$$\phi_{LE}^{F} = k_1/(k_F + k_7) \tag{46}$$

The total quantum yield of LE emission is

$$\phi_{LE} = f_S \phi_{LE}^{S} + f_F \phi_{LE}^{F} \tag{47}$$

$$= k_1 \left[\frac{f_S}{k_S + k_7} + \frac{f_F}{k_F + k_7} \right] \tag{48}$$

$$= \frac{k_1(k_7 + f_S k_F + f_F k_S)}{(k_S + k_7)(k_F + k_7)} \tag{49}$$

The quantum yield of exciplex emission from the slow (ϕ_E^{S}) and the fast conformations (ϕ_E^{F}) is given by

$$\phi_E^{S} = \frac{k_5}{k_8} \frac{k_S}{(k_S + k_7)} \tag{50}$$

and

$$\phi_E^{F} = \frac{k_5}{k_8} \frac{k_F}{(k_F + k_7)} \tag{51}$$

The total quantum yield of exciplex emission is then given by

$$\phi_E = f_F \phi_E^{F} + f_S \phi_E^{S}$$

$$= \frac{k_5}{k_8} \left[f_F \frac{k_F}{k_F + k_7} + f_S \frac{k_S}{k_S + k_7} \right] \tag{52}$$

$$= \frac{k_5}{k_8} \frac{k_S k_F + k_7(k_F f_F + k_S f_S)}{(k_F + k_7)(k_S + k_7)} \tag{53}$$

References and Notes

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(23) Between −30 and −85 °C the calculated values of λ_2^{280} are irreproducible (vide supra). Nevertheless it is possible to determine k_F from λ_2^{330}, whose values remain reproducible in this temperature region.

Thermodynamic and Kinetic Aspects of the Intermolecular Exciplex Formation between 2-Methylnaphthalene and Aliphatic Amines

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Abstract: The fluorescence quenching of 2-methylnaphthalene with aliphatic amines in polar and nonpolar solvents is investigated using stationary and nonstationary techniques. The results in polar medium are interpreted in terms of the Marcus theory. In acetonitrile, the intrinsic barrier prior to electron jump was determined to be 5.2 kcal mol^{-1}. In nonpolar solvents $\Delta H°$ and $\Delta S°$ as well as the repulsion energy of the exciplex are found to be solvent dependent.

Introduction

The formation of excited-state complexes where aromatic amines participate as electron donors is a well-known phenomenon.[1-5] Exciplex stabilization enthalpies, $\Delta H°$, entropies, $\Delta S°$, and ground-state repulsion energies, E_R, are reported for several such systems.[6-8] Correlations between the maximum of exciplex emission and the redox potentials of the donor and acceptor have been put forward.[9] The influence of the electron-transfer energetics upon the observed overall rate

constant for fluorescence quenching has been analyzed.[10,11] Data related to the influence of the solvent polarity upon the lifetime and fluorescence quantum yield of exciplexes have led to different interpretations,[12-15] supported by different theoretical approaches.[4,5] The small number of data available on the solvent dependence of $\Delta H°$, $\Delta S°$, and E_R fit to no consistent pattern.[16] Whether or not a universal trend is at work, the "inconsistency" between the too few data reported in the literature for solvent-dependent variations of $\Delta H°$, $\Delta S°$, and the radiative and nonradiative rate constant for exciplex decay
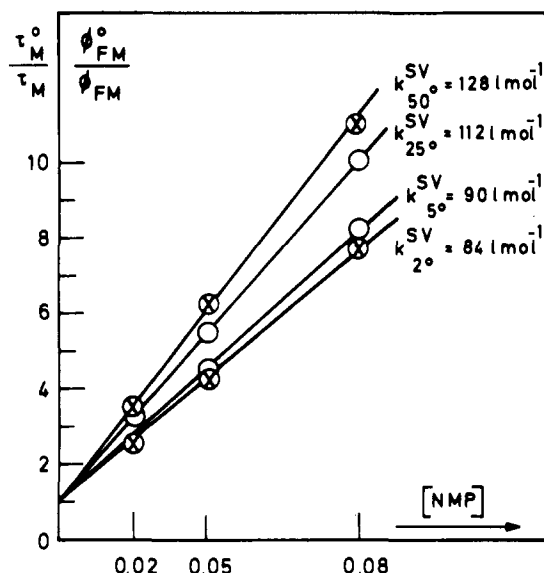
Figure 1. Stationary ⊗ and nonstationary O Stern–Volmer plots for the system 2MN–NMP in acetonitrile at different temperatures.

could be due to experimental difficulties in obtaining these data, since both steady-state and transient measurements should be made over a large temperature interval. Only a few studies have used transient measurements to determine the activation parameters associated with the individual rate constant involved in exciplex formation.[17,18]
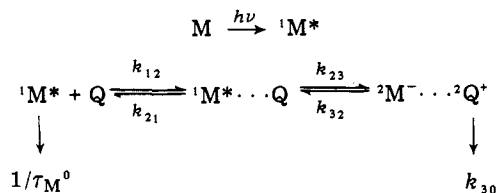
Information about exciplexes where tertiary aliphatic amines act as donors is even more scarce.[7,19,20] In this paper a detailed study will be made of the fluorescence quenching of 2-methylnaphthalene (2MN) by the tertiary amine N-methylpiperidine (NMP) in polar and nonpolar solvents, using both techniques of light excitations. The results will be compared with the data reported in a previous paper, where the fluorescence quenching of 2MN by NMP and triethylamine (TEA) was studied.[21]

Results and Discussion

(a) Absorption and Emission Spectra. The absorption spectra of NMP in n-butyl ether and acetonitrile do not extend above 300 nm. Since the S_0–S_1 band of 2MN has a 0–0 transition at 315 nm, selective excitation of 2MN is possible. Mixtures of 2MN with NMP in the experimental range used in this study do not show deviations from Beer's law or formation of a new band. Upon excitation at 304 nm of a 8×10^{-5} M solution of 2MN in n-butyl ether at 25 °C in the presence of 0.02 M NMP a new band, to the red of the naphthalene emission, with a maximum at 430 nm is observed. Excitation spectra at respectively 324 and 450 nm are identical with the absorption spectra of 2MN, indicating that this new bathochromic emission is due to excited state complex formation. No exciplex emission is observed in acetonitrile.

