trogen since the shape of the emission curves is not affected and the quantum yields of fluorescence only slightly increased in nonpolar solvents (unchanged in medium- and high-polarity solvents) by such purging. Sample temperatures were controlled at 25.0 ± 0.5 °C. Dioxane was from E. Merck, Darmstadt (spectrograde). Plots were executed with a Hewlett-Packard 9810-9862 calculator–plotter combination.

References and Notes

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Intramolecular Donor–Acceptor Systems. 4. Solvent Effects on Radiative and Nonradiative Processes for the Charge-Transfer States of *N*-Arylaminonaphthalenesulfonates

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Abstract: Fluorescence lifetimes and fluorescence quantum yields for 6,2- and 8,1-*N*-arylaminonaphthalenesulfonates (ANS) have been measured in dioxane–water solutions having a wide range of solvent polarities, as measured by the empirical solvent polarity parameter, $E_T(30)$. The radiative rate constants for change-transfer emission ($S_{1,ct} \rightarrow S_{0,np}$) and the nonradiative rate constants for electron-transfer reaction ($S_{1,ct} \rightarrow S_{0,np}$) are both sensitive to solvent. The greater sensitivity of the latter, k_{nr}, than the former, k_r, to changes in solvent polarity accounts for the strong quenching observed for ANS derivatives in polar solvents. The solvent dependence of $(k_r)^{1/2}$ can be accounted for reasonably well in terms of a relationship based on substituent effects on emission energies. The linear dependence of the transition state free energy $\Delta G^{\ddagger}$ (for k_{nr}) on $E_T(30)$ is explained by the "migration" of charge (i.e., screening) into the solvent shell. The $\Delta G^{\ddagger}$ correlations for many of the ANS derivatives extrapolate to a common region, which corresponds roughly to the dielectric relaxation rate for water. The intramolecular electron-transfer rate is thus limited by a property of a suitable reaction field, R_s, in the solvent, with intramolecular factors such as donor–acceptor overlap and bond distance changes all being compatible with still higher electron-transfer rates. A mechanism for an intramolecular electron-transfer reaction is thus established. The relationship of the strong solvent effect on emission energies to the strong effect upon $\Delta G^{\ddagger}$ is explained. Analysis of other results from the literature, using the ANS results for k_r and k_{nr} as references, reveals that some quenching reactions may be electron transfer and some most certainly are not. A new quenching mechanism, formation of an unstable covalent bond, is proposed for several molecules. A classification of decay processes for excited charge-transfer states is also given.

Introduction

In 1954, Weber and Laurence[2] made the discovery that certain arylaminonaphthalenesulfonates (ANS), highly fluorescent in nonpolar solvents, were strongly quenched in very polar solvents like water. The application of the phenomenon to the measurement of protein binding site polarity[3] stimulated several studies[4,5] which, however, did not lead to an explanation for the solvent effect. Even sophisticated investigations like

Table I. Quantum Yields, Lifetimes, Radiative and Nonradiative Constants, and Nonradiative Transition State Free Energies for 6-*N*-Phenylamino-2-naphthalenesulfonate in Dioxane–Water Mixtures[a,b]

Solvent % dioxane–water[c]	$E_T(30)$ value[d]	Quantum yield (ϕ_F)[e]	Lifetime (τ_{obsd}), ns	Radiative rate constant $10^{-7}k_r$, s^{-1}	Nonradiative rate constant $10^{-7}k_{nr}$, s^{-1}	$\Delta G_{nr}^{\ddagger}$,[f] kcal/mol
100	36.1	0.71	7.4	9.5	4.0	7.08
98.3	40.6	0.74	8.1	9.1	3.2	7.20
95.2	43.5	0.76	9.3	8.2	2.6	7.33
90.3	46.6	0.77	9.2	8.5	2.5	7.35
80.6	48.9	0.81	9.8	8.3	1.9	7.50
71.0	50.7	0.79	9.6	8.3	2.2	7.44
57.7	52.6	0.53	8.7	6.1	5.4	6.89
48.3	53.9	0.43	7.5	5.8	8.9	6.59
38.9	55.8	0.28	5.4	5.0	14	6.35
29.6	57.3	0.14	3.1	4.4	28	5.92
20.2	58.6	0.064	1.9	3.4	49	5.58
10.8	60.9	0.027	1.0	2.6	95	5.19
6.1	61.9	0.014	0.78	1.8	130	5.02

[a] Temperature 25.5 ± 0.2 °C. Temperature effects on the position of the fluorescence maximum or the intensity of the emission over this temperature range are small. [b] For details of the measurements and the instrumentation, refer to the Experimental Section. [c] Percentage of dioxane by volume mixed with water. [d] Values were either taken from Table 2, p 28, in C. Reichardt and K. Dimroth, *Fortschr. Chem. Forsch.*, **11**, 1 (1968), or derived from values in that table by linear interpolation. [e] ±10%, or less, according to reproducibility. Quinine sulfate in 0.1 N H$_2$SO$_4$, ϕ_F = 0.55, quantum yields in each solvent are corrected for refractive index, and all measurements were made on solutions purged with nitrogen. [f] Transition state free energies at 25 °C.

those of Chakrabarti and Ware[6] did not properly distinguish between the states generated on excitation and those responsible for emission. An important advance was made by Kosower and Tanizawa[7] who utilized comparisons of emission energies and quantum yield data with solvent polarity parameters to identify two emitting states for 6,2-ANS derivatives (**1**). The multiple fluorescences arose from a locally excited state, $S_{1,np}$, and a charge-transfer state, $S_{1,ct}$. The sequence shown in eq 1 explained why absorption maxima are

$$S_{0,np} \xrightarrow{h\nu} S_{1,np} \underset{e^-}{\overset{e^-}{\rightleftarrows}} S_{1,ct} \qquad (1)$$
$$\downarrow h\nu \qquad \downarrow h\nu$$
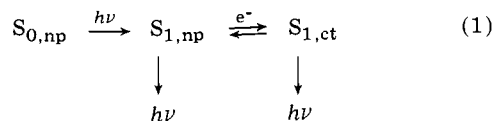
relatively insensitive to solvent polarity and emission maxima are sensitive to the nature of the solvent only in fairly polar solvents.

