

vacuo. The crude product was purified by radial chromatography.

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Supplementary Material Available: Details of the preparation and physical and spectral data for compounds **1-5**, **10**, and **11** (14 pages). Ordering information is given on any current masthead page.

Photophysical Analysis of Ion Pairing of β -Naphtholate in Medium Polarity Solvents: Mixtures of Contact and Solvent-Separated Ion Pairs

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Abstract: Absorption and emission properties of β -naphtholate are analyzed including lifetime measurements. It is shown that, in solvents of medium polarity, the broad absorption and emission bands of the β -naphtholate anion consist of overlapping spectra of contact (CIP) and solvent-separated (SSIP) ion pairs. In spite of the absence of spectral resolution, this is demonstrated by the following: (1) The shift of the emission maximum with excitation wavelength. (2) The biexponential decay measured by single photon counting. (3) The dependence of the decays on the excitation and emission wavelengths and on the nature of the cation used. (4) The dependence of Stern-Volmer quenching constants on the cations and on the excitation and emission wavelength. The ground-state equilibrium and the dynamics of the excited state are characterized. The estimated exchange rates are of the same order of magnitude and of about 2.10^7 s^{-1} in the excited state. NMR measurements have shown that the lifetimes of CIP and SSIP in the ground state are much shorter than 6.10^{-5} s .

Ion properties are strongly solvent dependent, and their reactivity may differ greatly according to the strength of their interactions with the surrounding molecules. In weakly polar solvents interionic interactions may dominate, and ion pairs will result. This ion pair concept was introduced by Bjerrum¹ and has been critically reviewed by Szwarc.² The definition of ion pairs is based on the mutual geometry of ions and solvent. Winstein³ and Sadek⁴ suggested the existence of "loose" and "tight" ion pairs. It is now of common use to speak about solvent-separated ion pairs (SSIP) or of contact ion pairs (CIP). Even more subtle distinctions were made by Y. Marcus: solvent-separated and solvent-shared ion pairs are distinguished according to the number (two or one, respectively) of solvent molecules separating the two paired ions.⁵

Predictions concerning ion pairs in solution are always delicate since many factors must be accounted for. Coulombic interionic interactions must be considered in competition with ion-dipole (solvent) interactions.⁶ The dielectric constant will play a role, but it is not expected as a relevant parameter since it reflects macroscopic properties of the solvent, while the considered interaction clearly does not. Specific ion-solvent interactions may take a part in solvation, and a marked difference between hydroxylic and nonhydroxylic solvents is often expected.⁷ Temperature will influence the status of ions in solution: when the

thermal energy kT decreases, ion pair formation is of course favored, but it is not easy to predict in which direction the equilibrium between SSIP and CIP will change. In general, SSIP are favored by lowering the temperature.⁸⁻¹⁰ Other factors like charge delocalization which favors SSIP,¹¹ steric effects, and aggregation phenomena¹²⁻¹⁴ will also play a role.

Among other techniques like EPR, NMR, IR, or Raman measurements, spectrophotometric results were often reported as a proof for ion pairing. The effects of ion pairing on the reactivities and spectral properties of carbanions^{6,8,15} and oxyanions¹⁶ have been reviewed. It is for instance well known that a decrease of the cation radius shifts the absorption peak of anions to shorter wavelengths.^{8,16} This hypsochromic shift is attributed to the higher association of the ion pair in the ground state when compared to the excited state and to an increasing association when the cation becomes smaller.

Absorption frequencies of ion pairs are shifted when the solvent changes: the direction of the shift depends on the change (increase

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Table I. Absorption and Fluorescence of 2-Naphtholate Anion

entry	solvent	cation	λ_{ex}^a	ϵ^b	λ_{em}^c
1	H ₂ O	Na	347	2700	420
2	H ₂ O	K	347	2700	420
3	CH ₃ OH	Na	349	2900	420
4	CH ₃ OH	K	349	2850	420
5	i-PrOH	Na	352		
6	benzene	Na(CE) ^e	380		427
7	benzene	K(CE) ^e	380	4300	431
8	DEE ^d	Na	355		
9	Diox	Li	353		399
10	Diox	Na	363	3300	412
11	Diox	K	370		424
12	Diox	(CH ₃) ₄ N ⁺	375	2100	454
13	THF	Li	357	3300	407
14	THF	Na	368	3600	421
15	THF	K	378	4000	430
16	THF	Na(EC) ^e	388	4200	431
17	DME ^f	Li	365		425
18	DME	Na	372		428
19	DME	K	384		434
20	CH ₃ CN	Na	380		451
21	DMF	Na	393	4300	456
22	DMSO	Na	396	4500	456
23	DMSO	K	396		456

^aAbsorption maximum in nm. ^bExtinction coefficient in M⁻¹ L cm⁻¹. ^cEmission maximum in nm. This measure was not necessarily made when using the absorption maximum for excitation. ^dDiethyl ether. ^eSodium and dibenzo-18-crown-6. ^f1,2-Dimethoxyethane

or decrease) of dipole moment upon the electronic transition.¹⁷ Carbanions show a bathochromic shift when the solvent polarity is increased, and this is often attributed to a separation of the charged particles. Solvation of ions is increased with a corresponding reduction of interionic attractions: CIP are transformed into SSIP.

The emission properties of ions have also been studied, and it has been shown that in certain cases, important changes may occur between ground and excited states, increasing the fraction of SSIP when the relaxed excited state is reached.¹⁸ Two different types of behaviors were observed. With highly delocalized carbanions like in fluorenyl salts, a red shift is observed in absorption, and a blue shift in emission, when the cation radius is increased. With nitrogen-centered anions like carbazolyl salts, absorption and emission shift together to the red.^{10,14,19}

The nature of ions in solution is also traced by their chemical reactivity in the ground state. Relevant of this is the change of the reaction site when ambident phenolates associated with different cations are alkylated²⁰ and the interdependence of solvent and cation effects has been clearly shown.^{20,21} Many other cases pertaining to nucleophilic additions or substitutions, protonations, rearrangements, and isomerizations have been reviewed.⁶

Fox^{22,23} and Tolbert²⁴⁻²⁶ drew the attention on the particular character of organic anion photochemistry. Their high reducing power, already seen in ground-state reactions,²⁷ became particularly apparent in the few reports on their excited state properties.^{24,28,29}

In certain cases absorption frequencies of anions may be distinguished for SSIP and CIP so that ratios of concentrations of

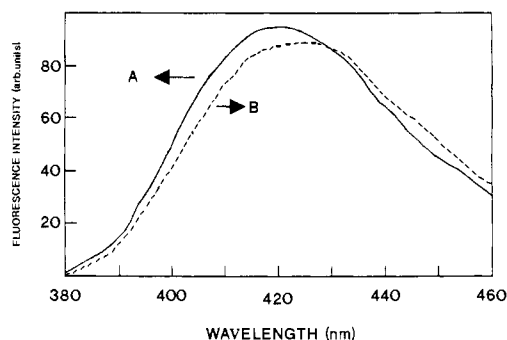


Figure 1. Time-resolved emission spectra of sodium β -naphtholate in THF. *A* = 0–3.5 ns spectrum; *B* = 100 ns delayed spectrum.

the different ion pairs may be measured.³⁰ In these cases, enthalpies governing the equilibrium are also estimated.^{8,9} In the case of the β -naphtholate anion, such a distinction is not possible. In the present paper, the photophysical properties of this anion in different solvents are investigated. Time-resolved measurements enabled us to understand the changes in ion pair solvation which were confirmed by a parallel change in reactivity.

