sodium acetate to neutralize the acid, but we were still unable to detect the tetrahedral intermediate. It is probable that the mixing in our system was inefficient and that there were still local concentrations of strong acid for short times after adding one reagent to the other. Possibly with the use of a flow system the tetrahedral intermediate could be detected.

In conclusion, this work and the complementary investigations of Kresge, McClelland, and their co-work-ers[34] show that the tetrahedral intermediates of O,O-acyl transfer reactions are sufficiently stable to be detected when generated from suitable precursors and for the kinetics of their breakdown to be measured by standard techniques. As more results accumulate, a much better understanding of acyl transfer reactions should emerge.

Ionic Photodissociation of Electron Donor–Acceptor Systems in Solution

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Photochemical generation of ionic species in solution has high potential for the investigation and design of various chemical systems, and its importance has increased rapidly over the last 10 years. The primary photoprocesses can be classified in two categories: photoionization and ionic photodissociation. In the former an electron is ejected from the excited state of an absorbing molecule and a cation radical and a solvated electron are produced (eq 1). On the other hand,

$$D \xrightarrow{h\nu} D^+ + e^- \qquad (1)$$

ionic photodissociation is brought about by an interaction between one excited- and one ground-state molecule to produce a free cation from the donor and a free anion from the acceptor (eq 2). Similar disso-

$$D + A \xrightarrow{h\nu} D^* + A \rightarrow D^+ + A^- \qquad (2)$$
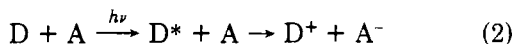
ciation phenomena are also observed by exciting the charge-transfer absorption band of electron donor–acceptor complexes stable in the ground state (eq 3).

$$(DA) \xrightarrow{h\nu} (DA)^* \rightarrow D^+ + A^- \qquad (3)$$
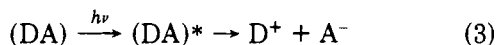
Whereas photoionization requires that the excitation photon have an energy larger than the ionization potential of the molecule in solution, ionic photodissociation can occur by low-energy photons available from sunlight, indicating a wide utility.

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Ionic photodissociation is important in various fields of chemistry. Some bimolecular photochemical reactions, e.g., cycloaddition and hydrogen abstraction, are very sensitive to the surrounding environment and correlated to the formation mechanism of ionic species in polar solvents. Generation of superoxide anion, reduction of metal ions, and polymerization are triggered by photoinduced electron transfer. Artificial photochemical storage of solar energy and water-splitting reactions are important problems in relation to the energy crisis. The design of photosensitive materials, photoconductors, and laser technology are developing rapidly, and some of these processes have ionic photodissociation as an elementary initial step. Furthermore it is well-known that primary photochemical reactions in green plant and bacterial reaction center are photoinduced electron transfer. Many kinds of chemical species of aromatic compounds and their derivatives, dyes, biological substances, polymers, metal ions, and transition-metal complexes are involved in ionic photodissociation under various kinds of conditions.

Although ionic photodissociation is a simple and common process, the following fundamental questions were unanswered when we started our investigation: What is the dissociative state from which ionic species are formed? What are the dissociation mechanisms? Can the dissociation be understood from the redox potentials of component molecules and of environmental effects? These important problems have been clarified by applying physicochemical methods to typical excited electron donor–acceptor systems.

The first indication of electron transfer in the excited state came from fluorescence quenching studies.[1] A direct demonstration in nonpolar solvents was given for the perylene–N,N–dimethylaniline system by measuring a broad, structureless emission due to the complex formed in the excited state (eq 4).[2] This complex is

$$D + A \xrightarrow{h\nu} D + A^* \rightarrow (DA)^* \qquad (4)$$
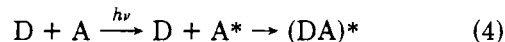
(1) Th. Förster, "Fluoreszenz Organischer Verbindungen", Vandenhoeck und Ruprecht, Göttingen, 1951, p 219.