(b) Fluorescence Quenching of 2MN in Polar Solvents. In ethanol the fluorescence decay of 2MN, as measured by single photon counting, in absence of quencher is a single exponential and a fluorescence lifetime of 47 ns at room temperature is obtained. The fluorescence quantum yield was found to be 0.26. Stationary quenching experiments, at 25 °C, of 2MN with varying concentration of NMP give a Stern–Volmer quenching constant equal to $K^{SV} = 11.4$ L mol^{-1}. This value is identical with the value of the quenching constant obtained from nonstationary measurements of 2MN quenched by NMP in the same concentration range.[21] Lowering the temperature causes a decrease of K^{SV}. Analogous observations are made for TEA as quencher, but a slightly higher value of $K^{SV} = 28$ L mol^{-1} at 25 °C is obtained.[21] In acetonitrile as solvent, the

Scheme I

$$M \xrightarrow{h\nu} {}^1M^*$$

$$^1M^* + Q \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} {}^1M^* \cdots Q \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} {}^2M^- \cdots {}^2Q^+$$

$$\downarrow \qquad\qquad\qquad\qquad\qquad\qquad \downarrow$$

$$1/\tau_M{}^0 \qquad\qquad\qquad\qquad\qquad k_{30}$$

lifetime of 2MN, in absence of a quencher, equals 54.8 ns, with a fluorescence quantum yield of 0.28 at 25 °C. On adding NMP as quencher, the decay of 2MN remained strictly exponential. As in ethanol, the Stern–Volmer analysis showed a positive temperature effect on the constant K^{SV}, which is found to be identical using both above-mentioned techniques of light excitation (Figure 1). From the work of Weller et al.[11] it is concluded that the mechanism for fluorescence quenching in these polar solvents is electron transfer, which is described in Scheme I, where M = 2MN; Q = NMP or TEA; $1/\tau_M{}^0$ = reciprocal of the lifetime of 2MN when [Q] = 0; k_{12} = bimolecular rate constant for diffusion; k_{21} = reciprocal of the duration of a collision due to Brownian motion; k_{23} = rate constant for the electron-transfer process; k_{32} = rate constant for the back electron transfer regenerating excited monomer; k_{30} = summation of rate constants for the processes by which the radical ion pair disappears.

Within the framework of Scheme I, the following useful relations for the fluorescence quantum yield of 2MN, ϕ_{FM}, and lifetime, τ_M, can be expressed:

$$\phi_{FM} = \frac{k_{FM}}{1/\tau_M{}^0 + k_q[Q]} \tag{1}$$

$$\left(\frac{\phi_{FM}{}^0}{\phi_{FM}} - 1\right)\frac{1}{[Q]} = k_q \tau_M{}^0 = K^{SV} \tag{2}$$

$$\tau_M = \frac{1}{1/\tau_M{}^0 + \dfrac{k_{12}k_{23}[Q]}{k_{21} + k_{23}}} \tag{3}$$

$$\left(\frac{\tau_M{}^0}{\tau_M} - 1\right)\frac{1}{[Q]} = \frac{k_{12}k_{23}}{k_{21} + k_{23}}\tau_M{}^0 \tag{4}$$

and the observed overall rate constant for the fluorescence quenching under steady-state conditions of light excitation, k_q, is given by

$$k_q = \frac{k_{12}}{1 + \dfrac{k_{21}}{k_{23}}\left(1 + \dfrac{k_{32}}{k_{30}}\right)} \tag{5}$$

The results indicate that in these polar solvents quenching takes place in such a way that, within the temperature range studied, regeneration of excited monomer does not occur. This means that $k_{32}/k_{30} \ll 1$ and eq 5 simplifies to

$$k_q = \frac{k_{12}}{1 + k_{21}/k_{23}} = \alpha k_{12} \tag{6}$$

The measured overall rate constants for fluorescence quenching, k_q, in ethanol at 25 °C by NMP and TEA are respectively 2.4×10^8 and 5.9×10^8 L mol^{-1} s^{-1}.[21] They are both considerably smaller than the rate constant for diffusion in ethanol at that temperature ($k_{12} = 5.5 \times 10^9$ L mol^{-1} s^{-1}), by a factor $\alpha = 0.04$ for NMP and $\alpha = 0.1$ for TEA. In acetonitrile k_q equals 2×10^9 L mol^{-1} s^{-1} for the system 2MN–NMP at 25 °C, and the quenching probability on collision, α, is found to be $\alpha = 0.1$. This means that $k_{21} \approx 9k_{23}$, and only one out of ten collisions caused by Brownian motion leads to fluorescence quenching. The overall rate constant for fluorescence quenching is then approximated by $k_q = (k_{12}/$
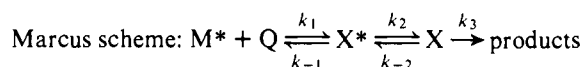
$k_{21})k_{23}$. The ratio k_{12}/k_{21} is not temperature dependent, and since k_{23} can be written as $k_{23} = \omega_{23}e^{-\Delta G^{\ddagger}_{23}/RT}$ where ω_{23} and $\Delta G^{\ddagger}_{23}$ are the frequency factor and free energy of activation, one obtains from a plot of $\ln k_q$ vs. T^{-1}, in acetonitrile as solvent, an activation energy $\Delta E^{\ddagger}_{23} = 2.8$ kcal/mol, and an intercept $I = 2.6 \times 10^{11}$ M^{-1} s^{-1} equal to $e(k_{12}/k_{21})\cdot$ $\omega_{23}e^{\Delta S^{\ddagger}_{23}/R}$ (Figure 2). The ratio k_{12}/k_{21} can be estimated using Smoluchowski's expression for the probability, ω, by which one particle is hit by one of the others as a result of their Brownian motion.[22] This probability is given by $\omega = 4\pi RD\nu_0$, where R is the interaction radius, D is the diffusion coefficient, and ν_0 is the number of particles per unit volume. This probability can be expressed as a bimolecular rate constant for diffusion by setting $k_{12} = \omega N/\nu_0 = 4\pi RD$.

Random walk theory predicts $k_{21} = 3D/R_2$.[23,27] The ratio k_{12}/k_{21} is then calculated to vary from 0.8 to 0.5 for collision distances of 7–6 Å.

