ir (Nujol, cm^{-1}) 1650 (C=O), 1590 (C=C); nmr ($CDCl_3$, δ) 1.92 (s, 3), 2.08 (d, 3, J = 1.5 Hz), 6.70 (q, 1, J = 1.5 Hz), 7.3–8.3 (m, 4).

Anal. Calcd for $C_{14}H_{11}NO_4$: C, 65.36; H, 4.31; N, 5.45. Found: C, 65.41; H, 4.73; N, 5.60.

2-Chloro-3,6-dimethyl-5-*p*-nitrophenyl-1,4-benzoquinone. A suspension of 5.0 g (19.4 mmol) of 2,5-dimethyl-3-*p*-nitrophenyl-1,4-benzoquinone in 100 ml of glacial acetic acid was saturated with HCl. The quinone rapidly dissolved, and a yellow precipitate formed. After stirring for 2 hr, the suspension was heated to dissolve the precipitate, and 20 g of $FeCl_3$ in 75 ml of water was added. The solution was heated on a steam bath for 15 min and then water was added to turbidity. Cooling and filtering gave 5.4 g (95%) of the brilliant yellow chloroquinone, mp 137–138.5°. The analytical sample from ethanol melted at 138.5–140°; ir (Nujol, cm^{-1}) 1665 (C=O), 1620 (C=O), 1600 (C=C); nmr ($CDCl_3$, δ) 2.00 (s, 3), 2.22 (s, 3), 7.3–8.3 (m, 4).

Anal. Calcd for $C_{14}H_{10}ClNO_4$; C, 57.64; H, 3.46; N, 4.80; Cl, 12.16. Found: C, 57.77; H, 3.42; N, 4.86; Cl, 12.26.

2-Azido-3,6-dimethyl-5-*p*-nitrophenyl-1,4-benzoquinone (1o). 2-Chloro-3,6-dimethyl-5-*p*-nitrophenyl-1,4-benzoquinone (2.0 g, 6.9 mmol) was dissolved, with heating, in 300 ml of methanol. Sodium azide (2.7 g, 41.5 mmol) in 15 ml of water was added. Dichloromethane (100 ml) was added to dissolve the resultant precipitate, and the solution was allowed to stand at room temperature in the dark for 4 days. The deep orange solution was diluted with water and extracted with dichloromethane. After drying ($MgSO_4$), the solvent was removed *in vacuo* at room temperature. The reddish orange semisolid was recrystallized from chloroform–ethanol to give 1.2 g (59%) of the yellow-orange azidoquinone, mp 122–130° dec. The analytical sample (chloroform–ethanol) melted at 131–133° dec.

Anal. Calcd for $C_{14}H_{10}N_4O_4$: C, 56.38; H, 3.38; N, 18.79. Found: C, 56.31; H, 3.17; N, 19.20.

Characteristic spectral properties of **10** follow: ir (Nujol, cm^{-1}) 2120 (N_3), 1660, 1640 (C=O); nmr ($CDCl_3$, δ) 1.98 (s, 6); 7.30–8.25 (m, 4).

Kinetics. The rates of azidoquinone decompositions described in this manuscript were determined by measuring the rate of nitrogen evolution. The apparatus employed was similar to that described by Martin and Timberlake.[35] The reaction vessel had a 25-ml capacity and was equipped with a magnetic stirrer. The solvent (10 ml) was equilibrated in the constant-temperature bath with the system open to the atmosphere. Then 4.0–4.5 mmol of the sample dissolved in 0.5 ml of the appropriate solvent was injected and nitrogen was passed through the solution for 1.5–2.0 min. The system was then closed and the rate of increase in nitrogen pressure was automatically recorded. The reaction was allowed to go to completion to obtain P_∞. In each case, the system was not disturbed for at least 2 hr after the highest pressure was obtained in order to check for leaks; none were found. The rate constants were then obtained by plotting ln ($P_\infty - P$) against time. Plots were linear for at least 4 half-lives and in most cases for 6 or more. All azidoquinones were of analytical purity and the solvents employed were purified immediately before use.

(35) J. C. Martin and J. W. Timberlake, *J. Amer. Chem. Soc.*, **92**, 978 (1970).