called an exciplex. It has a polar electronic structure and can be thought of as a kind of contact ion pair. In polar solvents the N,N-dimethylaniline cation and the perylene anion were observed instead of the thermalized exciplex, which was confirmed by the microsecond flash photolysis.[2,3] Since then flash photolysis studies have been carried out for similar systems.[4] On the other hand, reports on ionic photodissociation of ground-state charge-transfer complexes are scarce. The first direct verification was performed by Ilten and Calvin, using ESR and photocurrent measurements.[5] Since the lifetime of ion radicals is short, it was difficult to follow formation processes directly and to measure the dissociation yield. Only the qualitative features had been clarified before the laser photolysis method was applied to these systems. With these technique, Potashnik et al. confirmed the dissociation of the pyromellitic dianhydride–mesitylene complex from the charge-transfer triplet state,[6] while we succeeded in demonstrating that the 1,2,4,5-tetracyanobenzene–toluene complex dissociates from the excited charge-transfer singlet state.[7] Direct proof of ionic dissociation in the fluorescer–quencher systems was provided by nanosecond laser-induced photocurrent measurements.[8] Since 1970, ionic dissociation processes of these typical excited electron donor–acceptor systems have been systematically studied. Investigations dealt with dissociative states, solvent effects upon ionic photodissociation yield, and a relation between the yield and redox potentials of donor as well as acceptor molecules. The dissociation mechanism has been considered from several points of view. These results provide practical concepts for understanding and designing various kinds of photoredox reactions and are the subject of this Account.

Dissociative States. In the following we consider electron donor–acceptor systems where free ions are formed through a solvent-shared ion pair (eq 5). The
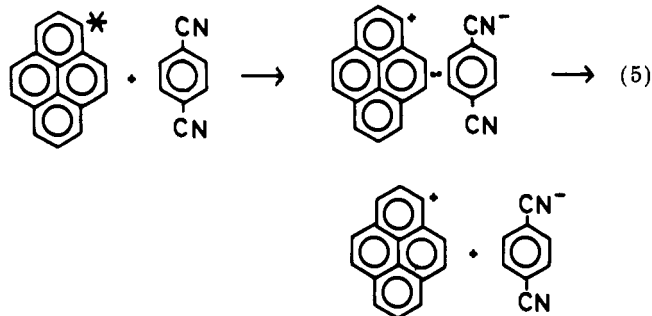
latter ionic species had originally been assumed to have an important role in the fluorescence quenching mechanism; however, its first direct confirmation was given for pyrene–1,4-dicyanobenzene in 1976.[9] Tran-

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Table I
Dissociation Rate Constants of the Solvent-Shared Ion Pair to Free Ions in the Pyrene-1,4-Dicyanobenzene System[a]

solvents	k_{exptl}, s^{-1}	k_{calcd}, s^{-1}
dichloromethane	1.3×10^7	1.5×10^7
1,2-dichloroethane	0.9×10^7	2.4×10^7
pyridine	9.0×10^7	6.3×10^7
acetone	$>10^8$	1.4×10^9
acetonitrile	$>10^8$	4.3×10^9

[a] Since an excitation pulse width of a used Q-switched laser is 15 ns, 10^8 s^{-1} is the maximum value measured.

sient absorption spectra of this system are reproduced by the superposition of bands of pyrene cation and 1,4-dicyanobenzene anion. The transmittance of the cation band is almost constant in the course of a few microseconds, while the peak photocurrent is attained in several hundred nanoseconds, corresponding to the formation of free ions. The dissociation rate constant (k_{exptl}) was determined from this exponential growth curve and compared with the diffusion-controlled dissociation rate constant (k_{calcd}).[10] In eq 6, D and ΔV

$$k_{calcd} = 4\pi N'Da\sigma/(\Delta V(1 - \exp(-\sigma)))$$

$$\sigma = e^2/\epsilon kTa \tag{6}$$

$$\Delta V = (4\pi/3)N'a^3$$

$$N' = 10^{-3}N_A$$

represent the sum of diffusion coefficients of the cation and the anion and molar volume of a solvated ion pair, respectively. The effective radius a of the latter was assumed to be 7 Å. The dielectric constant of the solvent is represented by ϵ, T is the temperature, and N_A is Avogadro's number. As listed in Table I, good agreement between k_{exptl} and k_{calcd} values was observed, suggesting that fluorescence quenching of the present system leads to a thermalized ion pair from which free ions are formed.