According to Marcus the overall rate constant for an outer-sphere electron-transfer reaction is given by

$$k_i = Z_i \exp[-\Delta G_i^*/RT] \qquad (7)$$

where Z_i is the bimolecular collision number in solution (taken to be 10^{11} L mol^{-1} s^{-1}) and ΔG_i^* is the Gibbs free activation energy needed to reorganize the nuclei of the reactants and the surrounding solvent molecules prior to electron transfer. However, the kinetic scheme used by Marcus,[24,25] for deriving this expression for k_i, takes different elementary steps into consideration:

Marcus scheme: $M^* + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X \overset{k_3}{\rightarrow}$ products

where X^* denotes the activated complex, and the ratio k_2/k_{-2} is the equilibrium constant for the interconversion of X^* into a state X with the same nuclear configurations but with an electronic configuration which is that of the species formed after the electron jump. These two states, X^* and X, have the same total energy, and the ratio k_2/k_{-2} is approximately set equal to unity on theoretical grounds. By assuming an electron jump mechanism, k_2 is estimated to vary between 10^{12} and 10^{14} s^{-1}. The rate constants k_{-1} and k_3 are considered to be essentially the same, both about 10^{13} s^{-1}, corresponding to the rate of disappearance of the state X^* (or X), either by a dissociation vibration within the solvent cage or by a disorganizing motion of the solvent destroying the state X^* (or X). The overall rate constant, k_i, for the reaction sequences considered in Marcus scheme is given by

$$k_i = k_1\left[1 + \frac{k_{-1}}{k_2}\left(1 + \frac{k_{-2}}{k_3}\right)\right]^{-1} \qquad (8)$$

which is formally identical with eq 5. But when the appropriate numerical values for k_{-1}, k_2, k_{-2}, and k_3 are taken into account k_i reduces to $k_i = \beta k_1$, where β is about $\frac{1}{2}$. Such a treatment has only physical significance if indeed k_2 is at least of the same magnitude as k_{-1}. If this condition is fulfilled, and by neglecting β, the overall rate constant for an electron-transfer process is given by eq 7. The difference between Scheme I and the scheme used by Marcus lies in the mode of conceptualization by using different rate constants which refer to different elementary steps. However, the physical process of electron transfer remains the same; thus k_q from Scheme I equals k_i and $(k_{12}/k_{21})k_{23}$ must correspond to βZ_1 $\exp[\Delta G_1^*/RT]$. As shown above the ratio k_{12}/k_{21} has a numerical value close to the factor β, so k_{23} from Scheme I represents the unimolecular equivalent of k_1 from Marcus scheme. Nevertheless, the numerical value of the preexponential factor, Z_1, is open to a minor criticism.[26] Marcus takes Z_1 to be 10^{11} M^{-1} s^{-1}, corresponding to the collision number in solution. This makes Z_1 explicitly solvent dependent. An easy way to calculate the collision number in solution makes use of the
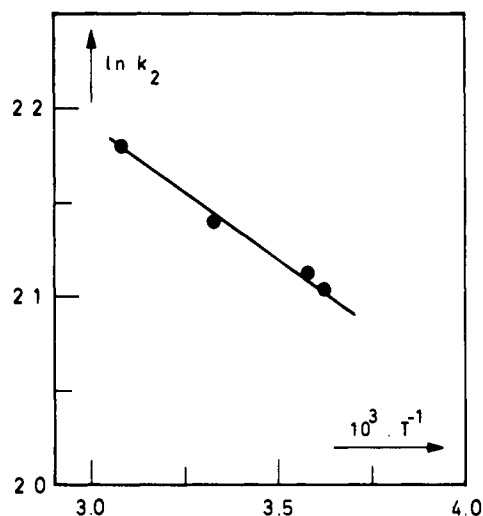

Figure 2. Arrhenius plot of $\ln k_q$ vs. T^{-1} for the fluorescence quenching of 2MN by NMP in acetonitrile.

Smoluchowski equation[22] $\omega = 4\pi RD\nu_0$. Such a calculation yields different frequency factors for different solvents. In acetonitrile, the frequency factor ω_{23} turns out to be 3.8×10^{11} s^{-1}, and the Gibbs free energy of activation ΔG^*_{23} is then calculated according to $\Delta G^*_{23} = \Delta E^{\ddagger}_{23} - RT \ln (Ik_{21}/\omega_{23}k_{12}) = 2.6$ kcal/mol. This Gibbs free activation energy for the cross electron transfer is related to the overall Gibbs free energy change, ΔG°, and to the so-called intrinsic barrier for electron transfer, $\lambda/4$, by the Marcus equation:

$$\Delta G^*_{23} = \frac{\lambda}{4}\left[1 + \frac{\Delta G^\circ}{\lambda}\right]^2 \qquad (9)$$

The overall Gibbs free energy change, ΔG°, can be calculated from the oxidation potential of the electron donor, $E_{(D/D^+)}$, the reduction potential of the electron acceptor, $E_{(A/A^-)}$, and the 0–0 excitation energy, by the expression[11]

$$\Delta G^\circ = E_{(D/D^+)} - E_{(A/A^-)} - E_{00} - e^2/\epsilon r$$
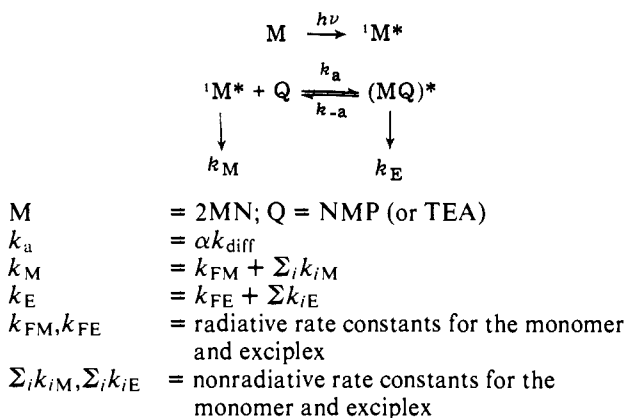
where $e^2/\epsilon r$ denotes the free energy gained by bringing the ions to encounter distance r. Such a calculation yields $\Delta G^\circ \simeq -7$ kcal/mol.[28] Putting the values of ΔG° and ΔG^*_{23} into eq 7, the intrinsic barrier for the electron-transfer process, $\Delta G^*_{23}(0)$, for the system 2MN–NMP in acetonitrile is equal to 5.2 kcal/mol. Compared to a value of $\Delta G^*_{23}(0) = 2.4$ kcal/mol found by Rehm and Weller[9] in their quenching experiments with aromatic amines, and to a value of $\Delta G^*_{23}(0)$ $= (2 \pm 1)$ kcal/mol obtained by Balzani et al.[29] for the fluorescence quenching of transition-metal complexes by aromatic amines, this relatively higher value explains very well why aliphatic amines do not lie on plots of $\ln k_q$ vs. ΔG° (or a related parameter like the half-wave oxidation potential of the electron donor by constant electron acceptor). This makes the assumption, which is made in such plots, of constant intrinsic reorganization energy, incorrect. Each electron donor–acceptor pair has its own intrinsic barrier for the cross electron transfer process, being the arithmetic mean of the particular self-exchange electron transfer reactions. If one assumes $\Delta G^*_{23}(0)$ $\simeq 3$ kcal/mol[30] for the self-exchange reaction between aromatic molecules with no appreciable Stokes shift, then the activation energy to reorganize the nuclei and the surrounding solvent molecules for the self-exchange electron transfer reaction for aliphatic tertiary amines is 7.2 kcal/mol in acetonitrile. This high activation free energy for an electron-transfer process in which the overall Gibbs free energy change is zero corroborates nicely the large geometrical changes which are known to take place in aliphatic amines after removal of an