Results

Absorption and Emission Spectra. The β -naphtholate anion shows a structureless absorption band with a maximum between 340 and 400 nm depending on the experimental conditions (solvent, counterion). The emission maximum is found between 410 and 460 nm. A bathochromic shift is observed as well as in absorption as in emission relative to the β -naphthol.

As can be seen in Table I, a red shift is observed, in absorption and in emission when the polarity of aprotic solvents is increased. In solvents of low polarity the λ_{max} also depends on the counterion: when the cation radius is increased, shifts to longer wavelengths are observed. On the contrary, no counterion effect is recorded in polar or protic solvents.

The data in Table I also show that the absorption coefficient of the anion increases as the absorption maximum shifts to the red.

Lifetime Measurements. Fluorescence decay times of β -naphtholate anions have been measured in different solvents and in the presence of different counterions (see Table II) by time-correlated single-photon-counting technique. Oxygen is a quencher of the anion since the lifetime was found to be shortened, in methanol, when the solution was not degassed. In water, this effect was not detected, due probably to the lower solubility of oxygen (0.265×10^{-3} M vs 2.12×10^{-3} M in methanol) in this solvent.³¹ Oxygen was also found to cause a rapid disappearance of the anion in THF. This was accompanied by the formation of the neutral form of naphthol.

In polar and in protic solvents, a single exponential decay was observed. In ethereal solvents, mono- and biexponential decays were found, depending on the cation. With lithium cation or with sodium in the presence of crown ether a single decay time was obtained. With sodium or potassium cations, the decay was analyzed as a sum of two exponentials from which two decay times were derived. It is also worth noting that in the monoexponential cases three different decay times can be found: in protic solvents (about 9 ns), in ethereal solvent with lithium cation (6 ns), and with the crowned sodium cation or in dipolar aprotic solvents (19 ns).

A time-resolved emission spectra of sodium β -naphtholate in THF was obtained in a time window between 0 and 3.5 ns after excitation and after a delay of 100 ns. Figure 1 indicates that the long-lived species is slightly red shifted.

Attempts have been made to obtain a monoexponential decay in THF by lowering the temperature (down to -60 °C). A small

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Table II. Decay Times^a of β -Naphtholate Anion as a Function of Solvent and Counterion

no.	solvent ^b	E^c	cation	τ (ns)	A^d	χ^2^e	D-W ^f	λ_{em}^g
1	H ₂ O*	63.1	Na	9.2		1.20	1.60	420
2	H ₂ O	63.1	Na	9.0		1.11	1.67	420
3	CH ₃ OH*	55.5	Na	9.6		1.15	1.67	420
4	CH ₃ OH	55.5	Na	6.2		1.06	1.74	420
5	THF*	37.4	Li	6.4		1.03	1.61	410
6	THF*	37.4	Na	7.0	0.43	1.04	1.72	430
				13.8	0.24			
7	THF*	37.4	K	6.5	0.18	1.19	1.77	430
				14.4	0.39			
8	THF*	37.4	Na (EC) ^h	19.2		1.2	1.68	430
9	Diox*	36.0	Na	5.0	0.46	1.2	1.71	440
				7.5	0.57			
10	DME*	38.2	Na	7.3	0.45	0.97	1.83	430
				15.0	0.52			
11	DME*	38.2	K	6.4	0.05	1.10	1.98	460
				12.1	.99			
12	DMF*	43.8	Na	17.0		1.15	1.75	480
13	DMF	43.8	Na	19.3		1.20	1.83	480
14	DMSO*	43.8	Na	17.8		1.27	1.66	480
15	DMSO	43.8	Na	18.0				480

^aAs measured by the single-photon-counting technique with an excitation wavelength of 330 nm. ^bWhen marked with an *, the solution was degassed by argon bubbling. ^cDimroth's solvent parameter. ^dPreexponential terms in cases of double exponential decays. ^e χ^2 parameter. ^fDurbin-Watson parameter. ^gEmission wavelength used for the single photon counting. ^hIn the presence of dibenzo-18-crown-6, 2×10^{-3} M.

Table III. Fluorescence Quantum Yield and β -Naphtholate Anion Lifetime^a

entry	solvent ^b	τ_F^c	τ_F^d	Φ_F^{exp}	Φ_F^{calcd}
1	H ₂ O	42.6	9.0	0.36	0.21
2	CH ₃ OH	41.0	6.2	0.23	0.15
3	CH ₃ OH*	41.0	9.6	0.32	0.23
4	DMSO	21.5	18.0	0.93	0.81
5	THF(CE)* ^e	24.0	19.2	0.75	0.80

^aAll values are given for sodium cation. ^bValues marked with an * are for systems degassed by argon bubbling. ^cCalculated with eq 2. ^dMeasured by the single-photon-counting method. ^eIn the presence of dibenzo-18-crown-6.

increase of the preexponential factor corresponding to the long decay time only was obtained.

Table III presents results on naphtholate anion under conditions where the cation does not influence the fluorescence or the lifetime. These values correspond to situations where a monoexponential decay was observed. Calculated radiative lifetimes as well as fluorescence quantum yields are presented.

Fluorescence quantum yields were measured by comparison with fluorescence of 9,10-diphenylanthracene (DPA) in cyclohexane (CYH) and calculated according to the formula³⁹

$$\Phi_F = \frac{n^2 F(\nu)d\nu}{n_{CYH}^2 F'(\nu)d\nu} \Phi_F^{DPA} \quad (1)$$

where n are the refractive indexes of the solvent used, Φ_F^{DPA} is the fluorescence quantum yield of the reference DPA,^{33,34} and $F(\nu)$ and $F'(\nu)$ are the fluorescence intensities of the naphtholate and DPA, respectively.