Another dissociation pattern is observed for pyrene–N,N-dimethylaniline. In moderately polar solvents this system shows exciplex fluorescence with a lifetime of 20 ns, while the rise curve of photocurrent consists of rapid and slow components. The rapid rise is in agreement with a time-integrated function of a 15-ns exciting pulse and completed before the exciplex decay.[8] This suggests that free ions are formed not from the exciplex but from its precursor state. Since both formation processes of free ions and exciplex involves electron transfer, this precursor state may be a nonrelaxed state with respect to solvent orientation, produced immediately after electron transfer. The slow rise was interpreted to be due to the dissociation from the solvent-shared ion pair. This dynamical behavior was confirmed for pyrene–aromatic amine systems in dichloromethane, 1,2-dichloroethane, and pyridine.[11] As the solvent polarity is increased, only the rapid component is observed.[7,11]

In the case of electron donor–acceptor complexes which are stable in the ground state, the problem of defining dissociative states is mainly the spin state.

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Transient absorption and photocurrent measurements on pyromellitic dianhydride (1) complexes with 2-
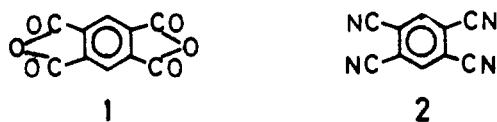
methyltetrahydrofuran, tetrahydrofuran, and 1,4-dioxane show the slow rise of free ions in moderately polar solvents.[12] The rise dynamics of several microseconds and effect of oxygen indicate that the dissociation into free ions occurs in the charge-transfer triplet state. In polar solvents such as butyronitrile and acetonitrile, most of free ions are formed within the time resolution of our nanosecond laser photolysis system (~15 ns), and the slow rise of about 50 ns is also observed. The rapid rise indicates that free ions are produced not only from the charge-transfer triplet state but also from its precursor state, namely, the excited charge-transfer singlet state. In the case of benzene and naphthalene donors, the main dissociation channel of pyromellitic dianhydride complexes is from the excited charge-transfer singlet state, which is almost independent of solvent polarity.

Other typical electron donor–acceptor complexes of 1,2,4,5-tetracyanobenzene (2) show different dissociation processes. Dissociation from the excited charge-transfer singlet state is observed for all these complexes examined in our laboratory.[7,12-14] The solvent-shared ion pair was observed for 1,2,4,5-tetracyanobenzene-2-methyltetrahydrofuran and -1,4-dioxane two-component systems, but not for complexes with aromatic hydrocarbons. These results on electron donor–acceptor complexes indicate that the dissociative state is determined by a delicate balance between molecular interaction and solvation. In other words, internal conversion to the ground state, intersystem crossing to the charge-transfer triplet state, and ionic dissociation are competing with each other in the excited charge-transfer singlet state of electron donor–acceptor complexes.

An Empirical Equation on the Relationship between Ionic Photodissociation Yield and Solvent Dielectric Constant. It is generally accepted that free ions are more stable in more polar solvents. However, previously there was no direct information on the relationship between yield and solvent properties. The present systems are quite suitable for obtaining such data, and we have studied the pyrene–N,N-dimethylaniline system by transient photocurrent measurements.[11] Although free ions are produced via two processes in moderately polar solvents, the photocurrent values, corresponding to dissociation from the nonrelaxed state with respect to solvation, were analyzed because this dissociative state is common to all the solvents used.

Yields were plotted against the solvent dielectric constant (ϵ), as shown in Figure 1 (a). The yield increases with the ϵ value, producing an S-shaped curve. Examining various possibilities, we found out a rela-
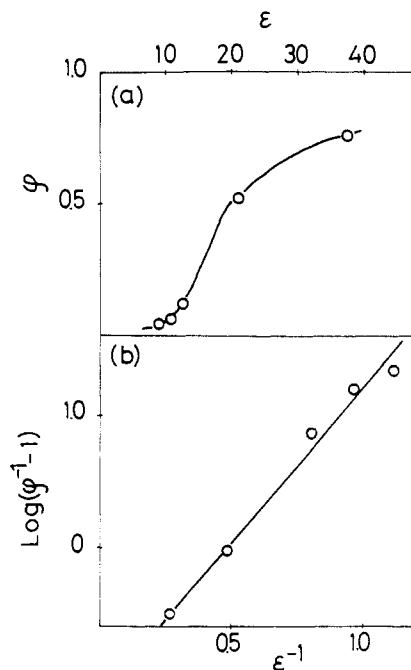
Figure 1. Solvent dependence of ionic photodissociation yield of the pyrene–N,N-dimethylaniline system: (a) yield vs. solvent dielectric constant; (b) relation between the yield and the inverse of the solvent dielectric constant.