Further clarification of the system dynamics was obtained through spectra of the excited states produced by 10-ns laser pulses and by varying the viscosity of the solvent used for both laser pulse and steady state experiments.[8] It was shown that the yield of triplet state molecules decreased sharply with increasing solvent polarity, excluding intersystem crossing as a quenching mechanism. In addition, high-viscosity solvents inhibited the formation of the charge-transfer state and medium-viscosity solvents inhibited quenching of the charge-transfer state, the latter effect implying that an electron-transfer reaction was responsible for the quenching process[8] (eq 2).

$$S_{1,ct} \xrightarrow{e^-} S_{0,np} \qquad (2)$$

Further results for *N*-methyl-6-arylamino-2-naphthalenesulfonates (**2**) led to the identification of two charge-transfer
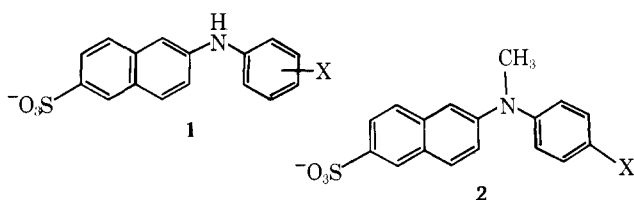
states, $S_{1,ct(U)}$ and $S_{1,ct(C)}$, which differ in whether or not the lone pair on the nitrogen is conjugated to the aryl group in the charge-transfer state.[9] Analysis of the substituent and solvent effects on the two different charge-transfer states gave insight into their nature and estimates for the effective charge on the aryl ring in different solvents.[9]

The foregoing facts and the detailed mechanism which could be formulated on the basis of those facts[8,10] nevertheless do not provide a clear understanding of the factors which govern the disappearance of the charge-transfer states, $S_{1,ct(U)}$ or $S_{1,ct(C)}$. Laser pulse experiments and detailed studies of what are normally minor side reactions like protonation[10] reveal that only two channels, either quenching or emission, are significant for the decay of the charge-transfer states. Understanding the decay thus becomes a problem in perceiving why the two channels should be so differently affected by solvent polarity (eq 3).

$$S_{1,ct} \xrightarrow{k_{nr}} S_{0,np} \qquad (3)$$
$$k_r \downarrow$$
$$h\nu$$
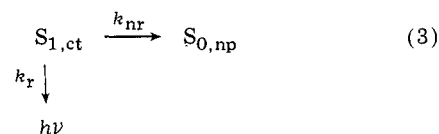
As stated, the problem is thus seen to be a question of understanding the dynamics of excited state behavior through quantitation of the effect of solvent on two rate constants, k_r (radiative) and k_{nr} (nonradiative, electron-transfer quenching). We have for this reason carried out fluorescence lifetime and quantum yield measurements on various 6,2-ANS and 8,1-ANS derivatives (**3**)[11] in various solvents, and now report that

3
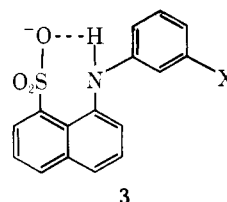
both the radiative and nonradiative rates are altered by changes in solvent polarity. With the aid of our data, we have been able to develop a fairly comprehensive understanding of the disappearance of the charge-transfer states of ANS derivatives.

1

2

Table II. Quantum Yields, Lifetimes, and Derived Rate Constants for 6-N-Arylamino-2-naphthalenesulfonates in Dioxane–Water Mixtures[a]

Substit-uent	Solvent % dioxane–water	$E_T(30)$ value	Quantum yield (ϕ_F)	Lifetime (τ_{obsd}) ns	Radiative rate constant $10^{-7}k_r$, s^{-1}	Nonradiative rate constant $10^{-7}k_{no}$ s^{-1}	$\Delta G^{\ddagger}$, kcal/mol
3-F	19.7	58.7	0.48	6.3	7.6	8.3	6.63
	13.4	59.5	0.37	5.3	6.9	12.	6.42
	10.0	61.1	0.21	3.5	5.9	22.	6.05
	6.8	61.7	0.15	2.8	5.4	30.	5.87
	3.5	62.4	0.084	2.1	3.9	43.	5.66
	3.2	62.5	0.066	1.7	3.8	54.	5.53
4-CH$_3$	61.4	52.1	0.22	5.3	4.1	15	6.29
	53.0	53.2	0.11	3.3	3.5	27	5.94
	43.6	54.8	0.055	2.0	2.7	47.	5.61
	37.4	56.0	0.032	1.5	2.1	65.	5.42
	31.1	57.0	0.019	1.1	1.7	86.	5.25
	21.8	58.4	0.0077	0.82	0.94	113	5.09
4-OCH$_3$	99.9	36.3	0.45	9.6	4.0	5.7	6.86
	99.6	37.2	0.43	9.9	4.0	5.8	6.86
	99.3	37.9	0.38	9.5	4.0	6.5	6.78
	99.0	38.5	0.30	8.1	3.7	8.6	6.62
	98.3	40.6	0.28	8.6	3.3	8.3	6.64
	96.8	42.3	0.19	7.0	2.7	12.	6.44
	95.2	43.5	0.11	4.5	2.5	20.	6.12
	93.6	44.8	0.086	3.6	2.4	25.	5.98
	92.5	45.6	0.071	3.6	2.0	26.	5.97
	90.5	46.5	0.045	2.2	2.1	44.	5.65

[a] All footnotes of Table I apply.

Table III. Quantum Yields, Lifetimes, and Derived Rate Constants for 6-N-Methyl-N-phenylamino-2-naphthalenesulfonate in Dioxane–Water Mixtures[a]

Solvent % dioxane–water	$E_T(3)$ value	Quantum yield (ϕ_F)	Lifetime (τ_{obsd}), ns	Radiative rate $10^{-7}k_r$, s^{-1}	Nonradiative rate $10^{-7}k_{nr}$, s^{-1}	$\Delta G_{nr}^{\ddagger}$, kcal/mol
99.9	36.3	0.70	12.4	5.7	2.4	7.37
98.1	41.1	0.56	11.1	5.0	4.0	7.07
94.4	44.2	0.50	11.5	4.3	4.3	7.02
81.3	48.7	0.44	12.2	3.6	4.6	6.99
57.7	52.6	0.27	9.5	2.8	7.7	6.69
48.3	53.9	0.18	7.6	2.4	11.	6.49
38.9	55.8	0.11	5.6	1.9	16.	6.25
29.6	57.3	0.045	3.5	1.3	28.	5.92
20.2	58.6	0.020	2.3	0.88	43.	5.66
10.8	60.9	0.0078	1.5	0.52	66.	5.41
6.1	61.9	0.0034	0.86	0.40	116.	5.07

[a] All footnotes of Table I apply.

Results

In order to obtain data suitable for detailed analysis, we took all possible precautions in preparing the solutions of arylaminonaphthalenesulfonates and in executing the lifetime measurements through single photon counting. Solutions were oxygen free, measurements were made at carefully controlled temperatures (25 ± 0.2 °C), the pulse width of the exciting light was measured frequently, quantum yield measurements were made on the solutions actually used for lifetime measurements (and refractive index corrections were made), and duplicate measurements were made in many cases. The well-defined character of the excited states of arylaminonaphthalenesulfonates, especially the fact that the charge-transfer state represents an intramolecular ion pair with a specified distance between the donor and acceptor moieties, makes information about the dynamics of the excited states useful for theoretical analysis. For this reason, we report our results in detail.

In Tables I and II we list the following data for 6-N-(X-phenylamino)-2-naphthalenesulfonates (**1**, X = 3-F, 4-H, 4-CH$_3$, 4-OCH$_3$); composition of the dioxane–water mixture used for the measurement and the corresponding solvent polarity, as measured by the parameter $E_T(30)$;[12,13] the quantum yield of fluorescence; the measured lifetime; the radiative rate constant; the nonradiative rate constant (equivalent to the rate constant for the electron-transfer reaction which leads to quenching of fluorescence); and the transition state free energy corresponding to the nonradiative rate constant. In Table III similar data are listed for N-methyl-6-N-phenylamino-2-naphthalenesulfonate (**2**). In Tables IV and V data are given for two derivatives of 8-N-phenylamino-1-naphthalenesulfonate (**3**, X = H, Br).