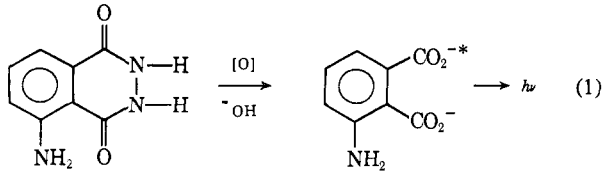
Differences between Excited States Produced Chemically and Photochemically. Ion Pairs of Excited States Derived from Luminol

Peter D. Wildes and Emil H. White*

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. *Received August 24, 1972*

Abstract: Differences in the emission spectra of 3-aminophthalate dianion produced by absorption of light and produced chemically by the oxidation of luminol in basic aqueous dimethyl sulfoxide are attributed to specific interactions of the aminophthalate ions with alkali metal cations (*e.g.*, sodium ion). Appreciable ground-state association is indicated by changes in the absorption spectra with increasing sodium ion concentration. The fluorescence spectrum of 3-aminophthalate in the presence of sodium ion is apparently determined largely by the degree of association in the ground state prior to excitation. In the chemically produced excited aminophthalate ion, the sodium ion distribution is determined largely at the transition state stage of the reaction; a lower fraction of the ion-pair species is apparently formed by this route compared to the fluorescence route.

The chemiluminescence of luminol (I) (5-amino-2,3-dihydro-1,4-phthalazinedione) and its derivatives involves the formation of substituted phthalate ions (II) in the excited singlet state (eq 1). The reaction has



(1)

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been studied in both aqueous and aprotic media (*e.g.*, dimethyl sulfoxide), and aminophthalate ion has been identified as the primary product in both cases.[1-4] In either pure medium, the chemiluminescence spectrum is identical with the fluorescence of aminophthalate ion.

In mixtures of water and dimethyl sulfoxide, however, the chemiluminescence of luminol has been reported to differ from the fluorescence of aminophthalate ion in the same solvent mixture, although aminophthalate was

(1) A preliminary communication on this work appeared in *J. Amer. Chem. Soc.*, **94**, 6223 (1972). For recent reviews see: (a) K. D. Gundermann, "Chemiluminesenz Organischer Verbindungen," Springer-Verlag, West Berlin, 1968; (b) K. D. Gundermann, *Angew. Chem., Int. Ed. Engl.*, **4**, 566 (1965); (c) F. McCapra, *Pure Appl. Chem.*, **24**, 611 (1970); (d) E. H. White and D. F. Roswell, *Accounts Chem. Res.*, **3**, 54 (1970).

(2) (a) E. H. White, O. Zafiriou, H. H. Kägi, and J. H. M. Hill, *J. Amer. Chem. Soc.*, **86**, 940 (1964); (b) E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964); (c) E. H. White and M. M. Bursey, *J. Org. Chem.*, **31**, 1912 (1966).

(3) (a) M. M. Bursey, Ph.D. Thesis, The Johns Hopkins University, 1963; (b) O. C. Zafiriou, Ph.D. Thesis, The Johns Hopkins University, 1966.

(4) (a) J. Lee and H. H. Seliger, *Photochem. Photobiol.*, 11, 247 (1970); (b) J. Lee and H. H. Seliger, *ibid.*, **15**, 227 (1972).

identified as the product of the chemiluminescent reaction and the final fluorescence of the spent reaction mixture matched the aminophthalate fluorescence.[2b] The present study was undertaken to determine the reason for the spectral differences between the chemiluminescence and the product fluorescence. We have found that the discrepancy is caused by a specific interaction of the aminophthalate dianion with the metal counterion (sodium in the previous work).