tionship connecting the yield (φ) and ϵ. This is given in eq 7, where p and q are constants independent of ϵ.

$$\log f\,(\varphi^{-1} - 1) = (p/\epsilon) + q \qquad (7)$$

The plot according to eq 7 is shown in Figure 1b. In addition to ϵ, there are many empirical solvent properties deduced from the spectroscopic and reaction kinetics data. We tried to correlate our data with E_T, Z, Y, S, log k_{ion}, and χ_R vaues[15] but found no clear relationship. Therefore, it was concluded that the ionic photodissociation yield is well determined primarily by ϵ. This suggests that solvent effects are not determined by the so-called microscopic interaction between radical ion and solvent molecule but by the stabilization of ions in dielectrics. Similar results were obtained also for the 1,2,4,5-tetracyanobenzene–toluene complex[11] and the p-chloranil–hydroquinone complex.[16] Furthermore, the solvent dependence of the ion-pair formation of the pyrene–1,4-dicyanobenzene was also fitted to eq 7. These showed that the present relation holds for typical excited electron donor–acceptor systems.

Relationships between Ionic Photodissociation Yield and Redox Potentials of Donor or Acceptor. The fluorescence quenching process of aromatic hydrocarbons caused by electron-transfer reactions has been extensively studied. A quantitative analysis was given by Rehm and Weller who established an equation representing the dependence of the quenching rate constant upon its free-energy change.[17] Similar experimental results have been given for the triplet dye systems,[18,19] transition-metal complexes,[20] inorganic

(12) M. Shimada, H. Masuhara, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **46**, 1903 (1973).

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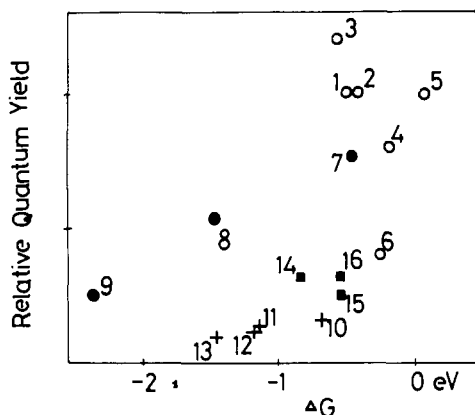
Figure 2. Relation between ionic photodissociation yield and free-energy change due to dissociation for the pyrene systems. Quenchers are as follows: (1) N,N-dimethylaniline, (2) N,N-diethylaniline, (3) N,N-dimethyl-m-toluidine, (4) N-methylaniline, (5) aniline, (6) triethylamine, (7) 1,4-dicyanobenzene, (8) 1,2,4,5-tetracyanobenzene, (9) tetracyanoethylene, (10) phthalic anhydride, (11) tetrachlorophthalic anhydride, (12) maleic anhydride, (13) pyromellitic dianhydride, (14) diethyl isophthalate, (15) diethyl phthalate, (16) diethyl terephthalate.
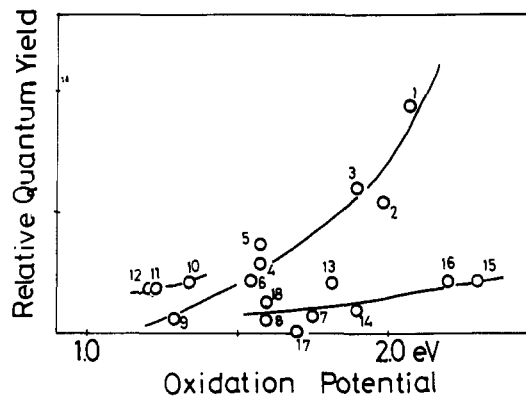

Figure 3. Relation between ionic photodissociation yield and oxidation potential of donors for the 1,2,4,5-tetracyanobenzene complexes. Used donors are as follows: (1) benzene, (2) toluene, (3) n-butylbenzene, (4) m-xylene, (5) o-xylene, (6) mesitylene, (7) anisole, (8) p-methylanisole, (9) durene, (10) naphthalene, (11) β-methylnaphthalene, (12) α-methylnaphthalene, (13) pyridine, (14) N,N-dimethylformamide, (15) β-methylpyridine, (16) 3,5-dimethylpyridine, (17) furan, (18) thiophene. Oxidation potentials are referrred to L. N. Weinberg and H. R. Weinberg, *Chem. Rev.*, 68, 449 (1968), and Figure 1 of E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, 85, 2124 (1963).