In Figure 1 are plotted the square roots of the radiative rate constants, k_r, against solvent polarity, $E_T(30)$, for all of the 6,2-ANS derivatives. Plots of $(k_r)^{1/2}$ vs. $E_T(30)$ for 8,1-ANS derivatives are given in Figure 2. The reason for this type of plot will become clear in the Discussion. The transition state free energies derived from the nonradiative rate constants are

Table IV. Quantum Yields, Lifetimes, and Derived Rate Constants for 8-*N*-Phenylamino-1-naphthalenesulfonate in Dioxane–Water Mixtures[a]

Solvent % dioxane– water	$E_T(30)$ value	Quantum yield (ϕ_F)	Lifetime (τ_{obsd}), ns	Radiative rate constant $10^{-7}k_r$, s^{-1}	Nonradiative rate constant $10^{-7}k_{nr}$, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol
99.9	36.4	0.65	12.4	5.3	2.8	7.28
98.3	40.6	0.53	11.9	4.5	4.0	7.08
95.2	43.5	0.426	10.8	4.0	5.3	6.90
90.5	46.5	0.311	9.4	3.3	7.3	6.71
84.3	48.1	0.222	8.0	2.9	10.	6.52
74.9	50.0	0.162	6.4	2.5	13.	6.37
67.06	51.3	0.115	4.9	2.3	18.	6.18
61.5	52.1	0.085	3.7	2.3	25.	6.00
57.7	52.6	0.077	3.6	2.2	26.	5.97
48.3	53.9	0.048	2.6	1.9	37.	5.95
43.6	54.9	0.028	1.7	1.7	57.	5.49
38.9	55.8	0.021	1.5	1.4	65.	5.41
29.6	57.3	0.014	1.3	1.1	78.	5.30
20.2	58.6	0.008	0.86	0.97	115.	5.08

[a] All footnotes of Table I apply.

Table V. Quantum Yields, Lifetimes, and Derived Rate Constants for 8-*N*-(3-Bromophenylamino)-1-naphthalenesulfonate in Dioxane–Water Mixtures[a]

Solvent % dioxane– water	$E_T(30)$ value	Quantum yield (ϕ_F)	Lifetime (τ_{obsd}), ns	Radiative rate constant $10^{-7}k_r$, s^{-1}	Nonradiative rate constant $10^{-7}k_{nr}$, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol
99.9	36.4	0.741	10.8	6.9	2.4	7.39
98.3	40.6	0.734	11.3	6.5	2.4	7.39
95.2	43.5	0.708	12.2	5.8	2.4	7.38
90.5	46.5	0.630	13.1	4.8	2.8	7.28
81.1	48.8	0.587	13.2	4.4	3.1	7.22
71.8	50.6	0.532	12.7	4.2	3.7	7.12
62.4	52.0	0.432	12.3	3.5	4.6	6.99
53.0	53.2	0.342	11.1	3.1	5.9	6.84
43.62	54.9	0.248	9.2	2.7	8.2	6.65
34.3	56.5	0.160	6.7	2.4	13.	6.39
21.8	58.4	0.076	4.0	1.9	23.	6.03
12.4	60.9	0.036	2.5	1.4	56.	5.50

[a] All footnotes of Table I apply.

plotted vs. $E_T(30)$ for all of the ANS derivatives in Figure 3. In order to make apparent the difference in the scale of the response of the nonradiative rate constants in comparison to the radiative rate constants to a change in solvent polarity, we present in Figure 4 plots of the k_r and k_{nr} for a number of 6,2-ANS derivatives as a function of $E_T(30)$. The quantities used are defined as shown in the equations

$$\phi_F = k_r/(k_r + k_{nr}) \tag{4}$$

$$k_r = \phi_F/\tau \tag{5}$$

$$k_{nr} = (1 - \phi_F)/\tau \tag{6}$$

ϕ_F, quantum yield of fluorescence; k_r, radiative rate constant; k_{nr}, nonradiative rate constant ($= k_e$, electron-transfer reaction rate constant); τ, observed lifetime.

Discussion

To begin with, the problem of quenching of fluorescence of arylaminonaphthalenesulfonates in polar solvents must now be regarded as solved. The conclusions reached by Chakrabarti and Ware,[6] on the basis of a relatively narrow range of radiative and nonradiative rate constants derived from measurements on 8,1-ANS in a group of solvents covering a modest
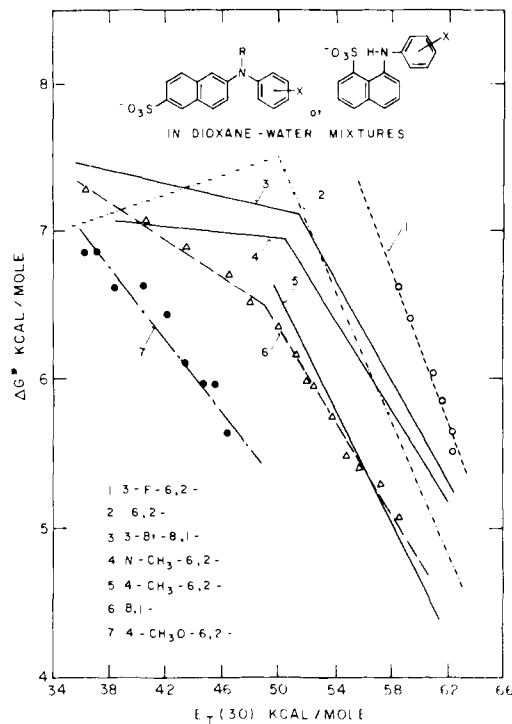
range of solvent polarities, are entirely confirmed and extended to 6,2-ANS and *N*-methyl-6,2-ANS systems. The fluorescence yield decreases in polar solvents because the radiative rate decreases and, more importantly, the nonradiative rate increases strongly. Our data, which constitute the most extensive and accurate set of constants available for the dynamic behavior of excited charge-transfer states, lead us to new insights into the reasons for the changes in the rate constants.

