan (Received: July 17, 1984)

A method of generating the molecular orbitals that take part actively in chemical interactions has been utilized for an examination of lone electron pairs in charge-transfer interactions with a proton. The molecules studied contain either nitrogen or oxygen atoms or both, ranging from ammonia to pyridine and from water to furan. The oribtals have been shown to be localized about 90% or more on the atom under attack of a proton. The interacting orbitals derived here are compared with the highest occupied frontier molecular orbitals and with the localized molecular orbitals that are obtained for those molecules in an isolated state.

Introduction

A couple of valence electrons belonging to the same atom but not involved in chemical bondings are familiar in chemistry, being called lone electron pair or simply lone pair. Not only physical properties but also molecular structures are influenced strongly by the existence of such electron pairs. For instance, ammonia has a pyramidalized geometry, showing a clear contrast to methyl cation. The valence-shell-electron-pair repulsion scheme has been applied conveniently to understand the structures of those molecules.[2-4] In the meantime, a unified explanation of a wide variety of molecular structures including molecules having a lone pair of electrons was presented recently on the basis of conjugation and hyperconjugation of localized σ orbitals.[5] In any case, the concept of hybridized atomic orbitals has been found to be quite useful for a simple theoretical interpretation of experimental findings.[6] One of the familiar methods of calculating numerically the hybridized orbitals has been due to Edmiston and Ruedenberg.[7]

On the other hand, lone electron pairs exhibit some characteristic behavior in chemical interactions. Coordination compounds are produced easily. For instance, an ammonia molecule gives an ammonium ion upon protonation and a borazane molecule upon charge transfer to a borine. It has been argued often that the highest occupied molecular orbital (MO) plays a critical role in electron donation to an electron acceptor.[8] However, the canonical MOs are delocalized substantially over the constituent atoms in a molecule. Thus, there seems to be a significant discrepancy between the lone-pair orbitals which are suited for understanding the structure of molecules and the orbitals which are thought to participate in charge-transfer interactions. An important question raised here is how local chemical interactions can be.

An ab initio MO calculation was carried out to guess the sizes and orientations of lone pairs from the profile of potential surfaces by placing a dummy atom as a probe.[9] No attempt appears to have been made so far, however, to obtain theoretically the orbitals that are actually taking part in charge-transfer interactions with an electron acceptor. By extending the concept of frontier orbital interactions, we proposed a method to obtain the orbitals for a reagent and a reactant that were most suited for representing delocalization of electrons between them.[10] In this paper we will examine how lone-pair orbitals look in chemical interactions.

Method of Calculation

The details of our theoretical treatment for yielding the orbitals which participate actively in chemical interactions were described in one of our previous papers.[11] Here, we mention only briefly a characteristic aspect of the method to clarify our following discussion. We consider a charge-transfer interaction between two systems, A and B. For the present purpose, we assume here that transfer of electronic charge takes place only from A to B. Then, the wave function of the system composed of A and B is written as[12]

$$\Psi = C_0\Psi_0 + \sum_{i=1}^{m}\sum_{l=1}^{N-n} C_{i\to l}\Psi_{i\to l} + \ldots \qquad (1)$$

where $\Psi_{i\to l}$ signifies the electron configuration in which an electron is shifted from the doubly occupied MO ϕ_i of A ($i = 1, 2, ..., m$) to the unoccupied MO ψ_l of B ($l = n + 1, n + 2, ..., N$) and Ψ_0 means the initial non-electron-transferred configuration (A·B).

---

(1) Present address: Institute for Molecular Science, Okazaki 444, Japan.

(2) Gillespie, R. J. *J. Chem. Educ.* **1970**, *47*, 18.

(3) Schmiedekamp, A.; Cruickshank, D. W. J.; Skaarup, S.; Pulay, P.; Hargittai, I.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2002.

(4) For a criticism of VSEPR theory and a new electrostatic model, see: Bills, J. L.; Steed, S. P. *Inorg. Chem.* **1983**, *22*, 2401.

(5) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.

(6) See, for example: Peters, D. *J. Chem. Soc.* **1963**, 2003, 2015, 4017; **1964**, 2901, 2908, 2916.

(7) Edmiston, C; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457.

(8) Fukui, K. "Theory of Orientation and Stereoselection"; Springer-Verlag: West Berlin, 1974.

(9) Rouse, R. A. *Theor. Chim. Acta* **1976**, *41*, 149.

(10) Fukui, K.; Koga, N.; Fujimoto, H. *J. Am. Chem. Soc.* **1981**, *103*, 196.

(11) Fujimoto, H.; Koga, N.; Hataue, I. *J. Phys. Chem.* **1984**, *88*, 3539.

(12) Fujimoto, H.; Kato, S.; Yamabe, S.; Fukui, K. *J. Chem. Phys.* **1974**, *60*, 572.

0022-3654/85/2089-0779$01.50/0