Calculated fluorescence quantum yields were obtained according to the relation

$$\Phi_F^{calcd} = \tau_F / \tau_F^c \quad (2)$$

Radiative lifetimes were approximated by the following expression^{32,35}

$$(\tau_F^c)^{-1} = 2.88 \times 10^{-9} n^2 (\bar{\nu}_F)^3 \frac{\epsilon_{max} \Delta\nu^{1/2}}{\bar{\nu}_{abs}} \quad (3)$$

In this equation, n is the refractive index of the solvent, while $\bar{\nu}_F$ and $\bar{\nu}_{abs}$ correspond to wavenumbers of the fluorescence and absorption maxima. $\Delta\nu^{1/2}$ represents the half width of the ab-

Table IV. Emission Wavelength and Intensity as a Function of Wavelength Excitation in THF

no.	cation	λ_{ex}^a	abs ^b	λ_{em}^c	Φ_F^d
1	Na	330	0.245	417	0.41
2		340	0.415	417	0.44
3		350	0.628	418	0.48
4		360	0.796	419	0.50
5		370	0.828	419	0.51
6		380	0.596	422	0.54
7		390	0.293	424	0.55
8		400	0.110	426	0.56
9	Na(CE) ^e	345	0.200	431	0.74
10	Na(CE) ^e	415	0.200	431	0.75
11	Li	340		408	
12		350		410	
13		360		411	
14		370		412	
15		380		414	
16		390		420	

^aExcitation wavelength in nm. ^bAbsorbance. ^cWavelength of the emission maximum in nm. ^dRelative fluorescence quantum yields. ^eIn the presence of crown ether.

sorption band, and ϵ_{max} is the molar extinction coefficient at the maximum.

When compared to the experimental lifetimes, the value of the radiative lifetime appear to change in opposite directions. On the contrary, the calculated and experimental values of fluorescence quantum yields do not show this antagonism.

Wavelength Effects on the Emitting Properties of Naphtholate.

Two types of wavelength effects were found, and the results are summarized in Tables IV, V, and VI. (1) A shift in emission wavelength may be related to the choice of excitation wavelength, and this was accompanied by a change of the fluorescence intensity. (2) The excitation and emission wavelengths were found to direct the relative contributions of the fluorescence intensities in the double exponential decays.

A shift in the emission maximum was found to be related to a change in the excitation wavelength (Table IV). A decrease of the excitation energy is accompanied by a red shift of the emission spectrum for sodium and lithium naphtholate in THF. At the same time variations in the fluorescence quantum yield were recorded and found to increase regularly. Neither the emission wavelength nor its intensity was changed for sodium naphtholate in the presence of crown ether.

In the cases where a double decay is observed, the wavelengths used for the excitation and for the measurement of emission are found to influence the relative fluorescence intensities of the two emitters. As can be seen from Table V the contribution of the

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Table V. Effect of Wavelength on the Relative Contributions of Fluorescence Intensities in Double Exponential Decays

no.	solvent	λ_{ex}^a	λ_{em}^b	τ_1 (ns)	% ^c	τ_2 (ns)	% ^c	χ^2^d
1	THF	300	400	6.7	48	10.0	52	1.38
2	THF	300	410	6.8	43	12.4	57	1.26
3	THF	300	420	6.2	41	9.6	59	1.32
4	THF	300	430	8.0	37	13.8	63	1.25
5	THF	300	490	6.9	24	13.6	76	1.22
6	THF	330	420	7.6	63	13.3	37	1.07
7	THF	330	430	6.5	50	10.9	50	0.97
8	THF	330	450	7.6	53	13.8	47	1.33
9	THF	330	460	6.4	40	11.0	60	1.29
10	THF	330	475	7.7	41	14.2	59	1.06
11	THF	360	421	6.2	36	11.2	64	1.83
12	DME	330	428	7.3	29	15.0	71	0.97
13	DME	330	460	7.4	19	15.6	81	0.94
14	DME	300	410	7.0	29	13.1	71	1.14
15	DME	300	430	7.0	24	13.3	76	1.02
16	THF ^e	330	390	7.0	87.7	13.8	12.3	1.20
17	THF ^e	330	400	7.0	81.5	13.8	18.5	1.17
18	THF ^e	330	420	7.0	67.0	13.8	33.0	1.03
19	THF ^e	330	430	7.0	59.3	13.8	40.7	1.17
20	THF ^e	330	450	7.0	51.6	13.8	48.4	1.02
21	THF ^e	330	470	7.0	43.2	13.8	56.8	1.04
22	THF ^e	330	485	7.0	39.2	13.8	60.8	1.08

^aExcitation wavelength in nm. ^bEmission wavelength in nm. ^cFractional emission intensity of each species in %. ^d χ^2 parameter. ^eMeasured and optimized by the global analysis technique.

Table VI. Lifetimes of Lithium Naphtholate as a Function of the Emission Wavelength

no.	λ_{ex}^a	λ_{em}^b	τ (ns)	% ^c	χ^2^d	D-W ^e
1	347	410	6.43		1.03	1.61
2	347	440	6.14	88	1.04	1.84
			11.3	12		

^aExcitation wavelength in nm. ^bEmission wavelength in nm. ^cFractional emission intensities in %. ^d χ^2 parameter. ^eDurbin-Watson parameter.

shortest decay time decreases when the emission is measured at longer wavelengths, while at the same time the longest decay part of the emission increases. On the other hand, when the emission wavelength is kept constant, the relative contributions undergo variations according to the excitation used.

In the lithium naphtholate case, a double exponential decay appears in THF when the anion emission is analyzed in the red edge of the fluorescence band (see Table VI). At the fluorescence maximum (410 nm), only a single exponential decay was found as mentioned in Table II, but at 440 nm a second contribution became apparent.

Water and Salt Effects. The effect of adding water or salts on the spectra and lifetimes of β -naphtholates has been evaluated, and the results are shown in Table VII. When small amounts of water are added to DMSO, a blue shift is recorded as well as in absorption as in emission, but the effect is smaller in the second case.

In THF, the same effect is observed on the absorption λ_{max} , but a red shift is obtained for the emission wavelength. This is also the case in dioxane and DME. More interestingly, in THF, the double exponential decay is no longer observed as soon as 1% of water is added to the solvent.

The addition of small amounts of salts as sodium perchlorate or iodide weakly perturbs the emission but does not affect the absorption spectrum. However, the excited state is affected in a significant manner since the double exponential decay is replaced by a monoexponential behavior with a decay time of 16 ns.

Addition of DMSO in THF results in a change of the relative contributions of the fluorescence intensities of the double exponential decay.

NMR Measurements. Chemical shifts in association with bandwidths values are commonly used to examine systems where an exchange is taking place. These parameters were measured for naphtholate anions using ¹³C and ²³Na NMR spectrometry, and the results are presented in Tables VIII and IX.

Ernst³⁶ identified the ¹³C NMR signals of the β -naphthol in deuterated chloroform, and a value of 153.35 ppm was found for the carbon bearing the hydroxy group. In THF a value of 156.2 ppm was obtained, and this was shifted to 165.8 ppm for the anion. As can be seen, the chemical shift of carbon 2 is sensitive to the cation or solvent used. A small variation is observed when the temperature of sodium naphtholate is lowered but the line width (less than 0.1 ppm) is insensitive to temperature changes.