Radiative Rate Constants. The constants, k_r, for most ANS derivatives exhibit two types of behavior with respect to solvent polarity change. In nonpolar solvents, the radiative rate decreases to a small extent as solvent polarity increases for emissions which have previously been assigned as $S_{1,np}$ emissions. In solutions of sufficient polarity, the behavior of k_r changes, the radiative rate becoming markedly dependent upon solvent polarity. The emissions in solvents which exhibit marked dependence of the radiative rate upon solvent polarity have previously been assigned as originating from charge-transfer states, $S_{1,ct}$. The two-phase behavior of k_r is new, independent evidence for the correctness of the assignments previously made on the basis of the changes in emission energy and quantum yield with solvent polarity and confirmed by other means (excited state spectra, substituent effects, solvent viscosity effects).[8-10]
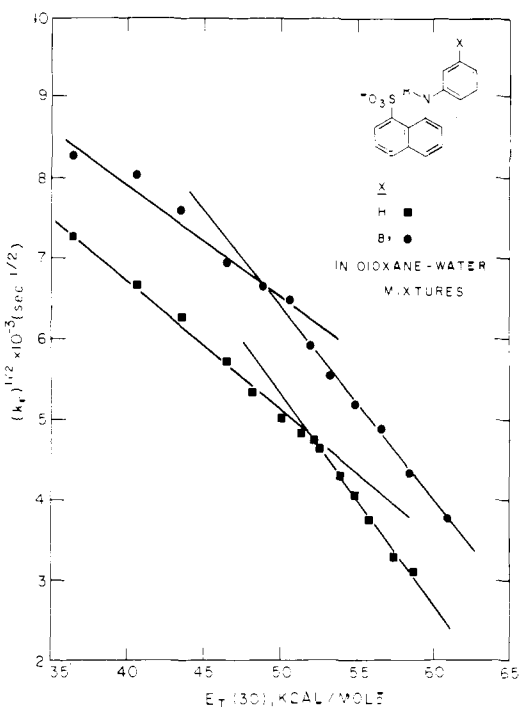
We shall now consider the quantitative changes in the radiative rate constants. The radiative rate constant is given
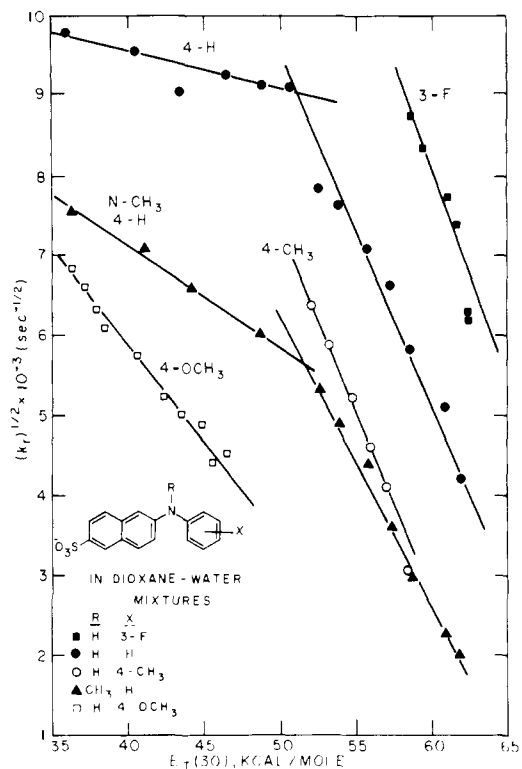
Figure 1. A plot of square root of radiative rate constants $((k_r)^{1/2})$ (in $s^{-1/2}$) vs. the solvent polarity parameters, $E_T(30)$ (in kcal/mol), for five 6-N-arylamino-2-naphthalenesulfonates ($\mathbf{1}$, X = 3-F, H, 4-CH$_3$, 4-OCH$_3$; $\mathbf{2}$, X = H) in a series of dioxane–water mixtures.

Figure 2. A plot of square root of radiative rate constants $((k_r)^{1/2})$ (in $s^{-1/2}$) vs. the solvent polarity parameter, $E_T(30)$ (in kcal/mol), for two 8-N-arylamino-1-naphthalenesulfonates ($\mathbf{3}$, X = H, Br) in a series of di-oxane–water mixtures.

Figure 3. A plot of the transition state free energies ($\Delta G^{\neq}$) (in kcal/mol) derived from the nonradiative rate constants vs. the solvent polarity parameters, $E_T(30)$ (in kcal/mol). The lines for different ANS derivatives are designated as follows: 1, $\mathbf{1}$, X = 3-F; 2, $\mathbf{1}$, X = H; 3, $\mathbf{3}$, X = 3-Br; 4, $\mathbf{2}$, X = H; 5, $\mathbf{1}$, X = 4-CH$_3$; 6, $\mathbf{3}$, X = H; 7, $\mathbf{1}$, X = 4-OCH$_3$.
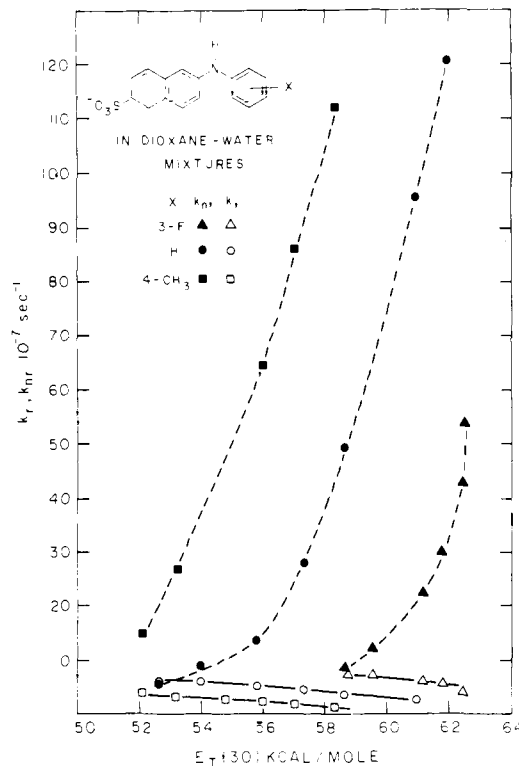
Figure 4. A plot of the radiative (k_r) (s^{-1}) and the nonradiative (k_{nr}) (s^{-1}) rate constants against the solvent polarity parameter ($E_T(30)$, in kcal/mol) for a number of 6,2-ANS derivatives ($\mathbf{1}$, X = 3-F, H, 4-CH$_3$) in a series of dioxane–water mixtures.

by eq 7. Comparison of the constants in two solvents of different polarity will be made with eq 8, which concentrates in one quantity, $q_{2/1}$, those factors responsible for the large and smooth dependence of the radiative rate constants on solvent

polarity. We must emphasize here that such large solvent effects on the radiative rate of a well-defined charge-transfer transition have only been rarely observed, and are worthy of

Table VI. Comparison of Ratios of Square Roots of Radiative Rate Constants and Ratios of Hammett "Reaction Constants" for a Series of Arylaminonaphthalenesulfonates in Solvent Pairs of Different Polarity

Compd	$E_T(30)_1{}^a/$ $E_T(30)_2$	$(k_r)_1{}^{1/2}{}^a/$ $(k_r)_2{}^{1/2}$	$\rho_1{}^b/$ ρ_2	$\nu_1{}^{3/2}{}^c/$ $\nu_2{}^{3/2}$	$Q_{1/2}{}^{c,d}$
6,2-ANS[e]	48.8	2.50	1.49	1.19	1.87
	62.5				
3-F-6,2-ANS	56.4	1.43	1.14	1.08	1.26
	62.0				
4-CH₃-6,2-ANS	44.3	2.50	1.43	1.24	1.84
	57.3				
4-CH₃O-6,2-ANS	35.0	1.75	1.32	1.22	1.62
	47.8				
8,1-ANS	47.5	2.00	1.60	1.12	1.87
	58.6				
3-Br-8,1-ANS	51.6	1.50	1.44	1.11	1.66
	60.0				
N-CH₃-6,2-ANS	53.5	2.50	1.69	1.23	2.16
	61.8				

[a] From Figures 1 and 2 based on data recorded in Tables I-V. [b] Derived from ρ values estimated for emissions from $S_{1,ct(C)}$ or $S_{1,ct(U)}$ states. See ref 9 and E. M. Kosower and H. Kanety, Intramolecular Donor–Acceptor Systems (ref 11). [c] See eq 9. [d] To be compared with the ratio of the square roots of the radiative rate constants, second column. [e] ANS = *N*-arylaminonaphthalenesulfonate. Substitutents are located on the *N*-aryl group in all cases except for the *N*-methyl group (N-CH₃).