Results and Discussion

The oxidation of luminol (eq 1) by hydrogen peroxide and a catalyst (*e.g.*, hemin) in basic aqueous solution results in visible chemiluminescence. The chemiluminescence spectrum peaks at 425 nm and is independent of base concentration and of the cation used; any alkali metal hydroxide or quaternary ammonium hydroxide may be used.[3,4] The fluorescence spectrum of 3-aminophthalate, which has been identified as a product of the chemiluminescent oxidation of luminol,[2] is identical with the luminol chemiluminescence spectrum in aqueous base; 3-aminophthalate fluorescence is also independent of the base concentration and type of cation in aqueous solution.[3,4]

In aprotic solvents, such as dimethyl sulfoxide (DMSO), the chemiluminescent oxidation of luminol requires only a strong base and molecular oxygen.[2] For example, in DMSO made basic by the addition of aqueous tetrabutylammonium hydroxide (TBH) (total water concentration <5 mol %) luminol reacts with oxygen to yield nitrogen and 3-aminophthalate ion accompanied by strong yellow-green chemiluminescence ($\lambda_{max} \approx 510$ nm).[5] The chemiluminescence spectrum is identical with the fluorescence of the product, 3-aminophthalate ion, in the same solvent mixture. Both the luminol chemiluminescence and 3-aminophthalate fluorescence spectra are independent of TBH concentration (0.002–0.04 *M*) provided the solution is sufficiently basic to convert the 3-aminophthalate completely to the dianion, or sufficient to form the reactive luminol dianion in the chemiluminescent reaction.[2b,3]

Protic Solvent Effect. In mixtures of DMSO and water, both luminol chemiluminescence and 3-aminophthalate fluorescence exhibit two bands corresponding approximately to the single bands observed in the pure solvents (the shorter wavelength band is slightly blue shifted in water-poor mixtures, λ_{max} 400–425 nm, depending on the amount of water present).[4,6] In water–DMSO mixtures *containing TBH*, the luminol chemiluminescence and 3-aminophthalate fluorescence spectra are identical (Figure 1c) and independent of TBH concentration (0.002–0.04 *M*). As the water content of the medium is increased, a gradual increase in the intensity of the short wavelength peak occurs with a concomitant decrease in the long wavelength peak.[7] The fluorescence spectra are constant for exciting wavelengths from 260–360 nm. Similar two-banded emission is observed in mixtures of DMSO and 2-methyl-2-propanol made basic with *potassium tert*-butoxide with the shorter wavelength band becoming relatively more intense with increasing alcohol content.[3a] The similarity of the results with water and 2-methyl-2-propanol indicates that the luminescence spectral shift is caused by an increase in the protic solvent concentration in the medium and not from changes in solvent dielectric constant, since addition of water increases the polarity of the solvent while addition of 2-methyl-2-propanol has the opposite effect. Thus under the foregoing conditions, two emitting states exist in the mixed solvents, one similar to that produced in water and one similar to that produced in DMSO, and the photo produced and chemically produced sets appear to be identical. In DMSO–water mixtures containing less than *ca.* 40 mol % water, the shift in favor of shorter wavelength emission with increasing water is accompanied by a decrease in luminol chemiluminescence and 3-aminophthalate fluorescence quantum efficiency. At higher concentrations of water these efficiencies increase again, with emission occurring largely from the short wavelength band. Apparently the species responsible for short wavelength emission has a lower fluorescence quantum efficiency in aprotic solvents than the species responsible for long wavelength emission.[3a,6]

Phototautomerization. Similar double emissions have been seen in aqueous DMSO for the chemiluminescence of several luminol derivatives[2b,c,3] and in the fluorescence of 2-aminobenzoate ion[4] and the corresponding 2-monomethylamino compound (see below). However, only a single emission (short wavelength) is seen in the chemiluminescence of 4-aminophthalic hydrazide (and its N-mono and -dialkylated derivatives) and in the fluorescence of 4-aminophthalate, 3-aminobenzoate,[4] and methyl 2-aminobenzoate. The existence of the double emission only in compounds having amino and free carboxylate functions in an ortho arrangement suggests that the long wavelength band in aprotic solvents arises from a phototautomerism involving an intramolecular proton transfer from the amino group to the adjacent carboxyl in the excited state (eq 2).[3,4,6] The explanation is reasonable since it is known that aromatic amino groups become more acidic and carboxyl groups become more basic on going from the ground state to the first excited singlet.[8,9]

In pure DMSO made basic with TBH, the proton transfer is complete and only the long wavelength band is observed. When protic solvents such as water or 2-methyl-2-propanol are added, the short wavelength emission band appears and increases in relative intensity with increasing concentration of the protic solvent.