For the ²³Na chemical shifts, comparisons are made with sodium perchlorate and iodide which are known to behave respectively as SSIP and CIP in THF.³⁷ A shift variation and a modification of the bandwidth occur when the temperature is changed. In the β -naphtholate case the shift modifications are rather weak, but the bandwidth and the effect of temperature on the bandwidth are much larger than for the two types of inorganic reference salts. On the other hand, the bandwidth and its variation as a function of the temperature are similar at different magnetic fields.

Reactivity of β -Naphtholate. The naphtholate anion may be expected to be highly oxidizable, and by measuring the quenching of its fluorescence by suitable acceptors the influence of its association state on its reactivity may be estimated. By measuring the decrease of the anion fluorescence intensity as a function of quencher concentration and by treating the results by the Stern-Volmer equation,³⁸ values of $k_{\text{SV}} (=k_q\tau)$ were calculated (see Table X). The quenching constants have been calculated when a monoexponential decay is measured as in the cases of the lithium naphtholate or for the crowned sodium salt (see entries 1, 3, 6, 11, and 23). In the other cases the values can only be approximated (see Discussion).

Quenchings have also been measured at different wavelengths of excitation and emission and important k_{SV} variations are recorded. The effect of additives on the fluorescence quenching was also estimated showing an important increase when a small amount of water is added to the solvent. As was already observed in Table VII (see entries 6 and 7), a further addition of water did not affect the results significantly.

Discussion

Absorption and Emission Wavelengths. Absorption of alkali naphthoxides at ca. 350 nm is due to a $\pi-\pi^*$ transition.^{15,43} The

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Table VII. Water and Salt Effects on the Spectra and Lifetimes of Naphtholates

no.	solvent	cation	add. (%) ^a	τ (ns) ^b	χ^2 ^c	D-W ^d	λ_{em} ^e	λ_{ab} ^f
1	DMSO	Na	A (0)	17.8	1.27	1.66	456	396
2	DMSO	Na	A (1)	17.4	1.39	1.68	455	388
3	DMSO	Na	A (2.5)				453	383
4	DMSO	Na	A (5)	16.9	1.22	1.75	450	378
5	THF	Na	A (0)	7.00 (59) 13.8 (41)	1.04	1.72	420	368
6	THF	Na	A (1)	14.2	1.18	1.79		361
7	THF	Na	A (2)	14.5	1.2	1.76	428	360
8	THF	Na	A (5)				429	359
9	Diox	Na	A (0)				412	363
10	Diox	Na	A (9)				423	355
11	DME	K	A (0)					384
12	DME	K	A (0.5)					365
13	THF	Na	B (5×10^{-3} M)				424	368
14	THF	Na	B (2×10^{-2} M)				427	
15	THF	Na	C (3×10^{-2} M)	16.0	1.21	1.50	428	368
16	THF	Na	C (5×10^{-2} M)	16.5	1.2	1.6	429	368
17	THF	Na	D (10)	6.54 (18) 18.0 (82)	1.16		452	377

^aAdditive with % in volume (or concentration when stated) under parentheses. A = water; B = NaI; C = NaClO₄; D = DMSO. ^bLifetimes in nanoseconds with the fractional intensities in % between parentheses. Single-photon-counting measurements with excitation wavelength at 330 nm and emission wavelength at 480 nm (entries 1-4) and 430 nm (entries 5-17). ^c χ^2 parameter. ^dDurbin-Watson parameter. ^eEmission maximum in nm. ^fAbsorption maximum in nm.

Table VIII. ¹³C NMR Shift for the β -Carbon of β -Naphtholate

no.	cation	solvent	δ^a (ppm)	T (°C)
1	Na	H ₂ O	165.8	25
2	Li	THF	166.6	25
3	Na	THF	168.8	25
4	K	THF	170.8	25
5	Na	THF	169.3	-50
6	Na	THF	169.5	-70
7	Na	THF	169.6	-80

^aRelative to TMS.

Table IX. ²³Na Shifts and Bandwidths for Sodium β -Naphtholate and Reference Compounds in THF

no.	anion used	T (°C)	δ^a (ppm)	$\Delta\nu^{1/2}$ (hz) ^b
1	perchlorate	20	-8.0	38 (40)
2	perchlorate	-60	-6.4	150
3	iodide	20	6.7	36 (37)
4	iodide	-60	1.4	140
5	β -naphtholate	20	2.0	260 (240)
6	β -naphtholate	-60	2.4	1320 (1310)

^aRelative to a water-saturated sodium chloride solution. ^bFrequency width at half height in hertz, measured for sample observation at 66.163 MHz. Values in parentheses were obtained at 132.29 MHz.

recorded shifts are of the same order of magnitude as those reported by Garst⁴⁴ and Zaugg¹⁶ in the case of phenoxides and enolates or by Hogen Esch⁶ and Velthorst¹⁹ in the cases of fluorenyl carbanions and carbazolyl nitranions, respectively. Hoijtink also obtained similar results with salts of radical ions.⁴⁵

The hypsochromic shifts of the absorption observed in Table I may be understood as a redistribution of the negative charge of the anion on excitation. Thus the blue shifts observed when an aprotic solvent is replaced by a protic one or when the cation radius is decreased may be attributed respectively to the stabilization of the anion ground state by hydrogen bonding or by the electrostatic field of the cation. The Franck-Condon excited state is not stabilized to the same extent since, by excitation, the charge density on the oxygen is reduced and spread over the aromatic part of the molecule.

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The emission λ_{max} has been found to shift to the red in weakly polar solvents when the cation radius increases. This is also the case for carbazolyl anions,¹⁹ while in the case of fluorenyl carbanions a blue shift has been reported. Since the electrostatic field of the cation is expected to stabilize the anion, the observed shifts may be explained in the following way: when the cation changes from potassium to lithium, the Franck-Condon ground state must be more stabilized than the relaxed excited state. This may be the case if the cation stays close to the naphtholate oxygen even in the excited state where the negative charge density has been redistributed. This means that the cation is more firmly retained by the oxygen lone pair than by the negative charge spread over the excited anion or that the density of the negative charge remains sufficient on the oxygen atoms to retain the cation in the excited state. That the same observation was made with carbazolyl anions is logical since in that case also, the lone pair on the nitrogen may retain the cation. As we already suggested in a previous paper⁴⁶ the opposite tendencies between these oxyanions and more delocalizable carbanions may be a consequence of the relative hardness and softness of the involved species.⁴⁷ According to this concept, carbanions with a widely dispersed negative charge may prefer larger cations, while anions with a higher electron density on a heteroatom may prefer tighter associations with less polarizable cations like lithium.

The possibility of aggregates formation was not taken into account since several authors already showed that, in solvents like THF, aggregation is unimportant in concentrations lower than 10^{-2} M.^{18,30,48} These phenomena are only significant in low polarity solvents. Furthermore, when sodium was used as counterion, an increase in the anion concentration from $5 \cdot 10^{-3}$ to $5 \cdot 10^{-4}$ M did not affect the spectra of the anions, even in dioxane.