Table VII. Transition State Free Energies Compared to Excited State Stabilization Energies Derived from Fluorescence Emission Energies[a]

Compd	$\Delta\Delta G^{\ddagger}/$ $\frac{1}{2}\Delta E_F$	Compd	$\Delta\Delta G^{\ddagger}/$ $\frac{1}{2}\Delta E_F$
N-CH₃-6,2-ANS	0.46	4-CH₃-6,2-ANS	0.73
3-F-6,2-ANS	0.45	8,1-ANS	0.93
6,2-ANS	0.72	3-Br-8,1-ANS	0.87.

[a] Fluorescence emission energies given in ref 8–10.

further investigation.

$$k_r = \frac{64\pi^4\nu^3 n^2}{3hc^3}\langle \Psi_E|\overline{er}|\Psi_G\rangle^2 \qquad (7)$$

$$k_{r_1}/k_{r_2} = n_1{}^2\nu_1{}^3/n_2{}^2\nu_2{}^3(1/q_{2/1}{}^2) \qquad (8)$$

The symbols in eq 8 are defined as follows: k_{r_1}, k_{r_2}, radiative rate constants for a particular ANS derivative in solvent mixtures 1 and 2; $q_{2/1}$, the fraction of charge contribution to the transition moment from the aryl ring in solvent 2, compared with that from the ring in solvent 1.

We are enabled to compare the radiative rate constants in two solvents by means of eq 8 with an independent evaluation of the charge contribution to the transition moment from the rings in the same solvents. The charge contribution to the transition moment from the *N*-aryl rings of ANS derivatives in the excited state may be estimated from the ρ values for the fluorescence emissions.[9] A comparison of the ratios of the square roots of the radiative rate constants can be made with the ratio $Q_{1/2}$, the product of a frequency factor and the ratio of ρ values for the same solvent polarities, the latter being obtained from the correlation of ρ value with solvent polarity illustrated previously.[9] Equations 9 and 10 express the appropriate forms of eq 8 above and a previously stated expression for the charge contribution to the transition moment from the aryl ring (eq 3b, ref 10).

$$(k_{r_1})^{1/2}/(k_{r_2})^{1/2} = 1/q_{2/1}(n_1\nu_1{}^{3/2}/n_2\nu_2{}^{3/2}) = Q_{1/2} \qquad (9)$$

$$1/q_{2/1} = \rho_1/\rho_2 \qquad (10)$$

Table VI lists the quantities derived on the basis of eq 9 and 10. Reasonably good agreement between the decrease in the square root of the radiative rate constant and the ratio $Q_{1/2}$ is obtained. We regard the approximate agreement shown in Table VI as satisfactory, although the mechanism for the decrease in radiative rate with increasing solvent polarity remains obscure.

Nonradiative Rate Constants. The radiationless process for the disappearance of the charge-transfer state is an electron-transfer reaction since (a) absorption spectra of the excited state produced by laser pulse show no other species of appropriate lifetime[8] and (b) the stability of most of the ANS derivatives to long-term irradiation in the absorption band requires that the original ground state be the ultimate product of the absorption of light. Radiationless decay of ANS derivatives is different in character in the nonpolar solvent range from that in the polar solvent range, as illustrated by the sharp breaks in the plots of $\Delta G^{\ddagger}$ (transition state free energy for k_{nr}) against the solvent polarity parameter (Figure 3). The regular behavior of $\Delta G^{\ddagger}$ as a function of solvent polarity is justification for treating the nonradiative rate constants according to transition state theory, at least insofar as the derivation of transition state free energies is concerned.

Closer examination of the nonradiative rate constants (for the electron-transfer reaction which converts $S_{1,ct}$ into S_0*) reveals a number of peculiarities: (1) electron-supplying substituents increase the rate of the electron transfer reaction (transfer being toward the moiety bearing the electron-supplying group; the opposite might have been expected), (2) an increase in solvent polarity augments the rate of the electron-transfer reaction (lowers the transition state free energy), whereas the opposite might have been expected. Plots which show the scale of the two effects on nonradiative decay in comparison to the influence of the same factors on the radiative process are given in Figure 4.

The close relationship of the $\Delta G^{\ddagger}$ values to solvent polarity ($E_T(30)$ values) and emission energies (E_F) together with the anomalous relationship (cited above) to molecular properties suggests the possibility that a property of the solvent controls the electron-transfer rate. Our analysis of the correlation coefficients (ρ values) for substituent effects on emission energies has already led to the notion that the charge within the aryl (i.e., the *N*-phenyl) ring "migrates" into the solvent.[9] Such migration is equivalent to screening of the charge and is classically expressed as the creation of a reaction field, R, in the solvent.[16]

To illustrate the parallelism between $\Delta G^{\ddagger}$ and ΔE_F, we summarize in Table VII the ratio $\Delta\Delta G^{\ddagger}/\frac{1}{2}\Delta E_F$. The use of the quantity $\frac{1}{2}\Delta E_F$ is based on the model for the energetics of the pyridinium iodide charge-transfer transition,[14] for which
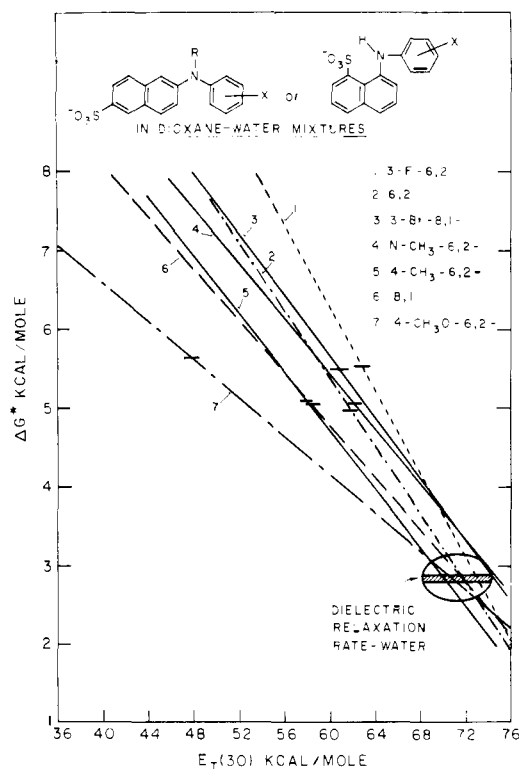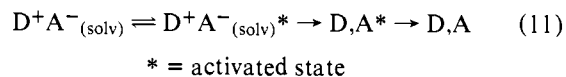
Figure 5. Extrapolation of correlation lines for $\Delta G^{\ddagger}$ (see Figure 3) to a "common region". The dielectric relaxation rate has a transition state free energy which corresponds to the $\Delta G^{\ddagger}$ in the "common region".