(5) (a) Most of our spectra were computer corrected for variations in spectral sensitivity of the spectrophotofluorometer.[5b] The relatively large correction required for wavelengths longer than *ca.* 500 nm renders the exact position of the maximum uncertain, but the uncertainty does not affect the present discussion. Uncorrected spectra are reported when only general spectral trends are important. (b) D. R. Roberts and E. H. White, *J. Amer. Chem. Soc.*, **92**, 426 (1970).

(6) J. D. Gorsuch and D. M. Hercules, *Photochem. Photobiol.*, **15**, 567 (1972). We thank Professor Hercules for making the results of his experiments available to us prior to publication.

(7) For example, in DMSO–water solutions containing 0.02 *M* TBH, the ratios of long wavelength to short wavelength fluorescence (corrected spectra)[5] in 17 mol %, 30 mol %, and 50 mol % water are 13.2, 4.8, and 1.0, respectively.

(8) (a) A. H. Weller, *Progr. React. Kinet.*, 1, 187 (1961); (b) E. Van der Donckt and G. Porter, *Trans. Faraday Soc.*, **64**, 3215 (1968); (c) Th. Forster, *Z. Elektrochem.*, **54**, 531 (1950).

(9) For other examples of excited state acid–base reactions or phototautomerisms which result in fluorescent excited state products, see (a) H. Beens, K. H. Grellmann, M. Gurr, and A. H. Weller, *Discuss. Faraday Soc.*, **39**, 183 (1965); (b) A. Tramer, *J. Phys. Chem.*, **74**, 887 (1970); (c) C. A. Taylor, M. A. El-Bayoumi, and M. Kasha, *Proc. Nat. Acad. Sci. U. S.*, **63**, 253 (1969); (d) G. Jackson and G. Porter, *Proc. Roy. Soc., Ser. A*, **260**, 13 (1961), and references therein; (e) J. Menter and Th. Forster, *Photochem. Photobiol.*, **15**, 289 (1972). For examples of triplet state phototautomerism, see P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968), and references therein.

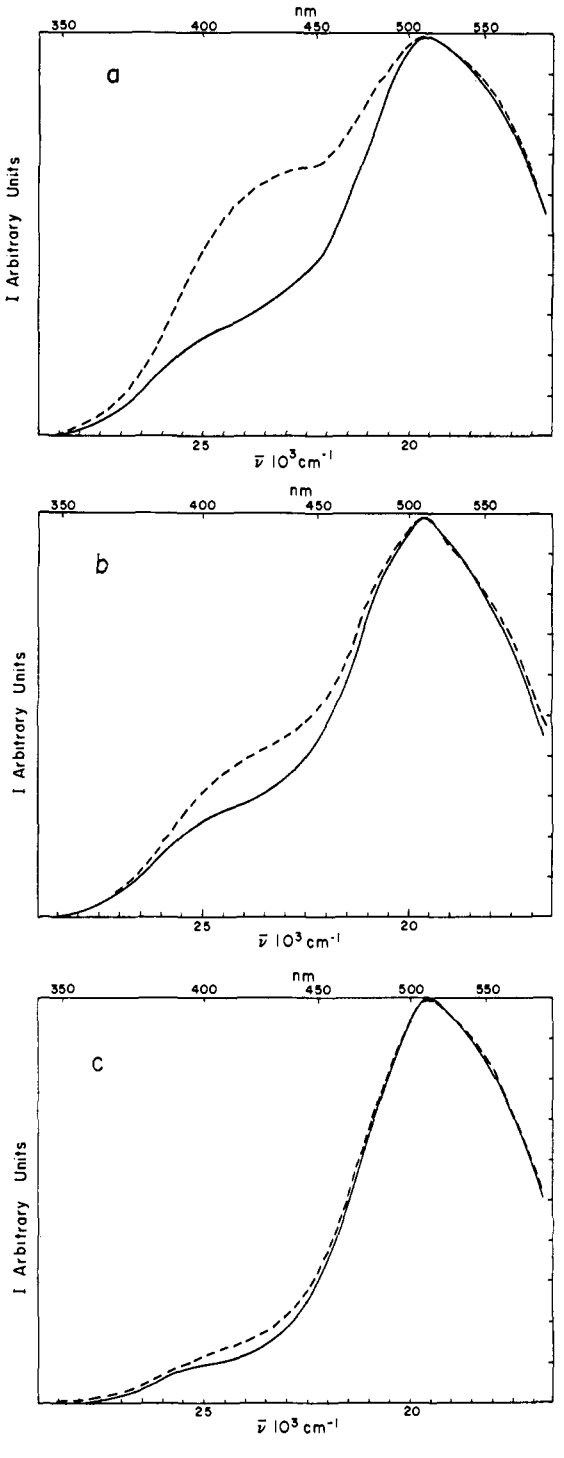
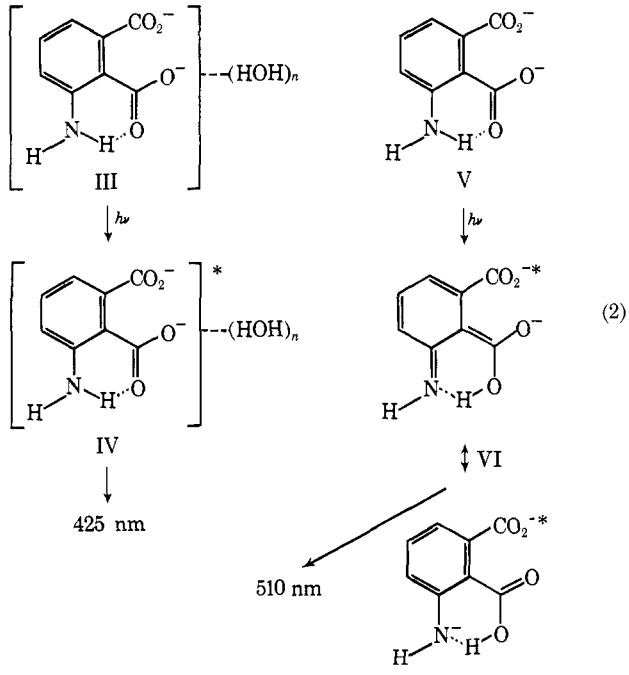
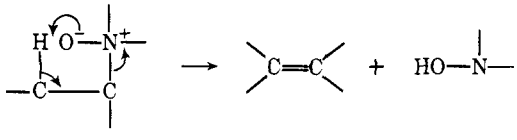