Double Exponential Decay: CIP and SSIP. In spite of the fact that absorption and emission spectra of the β -naphtholate only show one structureless band, two emitters are detected by the single-photon-counting measurements in solvents of medium polarity like THF when sodium or potassium cation were used (Table II). Since aggregation phenomena are unimportant under the conditions used, this may be related to the presence of two types of ion pairs: CIP and SSIP.

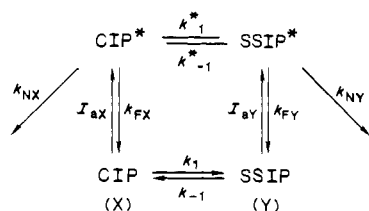
With the lithium β -naphthoxide, only one species is detected when the emission is observed at the maximum, and the corresponding lifetime may be attributed to a CIP. The strongest

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Scheme I



interaction between anion and cation is indeed found in this case as is shown by the absorption and emission wavelengths of Table I. This is expected since the smallest cation exerts the most intense electrostatic field. The fluorescence of the sodium naphtholate in the presence of crown ether may be attributed to an ion pair which may be considered as a SSIP. The interaction has been here largely reduced by the association of the sodium cation with the crown adduct. In the presence of sodium or potassium alone, two types of ion pairs are clearly present, and Scheme I may be an explanation of the observed results.

As apparent from Table II, when double exponential decays are observed, the two decay times are very close to the values obtained for the CIP in the lithium case or for the SSIP in the crowned sodium case. This means that these decay times represent the real lifetimes of the two emitters. This is only possible if the exchange between the two types of excited state ion pairs is slower than their respective rates of decay: $1/k^*_1$ and $1/k^*_{-1}$ must be lower than the lifetimes of excited CIP and SSIP.

Hogen Esch has already shown that carbanion lifetime increases when changing from CIP to SSIP or to free ions.⁴⁹ This result is analogous to our experimental observations and supports our interpretation.

The observed shifts of λ_{\max} in absorption and in emission must now be understood as the result of two simultaneous phenomena: when the cation is changed from a lithium to a potassium, the CIP feels the decrease in the electrostatic field of the cation, whereas in the SSIP the same effect is probably much less important. At the same time, the proportions in CIP and SSIP change in a way that favors the SSIP when a larger cation is used. This last change also occurs when the solvent polarity is increased.

Wavelength Effects. All our observations may be explained by overlapping spectra of mixed CIP and SSIP where CIP absorbs and emits light at lower wavelength than the corresponding SSIP.

In Table IV, when exciting the lithium naphtholate at 347 nm, the CIP is the only detected species at 410 nm, whereas the two ion pairs are seen at 440 nm. This shows that in view to observe the two ion pairs restrictions may exist concerning the wavelength at which fluorescence is measured. On the other hand, the presence of the corresponding ground-state species is demonstrated by the shift of the emission maximum with the excitation wavelength.

Two overlapping spectra also explain the red shift of the emission maximum associated with an increase in excitation wavelength. When changing the excitation wavelength to lower energy, an increasing percentage of SSIP absorbs the light, and since the equilibrium is not completely achieved in the excited state, an increased emission from the SSIP results, explaining the emission red shift.

The variations of relative fluorescence intensities recorded in Table VI clearly demonstrates the spectral overlaps in the absorption as well as in the emission spectra of the ion pairs. When the emission wavelength is progressively increased, an increasing percentage of fluorescence arising from the SSIP is found. This is particularly evident when the more accurate results of the global analysis are considered.

The time-resolved spectrum of Figure 1 is also in agreement with the explanation given for the wavelength effects. After a 100-ns delay the spectrum corresponds to an increased contribution from the SSIP, and the maximum is effectively red shifted ($\lambda_{\max} = 426$ nm).

The Dynamics of the Excited State. Quantitative information about the excited state exchange between CIP and SSIP is not

easy to gain since we are dealing with a photodynamic state rather than with an equilibrium. The emission intensities at a given set of excitation and emission wavelength depend on four factors: the relative concentration of the ion pairs in the ground state, the molar extinction coefficients of the two ion pairs at the excitation wavelength, the relative values of the fluorescence quantum yields of CIP and SSIP, and the relative values of the emission intensity at the chosen emission wavelength.

If the exchange between the excited states of CIP and SSIP is much slower than their respective decays, the excited state concentrations are determined by the ground-state equilibrium after correction for the relative absorbance at the excitation wavelength. If this condition is fulfilled, the 100 ns delayed spectrum of Figure 1 may be considered as arising from pure SSIP.

It seems however that this is not the case. If the 13.8 ns decay time observed in the case of sodium naphtholate in THF is considered as the SSIP lifetime, it means that SSIP lifetimes may be different depending on the cation or on the presence of a crown ether. This is not expected since spectroscopic properties of SSIP do not depend on such changes.⁵⁰ Therefore it has to be considered that the exchange rates between SSIP and CIP, even if slower than the decay of CIP or SSIP, are not negligible and must be taken into account.

If the kinetic scheme is considered the following equations may be deduced for the fluorescence decay as a function of time:

$$I_F(t) = R e^{\lambda_1 t} + S e^{\lambda_2 t} \quad (4)$$

where λ_1 and λ_2 may be defined by

$$\lambda_{1,2} = -1/2\{k_{DX} + k_{DY} \pm \sqrt{\rho}\} \quad (5)$$

$$\rho = \{(k_{DX} + k_{DY})^2 - 4(k_{DX}k_{DY} - k^*_1 k^*_{-1})\} \quad (6)$$

$$k_{DX} = (1/\tau_{CIP}) + k^*_1 \quad k_{DY} = (1/\tau_{SSIP}) + k^*_{-1} \quad (7)$$

$$(1/\tau_{CIP}) = k_{NX} + k_{FX} \quad (1/\tau_{SSIP}) = k_{NY} + k_{FY} \quad (8)$$

The significance of the R and S constants may be found in the appendix.

It may easily be shown with the help of eq 5 that for sodium β -naphtholate in THF, that $1/\lambda_{1,2}$ (the decay times) can only be considered as the τ_{CIP} and τ_{SSIP} if $1/k^*_1$ and $1/k^*_{-1}$ are comparatively negligible. If this is not the case the real lifetimes of CIP and SSIP are necessarily higher than the 7 and 13.8 ns found by the global analysis. If 19 ns is accepted for τ_{SSIP} (see Table II, entry 8) and if reasonable values are used for τ_{CIP} (from 7 to 9 ns), exchange rate constants can be calculated based on the experimental decay times. This simulation leads to the following limited values

$$k^*_1 \text{ (s}^{-1}\text{)} < 2 \times 10^7 \quad 1.9 \times 10^7 < k^*_{-1} \text{ (s}^{-1}\text{)} < 2.2 \times 10^7$$

This confirms that the excited states of CIP and SSIP interconvert but that, to a major extent, their respective population in the excited state depends on the ground-state equilibrium and on the respective extinction coefficient of each species at the excitation wavelength.