Figure 6. A representation of the solvation energetics for intramolecular electron transfer. The emitting state levels are shown in the lower part of the figure, and decrease in energy with increasing solvent polarity in the order S_1, S_2, S_s. The subscript s represents "suitable". The effect of electronic polarization on the S levels is not shown for the sake of simplicity. The reaction field, in the usual convention, represents the field in the solvent produced by the organization of the solvent dipoles, and increases in magnitude with increasing solvent polarity. To be exact, the levels shown (R_1, R_2, R_s) represent hypothetical energy states of the solvent portion of the solvent–solute system, in which the solvent has been "prepared" to accept the solute dipole, i.e., the dipole of the charge-transfer excited state. R_s represents a "suitable" reaction field, in which all of the dipolar charge has been screened or, in the language used in the text, all of the charge has "migrated" into the solvent.

the changes in transition energy are divided equally between the excited and ground states. In some cases, the ratios listed in the table approach 1.

The electron-transfer reaction would proceed if the solvent shell responsible for the reaction field, R, were activated to an appropriate value, a transformation we express in eq 11. The greater the solvation of the charge-transfer state, the greater the screening and the faster the electron-transfer reaction. In principle, we can increase the screening to the point where the reaction field R has reached a limit. We label the limiting reaction field R_s (s = suitable). Can we identify a limit to $\Delta G^{\ddagger}$? It is remarkable that extrapolation of the correlations shown in Figure 3 lead to a common region, as shown in Figure 5. The common region corresponds to the dielectric relaxation rate for water.[17]

$$D^+A^-_{(solv)} \rightleftharpoons D^+A^-_{(solv)}{}^* \rightarrow D,A^* \rightarrow D,A \qquad (11)$$

$$* = \text{activated state}$$

We can restate the foregoing in terms of the reaction field created for the dipole of the charge-transfer excited state. Electron transfer will occur only when a suitable reaction field, R_s, has been created in the solvent and an appropriate activation energy added, that required to maximize screening of the solute dipole. Our discussion implies that the electron transfer is, in fact, taking place much faster but in a reversible fashion. Only the transition state corresponding to an appropriately activated R_s will permit the product of electron transfer from the charge-transfer excited state (e.g., a species we might label D,A**) to evolve into vibrationally excited ground state, D,A*. Charge-transfer states, which are less stabilized by solvent than the state corresponding to the R_s, will have correspondingly smaller reaction fields and require correspondingly more energy to achieve R_s. We have tried to illustrate these points with a diagram (Figure 6).
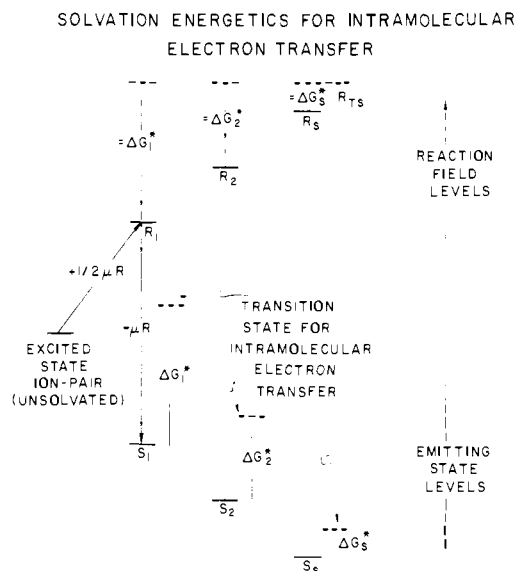
The solvent region in which the reaction field is produced

is sometimes called the cybotactic region.[14] Our analysis identifies the dielectric relaxation time of the cybotactic region as the critical factor in determining intramolecular electron-transfer rates, in cases for which other factors like overlap do not lower the electron-transfer rate below the dielectric relaxation rate. A more careful analysis of effects on nonradiative rates (or overall fluorescence quenching) which were previously assigned to "viscosity" must be made in the light of our conclusions. We have not included polarization since, as Schmickler has pointed out, this factor would change very little between the initial state and the transition state for electron transfer.[18] Our work constitutes a determination of mechanism for an intramolecular electron-transfer reaction.

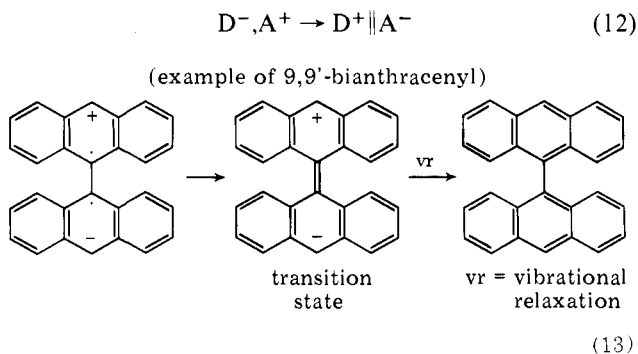**Mechanisms of Decay of Charge-Transfer Excited States.** In order to put a proper perspective on other work on the radiative and nonradiative disappearance of charge-transfer excited states, we have summarized in Table VIII the mechanisms of decay of charge-transfer excited states, along with a note as to the effects expected for a substantial increase in solvent polarity. Only light emission, intramolecular electron transfer (either to S_0 or S_1), and dissociation to either solvent-separated ion pairs or to free ions will exhibit a considerable response to solvent polarity change. The present results on ANS derivatives provide a well-defined standard with which we may compare results on other complexes and charge-transfer excited states. In Table IX we have collected the little information of which we are aware on charge-transfer excited states which are produced without the intervention of a diffusion-controlled step. The charge-transfer emissions all show rather similar changes in response to a solvent polarity change. In contrast, it is quite clear that the nonradiative rates fall into two classes, ones with a substantial response to a change in solvent polarity and those with a small or modest response to such a change. We are forced to conclude that the unresponsive

Table VIII. Decay Mechanisms for Charge-Transfer Excited States

| Decay mechanism[a]	Effect of increase in solvent polarity
1. Light emission	Emission energy decreases
$(D^+,A^-) \rightarrow (D,A)_0 + \hbar\nu$	Radiative rate decreases
2. Intramolecular electron transfer (to S_0) $(D^+,A^-) \rightarrow (D,A)$	Nonradiative rate increases
3. Intramolecular electron transfer (to S_1) $(D^+,A^-) \rightarrow (D,A)_1$	Nonradiative rate decreases (can be accompanied by emission from $(D,A)_1$
4. Intersystem crossing $^1(D^+,A^-) \rightarrow {}^3(D^+,A^-)$	Insensitive
5. Intramolecular covalent bond formation $(D^+,A^-) \rightarrow (D^+,A^-) \rightarrow (D-A)$ transition state a, b, with/without proton transfer c, d, with/without return to S_0	No change
6. Extramolecular electron transfer	Diffusion controlled, depends upon viscosity
$(D^+A^-) + Q \rightarrow Q^{\pm} + D^+,A$ (or D,A^-)	Little change with polarity
7. Extramolecular covalent bond formation a, b, with/without proton transfer c, d, with/without return to S_0	Limited by diffusion control
8. Ionic dissociation $(D^+,A^-) \rightarrow (D^+\|A^-) \rightarrow D^+ + A^-$	Increase for solvent-separated ion pairs; larger increase for free ions. Both dissociation rates and equilibrium constants are favored
9. Energy transfer $(D^+,A^-) + (D,A) \rightarrow (D,A) + (D^+,A^-)$	Intramolecular should follow rules for intramolecular electron transfer; intermolecular should be limited by diffusion control