Figure 1. Corrected[5] luminol chemiluminescence (——) and 3-aminophthalate fluorescence (--------) in 30 mol % water–70 mol % DMSO with (a) 0.02 *M* sodium hydroxide; (b) 0.02 *M* potassium hydroxide; (c) 0.02 *M* TBH. Fluorescence spectra were excited at 300 nm. Initial luminol or 3-aminophthalate concentration 1×10^{-4} *M*.

Presumably protic solvents inhibit the intramolecular proton transfer by means of intermolecular hydrogen bonding to the carboxylate group, which lowers the net negative charge density on the group (IV). In addition, hydrogen bonding to the amino group would favor back-tautomerization of VI to forms related to IV. A similar effect of hydrogen bonding has been noted in comparisons of the Cope elimination in DMSO and in



protic solvents;[10] rate decreases of four to five powers of 10 by protic compounds were observed.[11]



Cation Effect. The experimental results are more complicated when alkali metal hydroxides are present in water–DMSO mixtures. In 30 mol % water–70 mol % DMSO (10% water by volume) made basic with a 0.02 *M* alkali metal hydroxide (MOH), the shorter wavelength emission band is markedly more prominent in 3-aminophthalate fluorescence than in luminol chemiluminescence when M = sodium, but the difference is smaller when M = potassium (Figure 1). The use of lithium hydroxide results in 3-aminophthalate fluorescence very similar to that observed with sodium hydroxide, while rubidium and cesium hydroxides yield spectra similar to that with potassium hydroxide (Table I). Calcium hydroxide (0.002 *M* in 30 mol % water–70 mol % DMSO) results in exclusively short wavelength fluorescence from 3-aminophthalate. The chemiluminescence of luminol is quenched by calcium or lithium hydroxide, possibly because their salts with luminol are covalent in character and not readily oxidized.