Table I. Kinetic and Thermodynamic Data for the Fluorescence Quenching of 2MN by NMP in Polar Solvents at 25 °C

	K^{SV}, L mol^{-1}	$\tau^0{}_M$, ns	$\phi^0{}_{FM}$	k_q, L mol^{-1} s^{-1}	k_i, L mol^{-1} s^{-1}	α	$\Delta E^{\ddagger}{}_{23}$, kcal/mol	ω_{23}, s^{-1}	$\Delta G^{\ddagger}{}_{23}$, kcal/mol	$\Delta G^{\ddagger}{}_{(0)}$, kcal/mol
ethanol	11.4	47	0.26	2.4×10^8	5.5×10^9	0.04				
acetonitrile	112	54.8	0.28	2×10^9	2×10^{10}	0.1	2.8	3.8×10^{11}	2.6	5.2

electron out of the lone-pair departing orbital.[31] The relevant data are summarized in Table I.

(c) Fluorescence Quenching of 2MN in Nonpolar Solvents. In the nonpolar solvent *n*-butyl ether ($\epsilon = 3$), the fluorescence quantum yield of 2MN in the absence of quencher at 25 °C equals $\phi^0{}_{FM} = 0.20$, with a lifetime of 32.3 ns. The fluorescence quenching of 2MN by NMP at room temperature is accompanied by a new bathochromic emission with λ_{max} at 430 nm, due to exciplex formation. The Stern–Volmer constant obtained from stationary measurements equals $K^{SV} = 13$ L mol^{-1}. This value increases with decreasing temperature (Figure 3), indicating that quenching occurs through reversible exciplex formation. The data are analyzed using the well-known kinetics associated with Scheme II.[18]

Scheme II

$$M \xrightarrow{h\nu} {}^1M^*$$

$$^1M^* + Q \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} (MQ)^*$$

$$\downarrow k_M \qquad \qquad \downarrow k_E$$

M $= 2MN; Q = NMP$ (or TEA)
k_a $= \alpha k_{diff}$
k_M $= k_{FM} + \Sigma_i k_{iM}$
k_E $= k_{FE} + \Sigma k_{iE}$
k_{FM}, k_{FE} $=$ radiative rate constants for the monomer and exciplex
$\Sigma_i k_{iM}, \Sigma_i k_{iE}$ $=$ nonradiative rate constants for the monomer and exciplex

The following useful relations for monomer, ϕ_{FM}, and exciplex fluorescence quantum yield, ϕ_{FE}, hold:

$$\phi_{FM} = \frac{k_{FM}}{k_M + \dfrac{k_a k_E [Q]}{k_{-a} + k_E}} \qquad (10)$$

$$\phi_{FE} = \frac{k_{FE} k_a [Q]}{(k_{-a} + k_E)\left[k_M + \dfrac{k_a k_E [Q]}{k_{-a} + k_E}\right]} \qquad (11)$$

$$\frac{\phi_{FE}}{\phi_{FM}} = \frac{k_{FM}}{k_{FE}} \frac{k_a [Q]}{(k_{-a} + k_E)} \qquad (12)$$

$$\ln\left(\frac{1}{\phi^0{}_{FM}} - 1\right) = Ct - \frac{\Delta E^{\ddagger}{}_{iM}}{RT} \qquad (13)$$

$\Delta E^{\ddagger}{}_{iM}$ refers to the Arrhenius activation energy of the temperature-dependent rate constant in the sum $\Sigma_i k_{iM}$, and the steady-state equation for Stern–Volmer analysis is given by

$$K^{SV} = \frac{k_a k_E}{(k_{-a} + k_E)k_M} = \frac{1}{[Q]}\left[\frac{\phi^0{}_{FM}}{\phi_{FM}} - 1\right] \qquad (14)$$

A plot of $\ln[(1/\phi^0{}_{FM}) - 1]$ vs. T^{-1}, in *n*-butyl ether, yields $\Delta E^{\ddagger}{}_{iM} = 0.9$ kcal/mol. This corresponds to an activation energy expected for the S^1-T^2 transition, as suggested by the energy levels in 2MN.[32]

From Figure 3 it is seen that K^{SV} changes appreciably with temperature. This negative temperature effect upon K^{SV} is
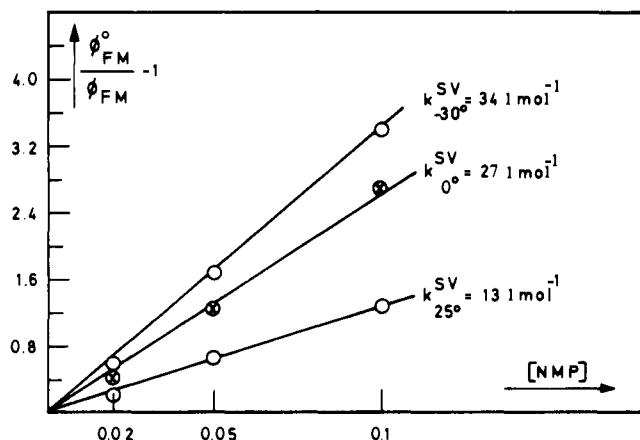
Figure 3. Stationary Stern–Volmer plot for the system 2MN–NMP in *n*-butyl ether at different temperatures.

caused by the much faster increase of the sum $(k_{-a} + k_E)$ compared to the product $k_a k_E$.

The exciplex stabilization energy, ΔH°, is obtained from a plot of $\ln(\phi_{FE}/\phi_{FM})$ vs. T^{-1} (Figure 4). The slope of the straight line drawn, using the most left-hand side of the curve, where k_E is expected to be negligible as compared to k_{-a}, equals $-\Delta H^\circ/R$. The slope of the straight line, drawn using the most right-hand side of the curve, where it is expected that $k_E \gg k_{-a}$, yields an overall Arrhenius activation energy which is approximately given by the activation energy of exciplex formation, $\Delta E^{\ddagger}{}_a$, minus $E^{\ddagger}{}_{iE}$, the activation energy associated with the temperature-dependent rate constant in the sum k_E.

However, from steady-state data alone it is not possible to know for certain from which temperature on k_{-a} is indeed much greater than k_E or vice versa.[33] Transient measurements, where individual rate constants are determined, will give the answer. Further information about the molecular properties of the exciplex is obtained by plotting the ratio of the exciplex fluorescence quantum yield over the fluorescence quantum yield of 2MN as a function of quencher concentration. The slope of this plot equals $S = k_{FE}k_a/(k_{FM}(k_{-a} + k_E))$ (Figure 5).