Fluorescence Quantum Yields and Radiative Lifetimes. Table III reveals that the experimental fluorescence quantum yields show the same trend as the calculated values: this means that the calculated radiative lifetime, at least as relative values, must be correct. Consequently, the decrease of τ_F , when a protic solvent is used, is due to an important increase of nonradiative decay of the excited state and not to the decrease of the fluorescence rate constant (k_F).

One explanation, already proposed by Klänig,⁵⁰ is the photoejection of an electron followed by the recombination of the radical cation and electron leading to the deactivation of the excited state. This photoejection would not take place in aprotic

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solvents where the electron is not solvated. Another possible deactivation way would be afforded by the hydrogen bonds between the anion and the solvents, giving to the system new ways of nonradiative relaxations.

In table VI, a continuous increase of the fluorescence intensity is observed when the excitation wavelength is increased. This must be the result of the higher fluorescence quantum yield of the SSIP when compared to a CIP. That a SSIP is probably a better fluorescer than a CIP is confirmed when the crowned sodium naphtholate, in THF, is compared to the other sodium naphtholates (Table V, entries 1–10). The electrostatic attraction between the cation and the excess of charge transferred to the aromatic part of the anion after excitation is probably responsible for a more rapid deactivation in the case of CIP, and this may be an explanation of the lowering of ϕ_F . If the lifetimes are considered it seems interesting to underline the progressive shortening observed when going from a SSIP (about 19 ns) to an hydrogen-bonded anion (about 9 ns) and finally to a CIP (6 ns in the lithium case).

Water and Salt Effects. In DMSO, a dipolar aprotic solvent, a significant blue shift of the absorption maximum is observed when water is added to the solution (see Table VII, entries 1–4). This results from a ground-state stabilization due to the preferential solvation of the anion by hydrogen bonding with water molecules. The weakness of the blue shift of the fluorescence and the absence of a significant change of the lifetime are certainly due to the decrease of the negative charge density on the oxygen in the excited state of the anion. This renders the excited naphtholate much less sensitive to water solvation.

In THF, the addition of water also leads to a blue shift of the absorption maximum. This type of effect has already been observed in the case of phenolates,⁴⁴ and the explanation is the same as in the case of DMSO. The strongest effect on the absorption spectra upon addition of water was obtained with a potassium cation: the cation–naphtholate interaction is weaker than in the cases of sodium or lithium. The values of the lifetime and of the fluorescence maximum come closer to the one obtained in the presence of a crown ether: surprisingly, a monoexponential decay, with a lifetime near that of an SSIP, immediately appears when a small amount of water is present. This is characteristic of a weakened interaction in the excited CIP between the oxygen bearing a weak negative charge and the sodium cation. As soon as water is present, the cation is retained by water more strongly than by the anion, and the ion pair gains the SSIP characteristics. Furthermore, the difference between the observed 14 ns and the SSIP 19 ns lifetime may be attributed to the specific anion solvation by water molecules.

Addition of salts does not influence the absorption wavelength but transforms the main part of the excited CIP into SSIP as traced by the observed lifetime (Table VII, entries 15 and 16). Here also, the naphtholate–sodium interaction in the excited CIP is too weak to maintain the association when other ions are present in the solution. This effect like the previous ones is probably a local and not a bulk effect since the change in ionic strength of the solution is not sufficient to explain the important variations observed here.

The addition of DMSO to THF, on the contrary, probably corresponds to such a bulk effect: here the global polarity of the medium is increased, and this results in a displacement of the equilibrium between CIP and SSIP. This displacement affects both the ground and the excited state.

NMR Results and Ground-State Equilibrium. In ¹³C measurements, the shift associated with the cation used may be understood as a trace of the progressive change from an almost pure CIP (the lithium case) into a mixture of CIP and SSIP. No line width change was observed when the temperature was lowered, showing that we are dealing with an exchange which is too fast to be detected by this method. It is known that in a mixture of two species with a mean lifetime of τ the product $2\tau \cdot \delta\omega$ is less than 1 if the two species give rise to one averaged signal.⁵¹ This

Table X. Quenching of the Naphtholate Anion Fluorescence in THF

no.	quencher ^a	$E^{1/2}_{RED}$ ^b	cation	λ_{ex} ^c	λ_{em} ^d	k_{sv} ^e	$k_q \cdot 10^{-10}$ ^f
1	HCB	1.41	Li	358	407	132	2.04
2	HCB		Na	367	421	180	
3	Q	2.18	Li	358	407	72	1.12
4	Q		Na	367	421	135	
5	Q		K	376	430	185	
6	1CN	2.26	Li	358	407	44	0.69
7	1CN		Na	367	421	96	
8	1CN		K	376	430	129	
9	4CBP	2.37	Na	367	421	36	
10	4CBP ^g		Na	367	428	114	
11	N	2.53	Li	358	407	3	0.05
12	N		Na	335	400	6	
13	N		Na	335	420	11.2	
14	N		Na	335	480	16.8	
15	N		Na	368	420	15	
16	N		Na	380	420	21.4	
17	N		Na	380	480	33.5	
18	N ^h		Na	361	428	70	
19	N ⁱ		Na	359	429	75	
20	N		K	376	430	75	
21	BP	2.59	Na	367	421	11	
22	BP		K	376	430	35	
23	BP		Na (CE) ^j	388	431	60	0.32

^aHCB = hexachlorobenzene; Q = quinoline; 1CN = 1-cyanonaphthalene; 4CBP = 4-chlorobiphenyl; N = naphthalene; BP = biphenyl. ^bReduction potential in DMF solvent vs standard calomel electrode.^{39–42} ^cExcitation wavelength in nm. ^dEmission wavelength in nm. ^eStern–Volmer constant in L·M⁻¹. ^fQuenching rate constant in L·M⁻¹ s⁻¹. ^gWith 1% of water added to the solvent. ^hWith 1.7% of water added to the solvent. ⁱWith 3.2% of water added to the solvent. ^jIn the presence of crown ether.

means, in our case, that if the CIP (lithium case, 166.6 ppm) appears at 4 ppm apart from the SSIP (potassium case, at least 170.8 ppm), the lifetimes must be much shorter than 6.10^{-4} s.