In contrast to the independence of aminophthalate ion fluorescence on the concentration of quaternary bases such as TBH (cited above), the fluorescence is affected by alkali metal hydroxides. For example, in DMSO–water mixtures, the relative intensity of the shorter wavelength band increases with increasing sodium hydroxide concentration (Figure 2). Potassium hydroxide, however, has only a slight effect (Figure 2). The specific dependence of 3-aminophthalate fluorescence on sodium hydroxide concentration suggests an

(10) D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Amer. Chem. Soc.*, **84**, 1734 (1962); (b) M. R. V. Sahyun and D. J. Cram, *ibid.*, **85**, 1263 (1963).

(11) S. W. Jacob, E. E. Rosenblum, and D. C. Wood, Ed., "Dimethyl Sulfoxide," Vol. 1, Marcel Dekker, New York, N. Y., 1971, p 54.

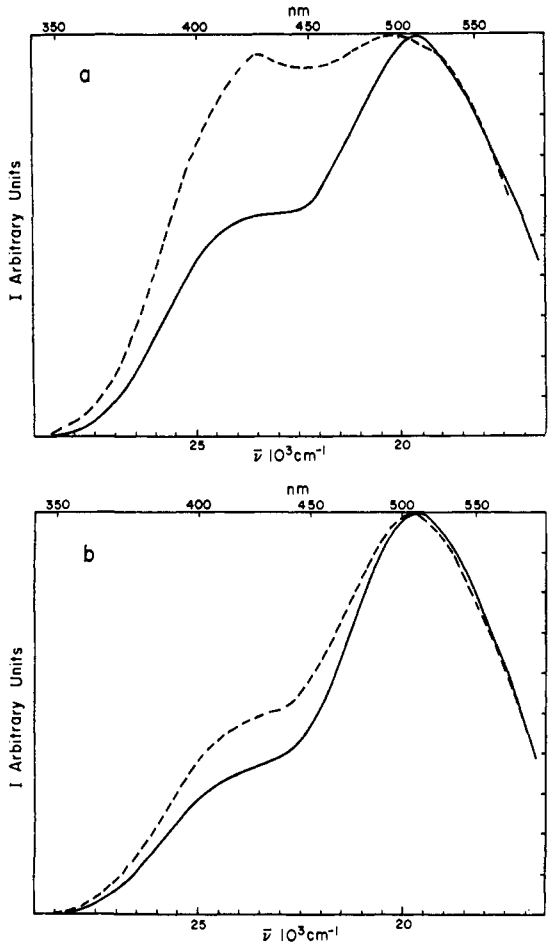


Figure 2. Corrected[5] fluorescence of 3-aminophthalate (5×10^{-5} *M*) in 30 mol % water–70 mol % DMSO ($\lambda_{excitation}$ 300 nm) with (a) sodium hydroxide 0.0036 *M* (——), 0.05 *M* (--------); (b) potassium hydroxide 0.0036 *M* (——), 0.03 *M* (--------).

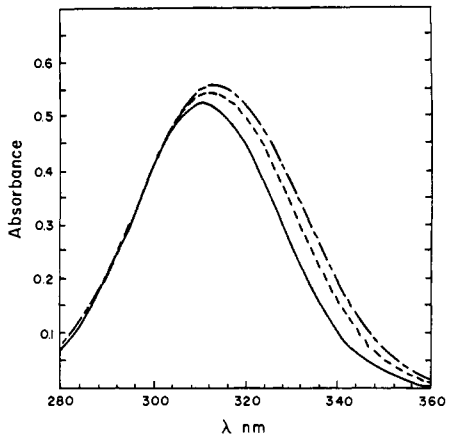


Figure 3. Absorption spectrum of 3-aminophthalate (2×10^{-4} *M*) in 30 mol % water–70 mol % DMSO containing 0.004 *M* TBH and sodium chloride 0.0 *M* (——), 0.003 *M* (--------), 0.007 *M* (—— · ——).