[a] Subscripts refer to electronic state.

nonradiative processes reflect a lack of change in charge separation on proceeding from the initial state to the transition state. Either dissociation to nonemitting solvent-separated ion pairs[19] or covalent bond formation can account for the results (eq 12 and 13).

$$D^-,A^+ \rightarrow D^+\|A^- \qquad (12)$$

(example of 9,9'-bianthracenyl)

$$\qquad\qquad\qquad\qquad\text{transition} \qquad \text{vr = vibrational}$$
$$\qquad\qquad\qquad\qquad\text{state} \qquad\quad \text{relaxation}$$

$$(13)$$

Our view of radiative decay rates varying as a result of migration of charge into the solvent ("screening") does not de-

pend upon any change in the separation of the donor and acceptor portions of the charge-transfer excited state, as suggested by Prochorow[20] for intermolecular complexes. It is unlikely in any case that a continuum of structures exists for the excited state, and only a solvent molecule coming into the region between the donor and acceptor could prevent the formation of the minimum distance of separation ion pair in the intermolecular charge-transfer state. In fact, the solvent sensitivity of the radiative rate for the charge-transfer emission of intermolecular complexes studied by Prochorow is almost as great as that of the radiative rate for the ANS derivatives (see Table IX). The explanation adduced for radiative rate changes of the ANS derivatives probably applies to the intermolecular complexes as well.

One set of interesting cases which is worthy of special attention and perhaps additional effort are some pyrene and anthracene derivatives studied by Mataga and co-workers.[21-23] One of the pyrene derivatives, P_2, and two of the anthracene derivatives, A_2 and A_3, listed in Table IX, show nonradiative rate constants for the loss of the charge-transfer excited state ("heteroexcimer" state is the terminology used by Mataga) which are similar to or greater than the k_{nr} for ANS derivatives with respect to sensitivity to solvent. In contrast A_0, A_1, and P_1 exhibit nonradiative rate constants which are much less sensitive to changes in solvent polarity than the k_{nr} of ANS. The decay of the latter cannot be electron-transfer quenching. A likely alternative is covalent bond formation, for which the transition state would have the same charge separation as that of the charge-transfer excited state. The process is illustrated for P_1 in eq 14, and is very similar to the process suggested for

$$\rightarrow S_0 \qquad (14)$$
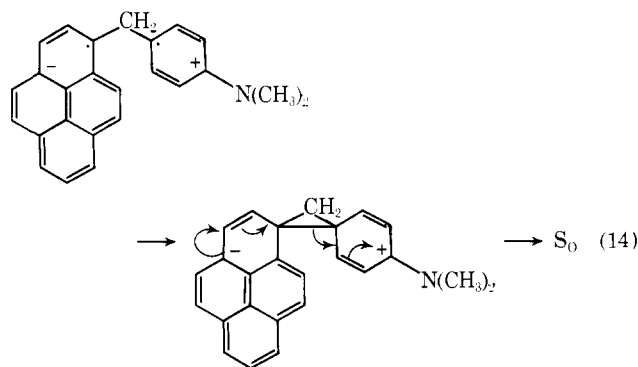
9,9'-bianthracenyl in eq 13. The case of P_3 should probably be looked at again in a series of dioxane–water solvents, to check whether or not the relatively low solvent sensitivity of k_{nr} is real. Fast covalent bond formation has been reported for polymethylene bis-2-anthroates as the quenching reaction which competes with fluorescence.[24]

Conclusions

1. Quenching mechanism for ANS derivatives in polar solvents: The classical observation of Weber and Laurence[2] with respect to the strong decrease in fluorescence of N-arylaminonaphthalenesulfonate derivatives in polar solvents can now be explained as being due to a significant decrease in radiative rate combined with a substantial increase in the nonradiative rate in polar solvents as compared with nonpolar solvents.

2. Utilizing solvent polarity parameters like $E_T(30)^{12}$ or Z^{14} for the purpose of evaluating the effect of solvent polarity on radiative and nonradiative rate constants is demonstrated to be valuable for obtaining a deeper understanding of the processes involved.

3. The decrease in radiative rate constant as a function of solvent polarity has been related to a decrease in the charge localized within the N-aryl group of the ANS as measured by the Hammett ρ value derived from substituent effects on emission energies.

Table IX. Solvent Effects on Radiative and Radiationless Processes for Charge-Transfer Excited States

Compd (complex)	Solvent range[a] $E_T(30)_1$; $E_T(30)_2$	$(k_r)_1^{1/2}$[b]/ $(k_r)_2^{1/2}$	$\Delta(k_r)^{1/2}/$ $\Delta E_T(30)$	$\Delta(\log k_{nr})^c/$ $\Delta E_T(30)$	$(k_{nr})_2$ $\times 10^{-8}$, s^{-1}	Ref
Pyromellitic acid anhydride (PMDA)-toluene	31.9 41.9[d]	3.08	286	0.017	5.5	j
PMDA-p-xylene	31.9 41.9[d]	2.30	169	0.019	4.3	j
PMDA-mesitylene	31.9 41.9[d]	3.0	200	0.021	5.0	j
6,2-ANS[e]	48.8 62.5	2.50	586	0.14	15.0	k
4-CH₃-6,2-ANS[e]	53.5 61.8	2.50	357	0.13	13.0	k
P₁[h]	34.60 42.2	11.94	175	−0.001	1.0	m
P₂[h]	34.6 42.2	3.54	115	0.14	1.2	m
P₃[h]	34.6 42.2	1.86	83	0.06	0.15	m
9-(4-(CH₃)₂NPh)-anthracene (A₀)	~36[f] 46	2.50	499	~0.02[g]	0.21	l
A₁[i]	34.6 42.2	2.12	66	0.05	2.5	m
A₂[i]	34.6 42.2	1.35	36	0.19	2.0	m
A₃[i]	34.6 42.2	1.83	98	0.19	1.1	m
9,9′-Bianthracenyl	34.6 46.	2.48	329	−0.01	0.22	n
Durene-1,2,4,5-tetracyano benzene	31.0 34.6	~1.0		0.09	1.7	o