In the ²³Na experiments the bandwidth of sodium naphtholate was found to be much broader than for sodium perchlorate, a known SSIP, or for sodium iodide, a CIP.³⁷ It was tempting to speculate that this enlargement is caused by an exchange between SSIP and CIP in sodium naphtholate. In this case, near the fast exchange regime, the line width would depend on the lifetimes of the exchanging species and also on the chemical shift difference between them. Of course, this difference, must vary as a function of the magnetic field of the spectrometer.⁵² Spectra were recorded at two different fields showing line widths at 66.163 and 132.29 MHz which are not significantly different (Table IX). It is thus concluded that in the sodium naphtholate case, the signal bandwidth is essentially due to quadrupolar relaxation: the signal broadening by lowering the temperature is caused by an increase of the correlation time.⁵³

Chemical shifts may however give information about limiting values for lifetimes or exchange rates between SSIP and CIP. An accurate location of the sodium naphtholate CIP and SSIP signal is not available. However, it seems reasonable to suppose that, in the SSIP case, sodium perchlorate and naphtholate will give a signal at about the same position. If we are dealing with a 50/50 mixture of SSIP and CIP naphtholate and since it gives an averaged symmetrical signal at 2.2 ppm (10 ppm above the sodium perchlorate), it is logical to estimate that the chemical shift difference between CIP and SSIP amounts to 20 ppm. Introducing this value in the already given inequality leads to a mean lifetime much shorter than 6.10^{-5} s for the ion pairs.

Quenching Measurements. As known from Marcus theory⁵⁴ and the empirical expression derived by Weller,⁵⁵ electron-transfer rates between donors and acceptors are related to the free energy

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of the reaction. The Weller formula⁵⁵ gives the following value

$$\Delta G \text{ (Kcal}\cdot\text{M}^{-1}) = 23.06(E_{\text{ox}} - E_{\text{red}} - E_{\text{oo}}) - \frac{e^2}{\epsilon r} \quad (9)$$

where E_{ox} (in V) is the oxidation potential of the donor, E_{red} (in V) is the reduction potential of the acceptor, E_{oo} (in V) is the excitation energy and $e^2/\epsilon r$ is the Coulombic interaction factor which equals zero in our case.

In the β -naphtholate fluorescence quenchings, only the reduction potential of the acceptor will vary from case to case. The values of k_q in Table X, when calculated for the lithium naphtholates, show an evident relationship with the reduction potentials of the acceptor quenchers, showing an increase with exothermicity of electron transfer. This confirms that our quenchings occur via this mechanism.

It is also obvious that differences in reactivity can only be observed if the reactions are not diffusion controlled as in the case of quenching by hexachlorobenzene. On the contrary, in non-diffusional cases as the quenching by naphthalene or by biphenyl an increase by a factor of 6 can be observed when the lithium cation is replaced by a crowned sodium (see entries 11 and 23). The naphtholate anion is more available in the last case which corresponds to an SSIP than for the lithium case where the CIP dominates.

A wavelength effect is observed in the quenching of the sodium naphtholate fluorescence by naphthalene: k_{SV} depends on excitation and emission. At constant excitation wavelength the k_{SV} value increases when the emission wavelength is red shifted; the same effect is observed at constant emission wavelength when the excitation is red shifted. This confirms that we are dealing with overlapping emission and absorption spectra of CIP and SSIP and that, according to the wavelength used, we are measuring the quenching of a changing percentage of the two species. This percentage is mainly made of CIP with a 335-nm excitation and a 400-nm emission (entry 12): if a lifetime of 7 ns is used, a value of 0.086×10^{10} is found for k_q , very close to what is observed for the lithium CIP. With a 380-nm excitation and a 480-nm emission wavelength, the quenching measurement concerns mainly SSIP (entry 17), and in this case, with a lifetime of 19 ns, a value of k_q of 0.18×10^{10} is found. This value probably underestimates the SSIP quenching constant since it has been shown that we are not able to select conditions where SSIP are only present: even when exciting at wavelengths where the CIP does not absorb the exchange in the excited state will generate a non-negligible fraction of CIP, and the same is true for SSIP.

The effect due to added water also confirms the previous observations: in THF, and in the presence of a small amount of water, the quenching must be considered as due to SSIP alone, in which the anion is specifically water solvated. If in the case of 4CBP (entry 10) a lifetime of 19 ns is used, a quenching constant of 0.6×10^{10} is found.

Lifetimes and Oxygen. The oxygen effect was probably due to an electron-transfer quenching from the excited naphtholate to oxygen. This quenching is probably diffusional since, according to the reduction potential of oxygen and to what may be expected for the oxidation potential of the naphtholate anion, the reaction must be largely exothermic. From 10 a ΔG value of -51.4 Kcal $\cdot\text{M}^{-1}$ may be calculated with a reduction potential of -0.33 V vs NHE⁵⁶ for oxygen, an oxidation potential of 0.7 V if the naphtholate is considered as a phenolate⁵⁷ and $E_{\text{oo}} = 3.26$ eV which corresponds to the energy of the transition in water.

If the two lifetimes observed in methanol are compared (9.6 and 6.2 ns in the absence and in the presence of oxygen, respectively), a rate constant of $2.3 \times 10^{10} \text{ M}^{-1} \text{ L s}^{-1}$ may be calculated for the quenching by oxygen.

Conclusions

In this paper, the exchange rate constants between excited state CIP and SSIP were estimated for the first time: this dynamic

aspect is characterized by a rate constant close to 10^7 s^{-1} . The ground state equilibrium is governed by rate constants which are only estimated to be much higher than 10^4 s^{-1} : exchange rates in the ground and in the excited state may well be very similar. By lowering the temperature down to -60 °C, only small changes were seen in the double exponential decays or in the shifts of the NMR signals. This suggests that the two equilibria in the excited and in the ground state have a standard free enthalpy change near zero.

It appears also that aromatic oxyanions are significantly different from carbanions^{10,49} since in our case an increase of the cation radius favors the SSIP over the CIP. This also originates from the high electron density on the very electronegative oxygen of naphtholate. As it prefers to associate with the hard lithium cation in a CIP, the naphtholate must be considered as a relatively hard anion at least when compared with carbanions.

Our results show that when analyzing the spectra of anions as a function of solvents and cations, shifts are not always a sufficient tool of investigation. In our case and in the absence of any resolution in the emission and absorption spectra, the combination of a time resolved technique and the wavelength effects on the lifetimes allows the understanding of the changes in the properties of the system.

It has also been shown that the addition of small amounts of water or salts in aprotic solvents may change the state of ion pairs in a different way in the ground and excited state.

Finally, it is worth pointing out that changes in reactivity and particularly in light induced electron transfer from the excited naphtholate anions may be expected when the excitation wavelength is changed as is evident from the Stern-Volmer constants.

Experimental Section

Reactants. β -Naphthol (UCB puriss.) was used both after several recrystallizations and as supplied without showing differences in optical spectra or lifetimes. The solvents were refluxed over the appropriate desiccants (ethereal solvents/sodium; acetonitrile and DMF/calcium hydride; DMSO/sodium hydroxide) and used freshly distilled. Quinoline has been distilled, sodium perchlorate has been dried in vacuum, and the crown ether was purified after washing with aqueous sodium hydroxide by repetitive crystallizations from toluene. Other reagents, hydrides, salts, and quenchers were proanalysis products.