anion quencher systems,[21,22] and biological molecules.[23] Theoretical treatments of such processes have been given, and presently this is an active area of research.[24] However, whether or not these electron-transfer processes are always followed by dissociation to free ions was not clear when we started our laser photolysis studies. Therefore we measured the quantum yields of ionic photodissociation in an attempt to establish a relationship between the yield and redox potentials of component molecules.

For the excited pyrene–quencher systems, relative yields were obtained by transient absorption and photocurrent measurements.[25] The results are given in Figure 2 where the free-energy change (ΔG) is the difference of energy level between the excited pyrene and free ions. This value is calculated by eq 8 where

$$\Delta G = E(D/D^+) - E(A^-/A) - E_i \qquad (8)$$

$E(D/D^+)$ and $E(A^-/A)$ represent the oxidation potential of the donor and the reduction potential of the acceptor, respectively, and E_i is the energy level of the fluorescent state. It should be noted that the quenchers employed are quite efficient so that the scattered values of the dissociation yield have nothing to do with the quenching

probability. When anhydride quenchers are used, the peak photocurrent is only a little larger than background, and a change of the absorption spectra after measurement was observed. This suggests that electron-transfer quenching is followed by chemical reaction and not by solvation to free ions. It should be noted that the yield of pyrene–nitrile systems decreases as the reduction potential increases, while pyrene–amine systems show rather large scatter.

Similar measurements of 1,2,4,5-tetracyanobenzene and pyromellitic dianhydride complexes were performed by exciting their charge-transfer absorption band. The yield was calculated by using absorption intensity of the acceptor anion and plotted against oxidation potential of the donor, as given in Figure 3.[26] In the case of substituted-benzene donors, the yield decreases along with the oxidation potential of the donor. The yield in naphthalene donor systems is larger than that expected from the relation established for benzene donors. It is worth noting that the yield of the complexes with donors containing nitrogen, oxygen, and sulfur atoms is small, in spite of the rather high oxidation potential.

These experimental results are summarized as follows. (i) The chemical property of donor-acceptor pairs (the nature of excited electronic state, the kind of groups contained in the component molecule, and molecular volume) determines the ionic photodissociation yield, independent of the redox potential of component molecules. (ii) In the case of the series of donors or acceptors with similar chemical character, the yields decrease as the oxidation potential of the donor does or the reduction potential of the acceptor increases.

Ionic Photodissociation Mechanism and Theoretical Considerations. On the basis of our experimental results, we have developed a simplified picture of the dissociation process. The ionic dissociation appears to consist of the following two steps:[11,25,26] (i) electron transfer of fluorescer–quencher systems or the

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electronic and vibrational relaxation from the excited Franck–Condon state of electron donor–acceptor complexes, leading to formation of a transient ionic complex, $(D^+A^-)^*$ (eq 9), and (ii) orientational relaxation of

$$D^* + A \rightarrow (D^+A^-)^* \text{ or } (DA)^*_{FC} \rightarrow (D^+A^-)^* \quad (9)$$
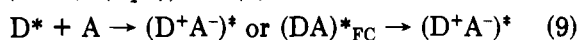
the solvent molecules around the latter complex, determining the solvation path to free ions or solvent-shared ion pairs (eq. 10).

$$(D^+A^-)^* \xrightarrow{k_d} D_s^+ + A_s^+, D_s^+ \cdots A_s^- \quad (10)$$
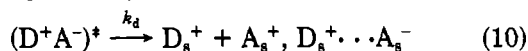
The latter process competes with other deactivation processes such as internal conversion to the ground state, intersystem crossing, and other chemical reactions (eq 11). Although the real nature of the transient ionic