When $[Q] \rightarrow \infty$, eq 11 reduces to $\phi^\infty{}_{FE} = k_{FE}/k_E$. Since $\phi^0{}_{FM}$ and K^{SV} are known from steady-state analysis, it follows that $S = (\phi^\infty{}_{FE}/\phi^0{}_{FM})K^{SV}$, and $\phi^\infty{}_{FE}$ can be calculated. The data are summarized in Table II, together with the previously reported[21] results obtained in isooctane as solvent.

The steady-state experiments revealed that with increasing temperature the λ_{max} of the exciplex emission shifted to the blue. The energy associated with this hypsochromic shift, measured over the temperature interval from -70 to $+30$ °C, was found to be 3.8 kcal/mol in *n*-butyl ether as solvent, and 0.9 kcal/mol in isooctane. This effect can be explained by assuming that the excess stabilization energy of the exciplex in *n*-butyl ether as compared to isooctane (which is about 6 kcal/mol) is caused mainly by solvent reorientation around the exciplex dipole. With increasing temperature, thermal motion will act against specific solvent reorientation in the reaction field of the exciplex dipole.[34] This means that with increasing temperature the stabilization energy for exciplex formation, arising from solvent interactions, will decrease. In

Table II. Kinetic and Thermodynamic Parameters at Room Temperature for the Donor-Acceptor Complex of 2MN and NMP in Nonpolar Solvents

	K^{SV}, L mol^{-1}	$\tau^0{}_M$, ns	$\phi^0{}_{FM}$	$\Delta H°$, kcal/mol	E_R, kcal/mol	$\phi^\infty{}_{FE}$	$\Delta E^{\pm}{}_a - \Delta E^{\pm}{}_{iE}$, kcal/mol
isooctane	5.7	57	0.30	−3.3	18	0.074	
n-butyl ether	)3	32.3	0.20	−9.6	19.6	0.037	2.2
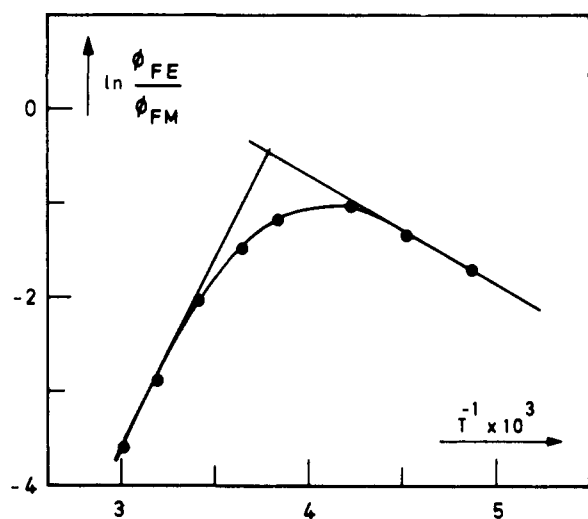
Figure 4. Plot of ln (ϕ_{FE}/ϕ_{FM}) vs. T^{-1} for the system 2MN-NMP in *n*-butyl ether with [NMP] = 0.02 M.

Figure 5. Plot of ϕ_{FE}/ϕ_{FM} vs. [NMP] for the system 2MN-NMP in *n*-butyl ether at 25 °C.

isooctane no appreciable temperature effect upon the λ_{max} is seen, since the stabilization energy due to solvent interactions is expected to be very small, because of low dielectric constant of the solvent.

Decay Measurements in *n*-Butyl Ether. From the assumed kinetic Scheme II it follows that the transient behavior of the monomer decay, $I_M(t)$, and exciplex decay, $I_E(t)$, after δ-pulse excitation are described by the equations[18]

$$I_M(t) = C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} = C_1(e^{-\lambda_1 t} + Ae^{-\lambda_2 t}) \tag{15}$$

$$I_E(t) = C_3(e^{-\lambda_1 t} - e^{-\lambda_2 t}) \tag{16}$$

where

$$A = C_2/C_1 = (X - \lambda_1)/(\lambda_2 - X) \tag{17}$$

$$\lambda_{1,2} = 0.5\{(X + Y) \mp [(Y - X)^2 + 4k_a k_{-a}[Q]]^{1/2}\} \tag{18}$$
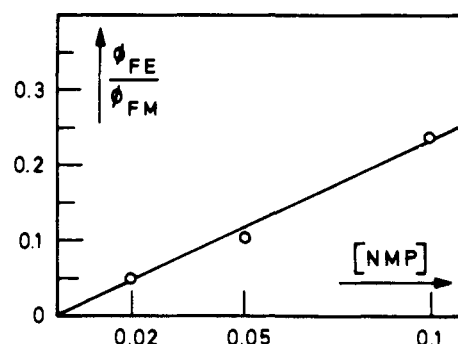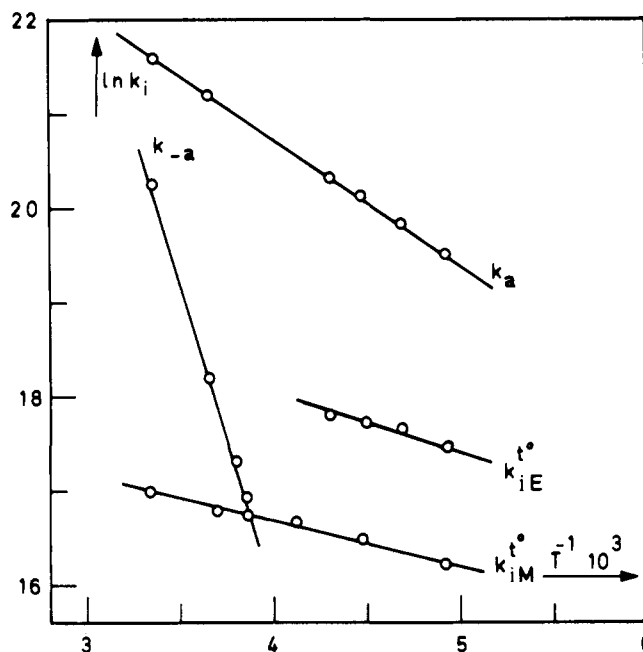
$$X = k_M + k_a[Q] = 1/T_M$$

$$Y = k_E + k_{-a}[Q] = 1/T_E$$

For the system 2MN-NMP, in *n*-butyl ether, a detailed study of the temperature effect upon the decay kinetics was undertaken in order to determine the individual rate constants, given by Scheme II.