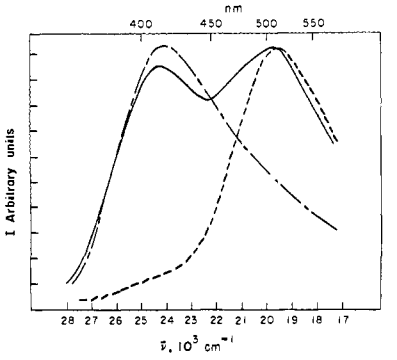


Figure 4. Corrected[5] luminol chemiluminescence (--------) and 3-aminophthalate fluorescence, $\lambda_{excitation}$ 300 nm (——) and $\lambda_{excitation}$ 350 (—— · ——), in 17 mol % water–83 mol % DMSO with 0.017 *M* TBH and 0.017 *M* sodium chloride.

Table I. Fluorescence of 3-Aminophthalate[a] in 17 mol % Water–83 mol % DMSO with Different Bases

Base (0.015 *M*)	$\lambda_{excitation}$, nm	$I(\lambda_1)/I(\lambda_2)$[b]
LiOH	300	0.94
	350	0.36
NaOH	300	0.92
	350	0.56
KOH	300	2.4
	350	2.2
RbOH	300	2.8
	350	2.5
CsOH	300	2.4
	350	2.5
$(CH_3CH_2CH_2CH_2)_4N^+OH^-$	300	~8.8
	350	~8.0

[a] 5×10^{-5} *M*. [b] Ratio of uncorrected fluorescence intensity at the longer wavelength maximum to that at the shorter wavelength maximum. All spectra consisted of two bands, λ_{max} 405 (bandwidth at half-height ≈60 nm) and λ_{max} 480 (bandwidth ≈90 nm).

interaction of 3-aminophthalate anion with the sodium ion.

The absorption spectrum of aminophthalate ion is also affected by the counterion. For example, the spectrum becomes appreciably broader upon addition of excess sodium ion. Increasing the concentration of sodium ion (up to *ca.* 0.006 *M*) by addition of sodium chloride or sodium nitrate to a solution of 3-aminophthalate in 30 mol % water–70 mol % DMSO made basic with 0.004 *M* TBH broadens the absorption spectrum of 3-aminophthalate at wavelengths longer than 310 nm and shifts the maximum from 310 to 315 nm (Figure 3). The shape of the fluorescence emission spectrum of aminophthalate ion under these conditions depends on the excitation wavelength,[3a] in contrast to the independence noted for the fluorescence with TBH as the base. Excitation at 310 nm or below results in two-banded emission while excitation at longer wavelengths results in increasingly predominant shorter wavelength emission (Figure 4 and Table I). Further, when excited with short-wavelength light (λ 310 nm), the shorter wavelength fluorescence band increases with a concomitant decrease in the longer wavelength band as the sodium chloride concentration increases, with an isoemissive point at ~480 nm over the midrange of sodium ion concentrations (Figure 5). Similar fluorescence shifts were observed on addition of sodium chloride to other DMSO–water mixtures. For example, in 2 mol % water with 0.004 *M* TBH, the exclusive 510-nm emission can be converted to exclusive 410-nm emission by addition of 0.006 *M* sodium chloride (excitation at 300 nm in both cases).

We propose that in water-lean mixtures the sodium ion shifts the 3-aminophthalate fluorescence in favor of the shorter wavelength band by virtue of its ability to

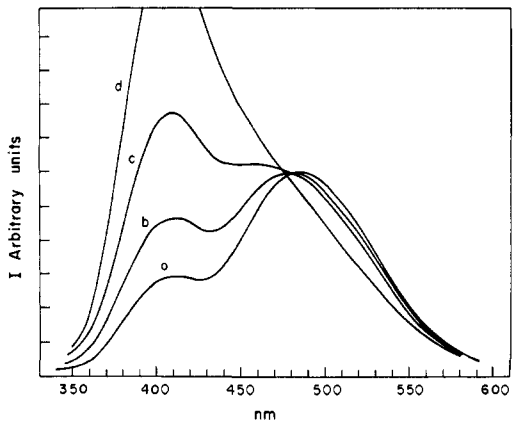
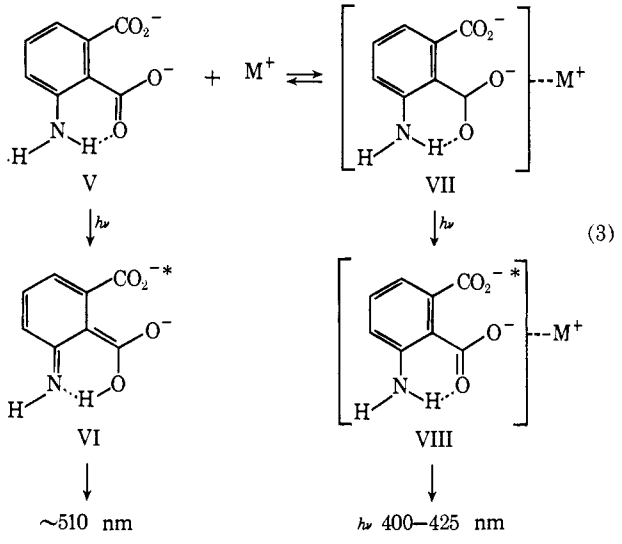