$$(D^+A^-)^* \xrightarrow{k_n} D + A, (DA), {}^3D + A, \text{ reactions ...} \quad (11)$$
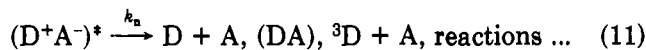
complex is beyond our knowledge at present, its electronic structure is quite polar, and it appears to be a kind of contact ion pair. This complex is stabilized with respect to electronic and vibrational relaxation. However, the solvent reorientation is incomplete, which is a quite different character from that of exciplexes and the fluorescent states of electron donor–acceptor complexes. This idea is supported by our data on the excited singlet-singlet absorption spectra of the 1,2,4,5-tetracyanobenzene complexes in nonpolar solvents at room temperature, 77 K, and 4.2 K.[27] The quite polar electronic structure of the fluorescent state was observed independent of the degree of the solvent orientation. On the other hand, their fluorescence spectra are very sensitive to the environmental conditions, and the stabilization energy due to the solvent orientation was estimated from their temperature dependence.[28] Very roughly speaking, the energy level of the transient ionic complex will be close to that of the fluorescent state of electron donor–acceptor complexes in rigid solvents.

In the following we explain our experimental results with the dissociation mechanism just described. First, the empirical eq 7 is considered with the yield defined as eq 12. It is assumed that k_n is characteristic of the

$$\varphi = k_d/(k_d + k_n) \quad (12)$$

donor–acceptor pair and independent of ϵ values. On the other hand the formation process of free ions (k_d) is a function of solvent, and its activation free energy is correlated with ΔG values of eq 8. The energy level of the transient ionic complex is independent of the solvent polarity because of the incomplete relaxation of solvation, while that of final free ions strongly depends upon ϵ. The latter energy level is usually estimated with redox potentials and Born's equation on the ion–solvent interaction,[29] so the change of ΔG value with the solvent dielectric constant (from acetonitrile, where both potentials are measured, to solvent with ϵ) is given by eq 13, where A and B are constants inde-

$$\Delta\Delta G = (A/\epsilon) + B \quad (13)$$

pendent of ϵ. Using the Horiuchi–Polanyi relation for the activation free energy change (eq 14),[30] the ratio

$$\Delta G_{act} = \alpha\Delta\Delta G, \qquad 0 < \alpha < 1 \quad (14)$$

of the rate constants of dissociation is given in eq 15.

$$k_d/k_d^0 \text{ (in acetonitrile)} = \exp(-\alpha\Delta\Delta G/RT) \quad (15)$$

From eq 13 and 15, k_d is represented as a function of ϵ (eq 16). Now the empirical eq 7 for the solvent effect

$$k_d \propto k_d^0 \exp(-A/\epsilon RT) \quad (16)$$

upon the yield can be derived from eq 12 and 16. If the solvent-shared ion pair is produced at first, its Coulomb force $-e^2/\epsilon a$ should be added to eq 8. However, this correction does not change the expression of eq 13 so that the above considerations hold also for the ion-pair formation of the pyrene-1,4-dicyanobenzene system.

In addition to interpretating the solvent effect, the relation between the yield and redox potential of donor or acceptor can be explained with the present mechanism. In this case the yields in the very polar solvents are compared with each other, so k_d is almost the same for all the donor–acceptor pairs. The value of k_n depends mainly upon internal conversion and intersystem-crossing processes, since no appreciable charge-transfer fluorescence from the transient complex is detected. Theoretically the radiationless transition rate constant is given by an electronic matrix element and Franck-Condon factor.[31] Provided the electronic matrix element is common for some donor–acceptor systems, k_n would be directly correlated with the Franck–Condon factor, which is a smooth function of the energy gap between the initial transient and the final ground (or the triplet) states. The energy level of the transient complex is lowered by decreasing the oxidation potential of the donor or by increasing the reduction one of the acceptor, leading to a large Franck–Condon factor. Therefore k_n is larger and the ionic photodissociation yield becomes smaller in the systems with lower oxidation potential of the donor or higher reduction one of the acceptor. This explanation is in qualitative agreement with the experimental results on 1,2,4,5-tetracyanobenzene as well as pyromellitic dianydride complexes with methyl-substituted benzenes and pyrene–nitrile quencher systems.

On the other hand, the yield is generally determined by the chemical property of donor–acceptor pairs, which requires other considerations. This suggests that the matrix element is related to the electronic structure of component molecules. As mentioned above, pyrene-acceptor systems other than nitriles and 1,2,4,5–tetracyanobenzene complexes with donors containing heteroatoms do not show a clear relation between the yield and redox potential. These compounds may have a larger value of matrix element than the aromatic hydrocarbon–nitrile systems, since the dissociation yield is quite small in spite of the large energy gap between the relevant states.