At −70 °C the monomer decay remains one exponential when NMP is added. For instance, when [NMP] = 0.02 M, the lifetime of 2MN equals $\tau_M = 1/\lambda_1 = 43.5$ ns and the decay of the exciplex could be analyzed as a difference of two exponentials according to eq 14. However, the parameter describing the observed exciplex decay, $e^{-\lambda_1 t}$, corresponds to the monomer lifetime τ_M, and hence the parameter describing the growing in of the exciplex emission, $e^{-\lambda_2 t}$, must correspond to the exciplex lifetime $\tau_E = 1/\lambda_2 = 23.3$ ns.

Two conclusions can be drawn: (1) At −70 °C no observable regeneration of excited monomer occurs. (2) It will be impossible to obtain λ_1, λ_2, and A from the monomer decay, because τ_E will always be shorter than τ_M, in the temperature range studied.

This last conclusion is made because the normally observed

Figure 6. Arrhenius plot of the rate constants k_a, k_{-a}, $k'^0{}_{iM}$, and $k'^0{}_{iE}$ for the system 2MN-NMP in *n*-butyl ether.

fast and slow components in the monomer decay can only be accurately measured if the regenerated excited monomer has been retarded long enough in spending, statistically spoken, "a little time" as exciplex species. When $\tau_E < \tau_M$, no significant retardation will manifest itself and the decay of the excited monomer does not show the normally observed fast and slow components. This forced us to use the following alternative procedure for obtaining an individual rate constant k_i, which is expressed as $k_i = A_i \exp[-\Delta E_i^{\pm}/RT]$.

(1) In the Temperature Range from −70 to −40 °C. (a) k_M is obtained from the monomer decay in absence of quencher by $k_M = 1/\tau^0{}_M$. (b) The monomer decay, in the presence of NMP, is one exponential over more than three decades. Thus $k_{-a} \ll k_E$ and eq 14 reduces to $I_M(t) = C_1 e^{-\lambda_1 t}$, where $\lambda_1 = 1/\tau_M = 1/X$. Under these conditions k_a is given by $k_a = [(\tau^0{}_M/\tau_M) - 1](1/[Q])$. By plotting ln k_a vs. T^{-1}, the activation energy, $\Delta E^{\pm}{}_a$, and the activation entropy, $\Delta S^{\pm}{}_a$, are determined (see Figure 6).

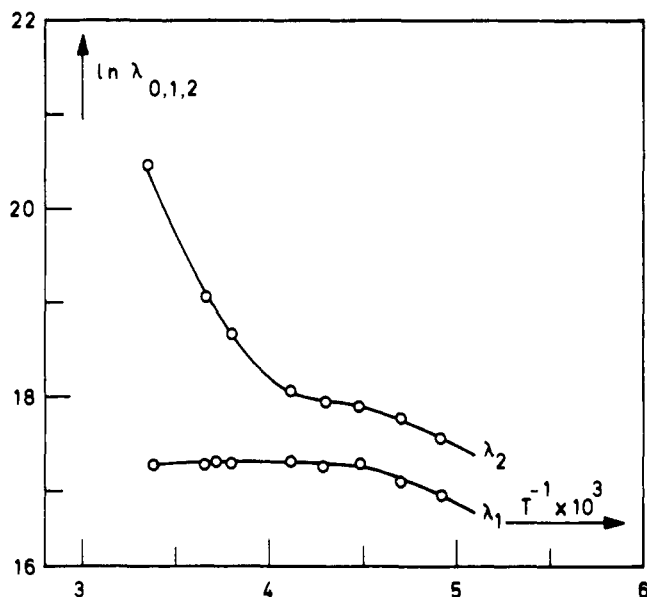(c) The exciplex decay is nicely described by the equation

Figure 7. Typical plot of the decay parameters for the system 2MN–NMP in n-butyl ether with [NMP] = 0.02 M.

Table III. Rate Constants for the System 2MN–NMP in n-Butyl Ether at Different Temperatures

t, °C	k_M, 10^7 s^{-1}	k_E, 10^7 s^{-1}	k_a, 10^8 L mol^{-1} s^{-1}	k_{-a}, 10^7 s^{-1}
−70	1.75	4.29	3.1	<1
−60	1.9	5.23	4.2	<1
−50	2.09	5.6	6	<1
−40	2.19	6	6.8	<1
−30	2.33	6.54	8.88	<1
−14	2.54	7.46	12.6	2.2
0	2.7	8.2	16.4	7.87
25	3.9	9.75	24.8	63.6

$I_E(t) = C_3 e^{-\lambda_1 t} - C_3' e^{-\lambda_2 t}$, where C_3/C_3' never deviates more than 5% from unity. The growing-in parameter yields the exciplex lifetime $\tau_E = 1/\lambda_2^{ex}$, and the parameter describing the actual observed exciplex decay $e^{-\lambda_1^{ex}}$ corresponds within 3% error range to the lifetime obtained from analysis of the monomer decay.

(d) The lifetime of the exciplex is exclusively determined by k_E, being a sum of a temperature-dependent and -independent part. The temperature-independent part is obtained by computer simulation in order to get ln $(k_E - Ct)$ linearized against T^{-1}. This constant turns out to be about 4×10^6 s^{-1}. This value corresponds to k_{FE}, which is calculated using $k_{FE} = \phi_{FE}/\tau_M \tau_E k_a[Q]$. The temperature-dependent rate constant, $k^{t^0}_{iE}$, in the exciplex decay is then given by $k^{t^0}_{iE} = (1/\lambda_2^{ex} - 4 \times 10^6)$. And from a plot of ln $k^{t^0}_{iE}$ vs. T^{-1} the activation energy $\Delta E^{\ddagger}_{iE}$ is obtained together with the preexponential factor $A^{t^0}_{iE}$ (Figure 6).

(2) In the Temperature Range from −30 to +30 °C. (a) The monomer decay is not resolvable, with sufficient accuracy, either as one or two exponential and λ_1 and λ_2 are exclusively obtained from the analysis of the exciplex decay which is described with high precision by eq 16.

(b) Upon increasing the temperature there exists a temperature where λ_2 begins to rise very fast and λ_1 reaches a plateau. This is easily understood, by remembering that in λ_2 the contribution of square root is cumulative, whereas in λ_1 the negative contribution of the square root is compensated by the growth of Y. This temperature effect upon $\lambda_{1,2}$ is illustrated in Figure 7 for [NMP] = 0.02. Above −30 °C λ_2 rises very fast, indicating that from this temperature on k_{-a} becomes
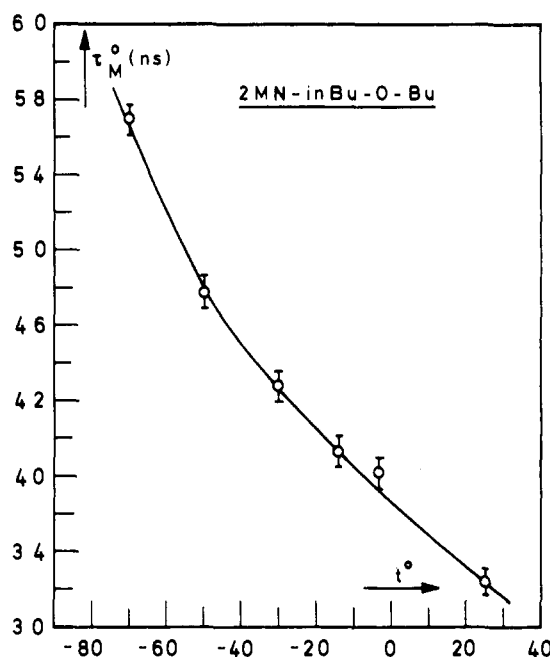

Figure 8. Lifetime of 2MN vs. temperature in absence of quencher in n-butyl ether as solvent.