[a] Solvent polarity parameter of K. Dimroth and C. Reichardt, *Fortschr. Chem. Forsch.*, **11**, 1 (1968); range of parameter $E_T(30) = 31$ (hexane) to $E_T(30) = 63.2$ (water). [b] Radiative rate constant, k_r. Use of square root is described in the text and results are given in Table VI. [c] Sensitivity of nonradiative rate constant, k_{nr}, to solvent change. [d] Estimated for solvent mixture actually used. [e] 6-Arylamino-2-naphthalenesulfonate; see Table VI. [f] Estimated for isobutyl acetate. [g] Approximate average based on available data. [h] 1-(4-(CH₃)₂NPh)(CH₂)ₙ-(pyrene); $n = 1$ (P₁), 2 (P₂), or 3 (P₃). [i] 9-(4-(CH₃)₂NPh)(CH₂)ₙ(anthracene); $n = 1$ (A₁), 2 (A₂), or 3 (A₃). Note that data for $n = 0$ (A₀) are also given in the table. [j] J. Prochorow and E. Bernard, *J. Lumin.*, **8**, 471 (1974). [k] Present work. [l] T. Okada, T. Fujita, and N. Mataga, *Z. Phys. Chem. (Frankfurt am Main)*, **101**, 57 (1976). [m] T. Okada, T. Saito, N. Mataga, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, in press. [n] N. Nakashima, M. Murakawa, and N. Mataga, *ibid.*, **49**, 854 (1976). [o] T. Kobayashi, K. Yoshihara, and S. Nagakura, *ibid.*, **44**, 2603 (1971).

4. Evaluation of the effect of solvent polarity on the transition state free energy for the nonradiative, electron-transfer reaction led to the conclusion that the rate of dielectric relaxation for water was the critical step in the course of the electron-transfer reaction. Such a step should only be evident in intramolecular electron-transfer processes, and our work constitutes a determination of mechanism for such a process.

5. A new mechanism (covalent bond formation) for the quenching of charge-transfer states has been identified by its lack of sensitivity to solvent polarity change.

6. Our understanding of the mechanisms involved in excited states processes of arylaminonaphthalenesulfonates is great enough (see complete scheme in ref 10) to suggest that the system might serve as a useful paradigm for molecules which might react through charge-transfer excited states.

Experimental Section

Compounds were synthesized and purified as described elsewhere.[8,11,25] Dioxane solvent was spectroquality (Merck, Darmstadt). Dioxane-water solutions of the compounds were prepared as follows. A stock solution of ANS derivatives (10^{-3}–10^{-4} M) in 98% dioxane-water was prepared. An aliquot (0.1 or 0.2 mL) of stock solution was placed in the fluorescence cell and additional solvent (of specific volume ratios) (3.0 mL) added; final compositions are recorded in the tables. After thorough mixing, the solutions (10^{-5}–10^{-6} M, OD ≤ 0.1) were purged with nitrogen immediately before measurements

were made. Quantum yields were measured for each sample using quinine sulfate in 0.1 N H₂SO₄ as a reference standard.

Quantum yields were calculated according to the equation[26]

$$(\phi_F)_s = \frac{F_s \epsilon_q C_q (0.55)}{F_q \epsilon_s C_s}$$

with excitation effected at the same wavelength for sample and quinine sulfate. A correction for refractive index was applied,[27] $(\phi_F)_s$ (corrected) $= (\phi_F)_s n_D^2(\text{solvent})/n_D^2(\text{H}_2\text{O})$. Corrected excitation spectra corresponded to the absorption spectra in all cases. Symbols are defined as follows: F, integrated area under fluorescence curve in arbitrary units; s, sample; q, quinine sulfate; C, concentration; ϵ, absorption coefficient.

For work reported in this paper, a single-photon counting technique was used, which has already been described in the literature.[28] A nanosecond air flash lamp monitored by a pick-up antenna was operated at 9 kHz to produce the exciting light. A monochromator (Jarrell-Ash 0.25-m grating) was used to isolate suitable wavelengths (314 nm for 6,2-ANS derivatives, 356 nm for 8,1-ANS derivatives) and an interference filter was used to exclude scattered exciting light and to pass fluorescence emissions (Special Optics, Cedar Grove, N.J.). The output from the filter was detected by a RCA-8850 photomultiplier. The pulse width of the lamp was checked several times in every set of measurements (average width at half-height 1.7 ns). The temperature was controlled during the experiments (25.5 ± 0.2 °C). The electrical pulse derived from the lamp discharge was attenuated, shaped by a discriminator, and then used to trigger a time-to-amplitude convertor (TAC, ORTEC). The ramp in a TAC cycle was terminated by the pulse from the photomultiplier, giving

rise to a pulse of a voltage determined by the time at which the termination occurred. The pulses emerging from the TAC were then stored in a multichannel analyzer (Hewlett-Packard) in which the pulses were distributed according to time elapsed from initiation of ramp. From 20 000 to 25 000 counts were accumulated in each measurement, using an appropriately low ratio between count rate and the exciting pulse rate. Data were transferred to paper tape and then to cards via the CDC 6600 computer of Tel-Aviv University. Data from the channels of the pulse height analyzer were fitted to single exponential decay curve by a least-squares program. It should be explicitly noted that a single exponential decay is observed even in intermediate solvent polarities because the $S_{1,np}$ and $S_{1,ct}$ states are in equilibrium.[8]

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Friedel–Crafts Isopropylation of a Bituminous Coal under Remarkably Mild Conditions[1a]

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Abstract: A bituminous coal, Illinois no. 6, has been treated under Friedel–Crafts alkylation conditions, some as mild as 0–5 °C and atmospheric pressure. The tools of mass spectroscopy and classical analytical techniques were employed to confirm unequivocally that the coal was alkylated. The alkylated product has both a higher hydrogen content and higher solubility in benzene and pyridine than the untreated coal. This work demonstrates that coal is very much more reactive than is conventionally believed.

"When I am asked what particular research on coal would be of most practical value to those who have to sell it, equally with those who wish to use it, I have no hesitation in saying: *'Research on the Composition of Coal'*." R. V. Wheeler (1928).

Introduction

Coal is considered to be an organic rock. A major challenge for organic chemists today is to gain a better understanding of the organic structural types which exist in coal, so that, ultimately, more efficient conversion to clean fuels and/or chemicals can be achieved.

Coal is largely insoluble in most common organic solvents,[2] and therefore the characterization techniques available to the chemist, which require samples in solution, cannot be applied to more than the about 25% of the coal which is soluble in pyridine. In hydrocarbon solvents such as hexane, benzene, or toluene, the solubility is only 2% or less. Furthermore, it is not possible to deduce all the structural types present in native coal from analysis of liquid products made during pyrolysis or liquefaction, because of the extensive bond making and bond breaking occurring under these high-severity conditions.

We have been investigating a mild chemical method to render large amounts of the coal soluble in organic solvents, i.e., Friedel–Crafts alkylation. While this reaction has been investigated earlier,[3-5] we have been extensively characterizing the alkylation products obtained, and wish to describe our results here.

Results and Discussion

All alkylations were performed on coal from the Illinois no. 6 seam as described in the Experimental Section. Some results are listed in Table I.

The extent of alkylation is not very sensitive to marked increases in the severity of reaction conditions. Thus the H/C ratio of the product of alkylation at 0–5 °C and 1 atm (sample