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One possible explanation is as follows. The carbonyl substituent and ring heteroatoms may place the n–π* triplet level between or near the initial π–π* charge-transfer singlet and the final triplet states, which may accelerate the intersystem crossing.[32] This notion is supported by the difference in the dissociation patterns of pyromellitic dianhydride and 1,2,4,5-tetracyano-benzene complexes with 2-methyltetrahydrofuran. The former dissociates from a charge-transfer triplet and the latter from an excited charge-transfer singlet state, although the molecular size and π-electronic structure of these acceptors are similar. The n–π* triplet level of pyromellitic dianhydride, whose location is not known precisely, may make the intersystem crossing faster than that of ionic dissociation in the excited singlet state. Another explanation for the rather low dissociation yield of 1,2,4,5-tetracyanobenzene complexes with *N,N*-dimethylformamide, furan, and thiopene can be based on the different types of complex for n donors and π acceptors. It may be that this complex has a larger electronic matrix element than that of aromatic hydrocarbon–nitrile systems.

In the above discussion, the dissociation mechanism is assumed to be common to both charge-transfer complexes and fluorescer–quencher systems, and no consideration was given for donor–acceptor configuration in the electron-transfer process of the latter one. Here we briefly discuss this problem, which leads to an alternative dissociation mechanism.

In general, electron transfer can be induced even by weak interaction, and, according to the outer-sphere type mechanism,[33] its rate constant is a parabolic function of the ΔG given in eq 8. For the excited pyrene–quencher systems considered in this Account, the maximum rate constant is attained at about –0.43 eV of ΔG.[17] In this case a loose ionic complex may be formed immediately after electron transfer. On the other hand, the rate constant of the electron-transfer process becomes small in the extremely exothermic and the isoenergetic ($\Delta G \sim 0$) regions. Donor and acceptor molecules can collide with each other before the outer-sphere type electron transfer occurs, and a more compact ionic complex may be formed.[34] Since the ΔG value is a function of the solvent polarity, the relative contribution of ionic complexes may depend also upon the solvent. This idea is supported by the recent picosecond studes on intramolecular exciplex systems,[35] which is in accord with the original concept of solvent-dependent exciplex structure.[36]

From this viewpoint the ionic photodissociation yield is determined by the relative formation ratio of the loose and compact ionic complexes. The dissociation from the former complex to free ions is more favorable than that from the latter compact one, and the radiationless deactivation will be easier in the case of the latter ionic complex due to the strong electronic interaction. With this idea we can qualitatively explain the decreased ionic dissociation yield in less polar sol-vents. Namely, the ΔG value increases and approaches zero with decrease of polarity, which accelerates the formation of the compact ionic complex, while the loose complex is more easily produced as the solvent polarity increases. Similar considerations are applied to the relations between the yield and the redox potential. In the ΔG region around –0.43 eV, the loose complex is formed predominantly, resulting in high quantum yield of ionic dissociation. On the other hand, the role of the compact complex increases in the regions of large negative ΔG or ΔG larger than –0.43, which reduces the dissociation yield. Very roughly speaking, we can see such a tendency in Figure 2. However, it is difficult to derive any conclusion using this alternative model because of the large scatter of points from compound to compound. The latter scatter might be ascribed to the fact that the relative contribution of both ionic complexes depends upon the nature of compounds.

A Comparison with Ionic Photodissociation of Dyes, Transition-Metal Complexes, and Porphyrins. Other systems studied in detail are dyes,[37,38] transition-metal complexes,[39] and porphyrins[40] whose dissociation is induced by the interaction of their triplet state and electron donors or acceptors. The triplet dye–halogen-substituted aniline systems show a heavy atom effect upon dissociation yield, which indicates that the intersystem crossing in the intermediate complex is increased by introducing halogen substitutent.[38] Namely, chemical property of component molecules are reflected in the yield, while clear relations between the yield and the redox potentials were observed in other cases. The dissociation yield of the chlorophyll–ben-zoquinone systems is nearly independent of the reduction potential of the quencher.[40] In the case of the triplet methylene blue quenched with amines and Fe(II) complexes, the yield decreases as the redox potential of the donor increases,[37,39] which is an opposite tendency to our studies on typical electron donor–acceptor systems. However, these results are not inconsistent with our mechanism of ionic photodissociation. The intermediate transient ionic complex of our systems has quite polar electronic structure which is common to all donor–acceptor pairs. This is due to rather large energy differences between the zero-order locally excited and charged-transfer states. On the other hand, the corresponding difference of the triplet molecule–quencher systems is in general small, and the expected mixing of both states may lead to the intermediate complex with partial charge transfer whose degree is correlated with the redox potential of component molecules. The higher degree of charge transfer may make the solvation to free ions easier and lead to higher quantum yield of ionic dissociation, since the competing deactivating processes may have very small values of k_n because of its spin-forbiddeness. A similar but more quantitative examination has been recently given for the triplet methylene blue–ferrocene systems.[41] Thus the different dependencies of the yield upon redox potentials