Table IV. Activation Energy and Entropy of the Rate Constants for the System 2MN–NMP in n-Butyl Ether

k_i	$\Delta E^{\ddagger}_i$, kcal/ mol	A_i	$\Delta S^{\ddagger}_i$, cal mol^{-1} deg^{-1}
k_2	2.66	2.2×10^{11} L mol^{-1} s^{-1}	−8.7
$k^{t^0}_{1M}$	0.9	1×10^8 s^{-1}	
$k^{t^0}_{1E}$	1.1	6×10^8 s^{-1}	
k_{-2}	12.8	1.7×10^{18} s^{-1}	+22.7

more and more important in determining the exciplex lifetime.

(c) k_a is obtained from the least-squares slope of $(\lambda_1 + \lambda_2)$ vs. [Q], which gives an intercept $I' = k_M + k_E + k_{-a}$.

(d) k_M is obtained from the monomer decay in absence of quencher, $k_M = 1/\tau^0_M$ (Figure 8).

(e) k_E is given by $k_E = k_{FE} + k^{t^0}_{iE}$, where k_{FE} is equal to 4×10^6 s^{-1} and $k^{t^0}_{iE}$ is known from 1d.

(f) k_{-a} is determined by using $k_{-a} = I' - k_M - k_E$. And from a plot of ln k_{-a} the activation energy and entropy are obtained (Figure 6).

Some numerical values of the rate constants obtained at different temperatures are shown in Table III. The activation energies and entropies associated with the individual rate constants are given in Table IV. From Table IV the enthalpy and entropy changes, $\Delta H°$ and $\Delta S°$, involved in exciplex formation are obtained according to $\Delta H° = \Delta E^{\ddagger}_a - \Delta E^{\ddagger}_{-a}$ and $\Delta S° = \Delta S^{\ddagger}_a - \Delta S^{\ddagger}_{-a}$. The results are shown in Table V, together with some relevant kinetic data in order to compare the influence of the solvent upon the exciplex formation at room temperature.

The slight discrepancy between $\Delta H°$ obtained from steady-state measurements is easily understood by remembering the dangers associated with determining $\Delta H°$ from the curve of ln ϕ_{FE}/ϕ_{FM} vs. T^{-1}.[33] From transient measurements it is seen that only above 20 °C $k_{-a} \gg k_E$. The increase in k_E with increasing solvent polarity (Table V) is explained on the basis of a ϵ-dependent rate constant[12,13] through the reaction
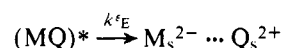
$$(MQ)^* \xrightarrow{k^f_E} M_s^{2-} \cdots Q_s^{2+}$$

Table V. Kinetic and Thermodynamic Properties of the 2MN–NMP Exciplex in Nonpolar Solvents at 25 °C

solvent	$\Delta H°$, kcal/mol	$\Delta S°$, cal mol^{-1} deg^{-1}	$\Delta G°$, kcal/mol	E_R, kcal/mol	ϕ^{∞}_{FE}	k_E, s^{-1}	k_{FE}, s^{-1}	τ_E, ns
isooctane	−3.3	−7.7	−0.9	18	0.079	1.9×10^7	1.4×10^6	<4[a]
n-butyl ether	−10.1	−31.4	−0.7	19,6	0.037	9.75×10^7	4×10^6	1,3

[a] At 25 °C the monomer and exciplex decay with an identical parameter $\lambda \simeq (k_M + k_E)/2$, and k_{-a} is estimated to be at least ten times greater than k_E, so $\tau_E \leqslant 4$ ns.[21]

The large increase of the exciplex stabilization enthalpy with increasing polarity is understood as caused by solvent interaction with the dipole of the exciplex.[5] The difference in Gibbs free solvation energy, ΔG_s, of an exciplex with dipole moment μ and cavity radius ρ, in a solvent of dielectric constant ϵ and isooctane, is given by[5]

$$\Delta G_s = -\frac{\mu^2}{\rho^3}\left(\frac{\epsilon - 1}{2\epsilon + 1} - 0.19\right) \quad (19)$$

The difference in solvation enthalpy ΔH_s is therefore given by[35]

$$\Delta H_s(\epsilon) = \Delta G_s + T\frac{\delta \Delta G_s}{\delta T}$$
$$= -\frac{\mu^2}{\rho^3}\left(\frac{\epsilon - 1}{2\epsilon + 1} + \frac{3T}{(2\epsilon + 1)^2}\frac{\delta\epsilon}{\delta T}\right) - 0.19 \quad (20)$$

yielding $\Delta H° = -8.4$ kcal/mol for the expected exciplex stabilization enthalpy in n-butyl ether.[40] The experimental obtained value amounts to −10 kcal/mol. The enhanced solvation with increasing polarity is also manifested in the much more negative value for $\Delta S°$ of about −30 cal K^{-1} mol^{-1} in n-butyl ether as compared to −7.7 cal K^{-1} mol^{-1} in isooctane, and in the relatively high preexponential factor of 10^{18} s^{-1} for k_{-a}. The exciplex ground state repulsion energy, E_R, is calculated using the equation

$$E_R = h\nu_{FM} - h\nu_{FM} + \Delta H° + 2T(\delta\Delta G_s/\delta T) \quad (21)$$

where the last term takes changes in solvation entropy into consideration.[36] As seen from Table III E_R increases slightly with solvent polarity, and E_R is larger compared to E_R values for exciplexes between aromatic donors and acceptors, which are about 7 kcal/mol.[9]

A high E_R value is only found in exciplexes when aliphatic amines are present. An E_R value of about 18 kcal/mol is also found for the intermolecular excimer formation of 1-azabicyclo[2.2.2]octane (ABCO).[37] The main factor causing this high ground-state repulsion energy for excited-state complexes where aliphatic tertiary amines are participating must be due to the severe differences between the nuclear configuration of a ground-state and an excited-state aliphatic amine. The increase in k_{FE} with solvent polarity can be explained by an increase in the transition dipole moment $M = (\Psi_E H'^{-1} \Psi_g^{-1})$, where Ψ_E is the exciplex wave function, Ψ_g denotes the Franck–Condon ground-state wave function, and H' is the electric dipole moment operator. This increase of M is due to a higher contribution of the matrix element $[\Psi(A^-D^+)/\mu_0/\Psi(A^-D^+)]$, where $\Psi(A^-D^+)$ is the charge transfer wave function with a dipole moment equal to μ_0 (5). An alternative explanation is a change of the matrix elements due to configurational changes caused by polar solvent molecules. Although there is also a difference between the calculated and the experimental value of $\Delta H°$, we do not want to emphasize these differences as being caused by important changes in exciplex geometry.