Anions Preparation. In protic solvents, the anions were prepared by reaction of the neutral form with an excess of hydroxide. In other solvents, the β -naphthol was treated with an excess of alkali hydride under an argon atmosphere and filtered directly into the cell through a fritted glass. The solutions were bubbled again under argon just before measurements. The anion concentrations were about $2.5 \times 10^{-4} \text{ M}$ in all cases.

Optical Measurements. Absorption spectra were taken on a Varian Cary 210 spectrophotometer. Emission spectra were recorded on an Aminco SPF 500 fluorimeter working in ratio mode and with excitation and emission bandpass of 1 nm. The lifetimes were measured by the time-correlated single-photon-counting technique. The instrument response function was reconstructed from the measured fluorescence decay of dimethylPOPOP. Laser characteristics and other details have been described elsewhere.⁵⁸ For the fluorescence quantum yields, corrections were made by using normalized spectra of β -naphthol, anthracene, diphenylanthracene, and perylene.

NMR Measurements. We used 10 mm o.d. tubes containing a 5-mm tube filled with CDCl_3 for field/frequency stabilization on the ^2H signal. The sodium salt solutions were 0.15 M, and the sample temperature was regulated at ± 1 °C.

^{13}C NMR measurements were carried out on a Bruker WM 250 spectrometer operating at 62.3 MHz. FT conditions were as follows: spectral width, 15 KHz; acquisition time, 0.54 s; data points, 16 384; number of scans, 200; pulse width, 7 μs (30°); pulse interval, 2 s; line broadening, 2 Hz.

For ^{23}Na NMR measurements two different Bruker spectrometers (WM 250 and WM 500) were used operating, respectively, at 66.163 and 132.29 MHz. FT conditions were as follows: spectral width, 25 and 100 KHz; acquisition time, 0.164 and 0.082 s; data points, 8192 and 16 384; number of scans, 1000 and 160; pulse width, 15 μs (45°) and 4.5 μs (25°); pulse interval, 0.4 and 1 s; line broadening, 5 and 10 Hz.

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Appendix

Starting from the kinetic Scheme I and considering equations for the rates of CIP and SSIP formations, the following classical differential equations are found

$$\dot{Y} + (k_{DX} + k_{DY})\dot{Y} + (k_{DX}k_{DY} - k^*_1k^*_{-1})[Y^*] = 0 \quad (10)$$

$$\dot{X} + (k_{DX} + k_{DY})\dot{X} + (k_{DX}k_{DY} - k^*_1k^*_{-1})[X^*] = 0 \quad (11)$$

where

$$\dot{Y} = d^2[Y^*]/dt^2, \quad \dot{X} = d^2[X^*]/dt^2, \\ \dot{Y} = d[Y^*]/dt, \quad \dot{X} = d[X^*]/dt$$

The solution of this system of equations is given by eq 4-6 from which the following R and S values may be extracted

$$R = \Lambda \{ (k^*_1k_{FY} - k_{FX}(k_{DX} + \lambda_2))\alpha + \\ (k^*_{-1}k_{FY} - k_{FY}(k_{DY} + \lambda_2))(1 - \alpha) \} \\ S = \Lambda \{ (k^*_{-1}k_{FY} + k_{FX}(k_{DX} + \lambda_1))\alpha + \\ (-k^*_{-1}k_{FX} + k_{FY}(k_{DY} + \lambda_2))(1 - \alpha) \}$$

where $\Lambda = 1/(\lambda_1 - \lambda_2)$, and α and $(1 - \alpha)$ represent the molar fractions of the excited CIP and SSIP, respectively.

Acetylenic Esters. Preparation and Characterization of Alkynyl Dialkyl Phosphates, $RC\equiv COPO(OR')_2$ [†]

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Abstract: The first synthesis of acetylenic phosphates is reported. Reaction of PhIO with $BF_3 \cdot OEt_2$, followed by treatment with aqueous $NaO_2P(OR')_2$, or anion exchange of alkynyl(phenyl)iodonium tosylates with $NaO_2P(OR')_2$, gives good yields of alkynyl dialkyl phosphates. These new phosphate esters are characterized by spectral means and show highly characteristic IR and ¹³C NMR absorptions. The scope and limitations of this methodology are discussed along with mechanistic considerations.

Acetylenic esters represent a distinct, new class of compounds that combine two of the most valuable and important functionalities in organic chemistry into a single, unusual derivative. Recently we reported the synthesis and characterization of alkynyl sulfonates² and alkynyl carboxylates,³ the first known members of the family of alkynyl esters. Besides sulfonate and carboxylate esters the third major and significant class of esters are phosphates. Phosphate esters play a key role in mechanistic and bioorganic chemistry.⁴ Despite the importance and variety of phosphate esters as well as the availability of numerous functionalized acetylenes⁵ alkynyl phosphates are to date unknown. Hence, we wish to report a general, simple procedure for the preparation as well as the spectral characterization of a variety of alkynyl dialkyl phosphates.⁶

Results and Discussion

Phosphate esters, like carboxylate esters, are normally prepared by reaction of an appropriate phosphorus halide with the respective alcohol, or an enolate if a vinyl phosphate ester is desired. As ynols, $RC\equiv COH$, are unknown,⁷ this simple, standard procedure cannot be employed for the formation of alkynyl phosphates. Likewise, the standard methods for acetylene formation⁵ are, at least in our hands, inapplicable to the synthesis of alkynyl phosphates. Hence, the lack of simple, standard methods for the preparation of alkynyl phosphates might at least partially account for the hitherto unknown nature of this unusual, albeit simple, class of functionalized organic derivatives.

Our recent success in the preparation of alkynyl sulfonate esters² and alkynyl carboxylates³ via tricoordinate iodonium species prompted us to examine this novel route as a possible means to the desired alkynyl phosphate esters. Specifically, we explored the formation, and subsequent decomposition, of alkynyl(phenyl)iodonium phosphates **5** as outlined in Scheme I.

Three different methods were examined for the formation of alkynyl(phenyl)iodonium phosphate **5**, the key intermediate in our tricoordinate iodine methodology for alkynyl esters preparation. Method A involves the interaction of readily available 1-alkynylsilanes **1** with iodobenzene, **2**, in analogy with our recently reported,¹¹ much improved, synthesis of the analogous tricoordinate

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(7) Alkynols, analogous to enols, are in tautomeric equilibrium with ketenes: $RC\equiv COH \rightleftharpoons RCH=C=O$. Ab initio calculations⁸ indicate that ketene is 36 kcal/mol more stable than the parent hydroxyacetylene. This is considerably greater than the calculated enol-keto energy difference of 11 kcal/mol for the vinyl-alcohol-acetaldehyde system. Yet the barrier to interconversion of $HC\equiv COH \rightarrow H_2C=C=O$ is very high at 73 kcal/mol as determined by calculations.⁸ Stable enols are well known.⁹ Recently the parent hydroxyacetylene $HC\equiv COH$ was observed by tandem mass spectrometry in the gas phase.¹⁰

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[†] Dedicated to Professor William G. Dauben on the occasion of his 70th birthday.