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in the triplet systems can be explained in terms of the electronic structure of the intermediate complex.

Concluding Remarks. We have described the ionic photodissociation processes of electron donor–acceptor systems as studied by nanosecond laser photolysis. Dissociative states, solvent effects on dissociation yield, and relationships between the yield and the redox potential of component molecules have been examined, and a simplified but satisfactory model of dissociation mechanism is presented. In this model, electron transfer of fluorescer-quencher systems, or electronic and vibrational relaxations from the excited Franck–Condon state of charge-transfer complexes, leads to formation of a transient ionic complex, where dissociation to ions and other radiationless transitions compete with each other. The nature of the transient ionic complex and the character of the latter transitions are discussed in detail. The proposed model should be examined further by using the absorption spectra of the complex in question, which will be possible in the near future by using picosecond laser photolysis method. Additional useful information is being obtained from magnetic field effects on the relevent processes.[42] For establishing a general concept of ionic photodissociation, various kinds of donor–acceptor systems should be examined by these experiments, since this process is very sensitive to the chemical properties of the component molecules.

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"Ligand-Free" Platinum Compounds

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Transition metals readily form complexes with ligated carbon atoms, and platinum is no exception. Indeed, organo derivatives of this metal[1] were studied intermittently for over a century prior to the discovery of ferrocene. Recognition of the sandwich structures of the metallocenes led to burgeoning research on π complexes and carbonyl compounds. In parallel with these developments it was discovered[2] that many organoplatinum species could be prepared from platinum halide complexes and organolithium or Grignard reagents. Although this route has afforded numerous alkyl-, aryl-, alkenyl-, or allylplatinum species, it is limited in scope. Indeed, the ease with which stable organoplatinum compounds are isolated from metathetical reactions between platinum halides and carbanion reagents has perhaps inhibited progress by causing investigators to focus on this method of carbon–platinum bond synthesis to the detriment of other possibilities. Certainly the development of organoplatinum chemistry has been less broadly based than that of the other subgroup 8 metals, notably nickel. There have been two reasons for this state of affairs.

Nickel forms a mononuclear tetracarbonyl, reasonably stable at room temperature but with CO ligands replaceable by other organic groups, e.g. RNC, RC≡CR, η^3-C_3H_5, or η^5-C_5H_5.[3] In contrast [Pt(CO)$_4$] is a laboratory curiosity, existing only in rare-gas matrices at very low temperatures,[4] and so is unsuitable for use as a reagent in synthesis. Even [Ni(CO)$_4$] has its limitations for use in preparing other organonickel compounds because of its toxicity and the difficulty of replacing all four CO groups in certain reactions where this would be a desirable end result. Hence reports commencing in 1960 that nickel formed compounds in which olefinic groups are the only ligands and, moreover, that these ligands were very labile proved to be of seminal importance.[5] Consequently, complexes such as [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene), and [Ni(cdt)] (cdt = *trans*-1,*trans*-5,*trans*-9-cyclododecatriene) have become standard reagents.[3] Their high reactivity, which is associated with the easy replacement of the diene or triene ligands by substrate molecules, has led to their being named "naked" nickel or "ligand-free" nickel compounds.[6,7] The impact of this discovery can be judged by the appearance in the last 20 years of several thousand primary publications on organonickel chemistry.[3]

Obviously, from the foregoing remarks, "ligand-free" Pt(0) compounds [P(olefin)$_n$] would be very desirable reagents for use in a variety of syntheses. That such compounds could exist was demonstrated by Müller and Göser,[8] who prepared [Pt(cod)$_2$] for the first time.

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