An interesting result is the remarkable resemblance between the rate constant for fluorescence quenching in acetonitrile and the rate constant for exciplex formation in n-butyl ether, both being smaller than the rate constant for diffusion, by a factor $\alpha = 0.1$, and both having a preexponential factor of about 3

$\times 10^{11}$ s^{-1} and an Arrhenius activation energy of about 2.7 kcal/mol. Whether this is pure coincidence or not, it seems worthwhile to point out the similarity between the Gibbs free activation energy required for the complete and "partial" electron transfer, suggesting that a similar activated complex may lie on both pathways.

In acetonitrile the results are analyzed using the concepts introduced by Marcus theory. However, it is argued that the physical reality of the frequency factor (and its numerical value) is not clear and open to some criticism. The procedure followed in this paper evaluates the intercept obtained from a plot of ln k_q vs. T^{-1} by considering Brownian motion leading to collisions with a mean lifetime given by $1/k_{21} = R^2/3D$,[38] and a probability of electron transfer within this lifetime equal to $\alpha = [1 + (k_{21}/k_{23})]^{-1}$. The rate constant for the electron-transfer process is then written as $k_{23} = \omega_{23} \exp[-\Delta G^*_{23}/RT]$, where ω_{23} is the collision frequency (s^{-1}) in solution, calculated by Smoluchowski's expression $\omega_{23} = 4\pi RD\nu_0$, and ΔG^*_{23} represents the Gibbs free activation energy required for the electron transfer which is given by $\Delta G^*_{23} = \Delta E^{\ddagger}_{23} - RT \ln (Ik_{21}/k_{12}\omega_{23})$. For an outer-sphere electron jump mechanism ΔG^*_{23} can be expressed as a function of the overall Gibbs free energy change, $\Delta G°$, by eq 7, where $\lambda/4$ represents the intrinsic barrier for electron transfer (when $\Delta G° = 0$), which is composed of two contributions, λ_i and λ_0; λ_i can be regarded as the intrinsic free activation energy to reorganize the nuclei of the reactants and λ_0 corresponds to the solvent reorganization parameter, given by

$$(\Delta e)^2\left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right]\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)$$

where a_1 and a_2 are the radii of the two reactants and r is their separation in the activated complex, D_{op} is the square of the refractive index of the medium, D_s is the static dielectric constant of the medium, and Δe is the transferred charge. Marcus calculated λ_i to be only about 2% of λ_0,[39] the latter being about 3 kcal/mol.[11] However, this study yields an intrinsic barrier for the electron transfer of 5.2 kcal/mol, indicating that λ_i is not negligible as compared to λ_0. This corroborates the large geometrical changes which take place in aliphatic amines after excitation.

Experimental Section

The purity of the solvents was checked by gas chromatography. The amines were refluxed and distilled over LiAlH$_4$, and 2-methylnaphthalene was purified by repetitive sublimation. Absorption spectra were taken on a Perkin-Elmer double-beam spectrophotometer. Corrected fluorescence spectra were taken on a Fica "spectrofluorimètre différentielle absolu." Quantum yields were determined using quinine sulfate in 0.1 N H$_2$SO$_4$. Fluorescence lifetimes and decay parameters were measured using the single photon counting technique. The observed decays were deconvoluted using a nonlinear least-squares program. All solutions were degassed by four freeze-pump-thaw cycles.

tively. Stimulating discussions with Professor Weller are gratefully acknowledged.

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Stepwise Bond Dissociation Energies in Sulfur Hexafluoride

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Abstract: The F_5S–F and F_3S–F bond dissociation energies are determined from studies of the chemiluminescent reactions of SF_6 and SF_4 with metastable calcium and strontium atoms under single-collision conditions. These results are combined with known heats of formation to deduce the following stepwise bond dissociation energies: $D_0°(F_5S–F) = 91.1 \pm 3.2$, $D_0°(F_4S–F) = 53.1 \pm 6.0$, $D_0°(F_3S–F) = 84.1 \pm 3.0$, $D_0°(F_2S–F) = 63.1 \pm 7.1$, $D_0°(FS–F) = 91.7 \pm 4.3$, $D_0°(S–F) = 81.2 \pm 1.6$ kcal/mol. The zigzag pattern of these successive bond dissociation energies is discussed in terms of bonding theory.

Introduction

Through advances in high-temperature chemistry, it is now possible to measure the stepwise bond dissociation energies of a number of polyvalent compounds in which a central atom is surrounded by identical ligands.[1] Central atoms belonging to groups 5–8 in the periodic table are of particular interest because these elements have the ability to form more bonds than the Lewis–Langmuir octet rule[2,3] permits. Studies of these "hypervalent"[4] molecules have been greatly stimulated by the discovery of the xenon fluorides.[5]

The sulfur fluorides, particularly the stable gaseous species sulfur tetrafluoride (SF_4) and sulfur hexafluoride (SF_6), are outstanding examples of hypervalent compounds. The present work reports the determination of the F_3S–F bond dissociation energy and slightly revises the F_5S–F bond dissociation energy determined previously in this laboratory.[6] The motivation of this study is that such measurements can be combined with existing thermochemical and mass spectrometric data to deduce the bond dissociation energies of $F_{n-1}S$–F, n = 1–6. This structural information can then be used to test various valency concepts in order to deepen our understanding of the bonding in the sulfur fluorides and other hypervalent species.

Experimental Section

Method. Chemiluminescent emission from elementary bimolecular reactions under single-collision conditions provides a means for placing bounds on the bond dissociation energy of the reactant, provided that the bond dissociation energy of the product is known.[6,7] We apply this technique to the reaction of a metastable alkaline earth atom, $M(^3P)$, with a sulfur fluoride, SF_n:

$$M(^3P) + SF_n \rightarrow MF^* + SF_{n-1} \tag{1}$$
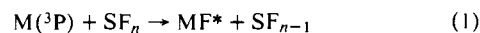
which yields an electronically excited alkaline earth monofluoride,