Figure 5. Effect of added sodium chloride on the fluorescence of 3-aminophthalate (5×10^{-5} *M*) in 30 mol % water–70 mol % DMSO; 0.004 *M* TBH: ($\lambda_{excitation}$ 300 nm). Sodium chloride concentration curves a–d: 0.0, 0.002, 0.005, and 0.007 *M*, respectively. The spectra are uncorrected[6] for instrument response (the long wavelength band is relatively more intense in the corrected spectra).

form an ion pair[12] with the aminophthalate ion, an ion pair which persists in the excited state (eq 3). Photo-



(3)

isomerization does not occur in VIII, presumably because of the resulting lower net charge on the carboxylate group.

The shift in 3-aminophthalate absorption with added sodium ion suggests that there is appreciable ground-state association. Thus, in the presence of sodium ions there are two distinct ground-state species present in the solution, free aminophthalate ions and aminophthalate ions associated with sodium ions. Excitation of the associated species leads to short wavelength emission while excitation of the free ion leads to predominately long wavelength emission (Figures 3 and 4 and Table I). In view of the short lifetime (*ca.* 5 nsec)[13] of the singlet excited state of aminophthalate in DMSO–water mixtures, it is unlikely that the excited state will reach a new equilibrium with the sodium ions. The rate of exchange of sodium ion with excited aminophthalate ion is not known, but even if the ion-pair exchange occurs at a diffusion limited rate of *ca.* 10^{10} l. mol^{-1} sec^{-1}, the exchange rate at a sodium ion concentration of 10^{-2} *M* is *ca.* 10^{8} sec^{-1}, which is comparable to the fluorescence rate of *ca.* 2×10^{8} sec^{-1}. Thus some ion-pair exchange may occur in the excited state, but not at a sufficient rate to reach equilibrium.

The intramolecular proton transfer and solvent cage relaxation on the other hand apparently occur at rates much faster than 3-aminophthalate fluorescence since the two-banded fluorescence spectrum in DMSO–water mixtures containing TBH is independent of excitation wavelength regardless of the solvent composition (see above).

In a given solvent mixture the concentration of sodium ion required to shift the aminophthalate fluorescence spectrum was found to depend on the hydroxide ion concentration; increasing the sodium ion concentration at constant hydroxide ion concentration shifts the fluorescence in favor of the shorter wavelength band whereas increasing hydroxide ion concentration while holding sodium ion concentration constant shifts the emission in favor of the longer wavelength band.[14] This suggests that the equilibrium $M^+ + {}^-OH \rightleftarrows M^+OH^-$ is important in the mixed solvents. Apparently the equilibrium favors the associated form (M^+OH^-), at least in DMSO–water mixtures containing less than *ca.* 30–40 mol % water. Thus in the presence of excess hydroxide ion, added sodium has little effect on 3-aminophthalate fluorescence since the sodium is paired with hydroxide ion, but when the sodium ion concentration is equal to or greater than the hydroxide ion concentration, pairing with the aminophthalate ion is significant and the fluorescence is shifted (Figure 5). In effect the fluorescence of 3-aminophthalate serves as an indicator for the titration of hydroxide ion with sodium ion in DMSO–water mixtures.

The addition of potassium chloride to a solution of 3-aminophthalate in 30 mol % water–70 mol % DMSO, 0.004 *M* in TBH, caused only a slight shift in the aminophthalate fluorescence spectrum; the shift in absorption was small but similar to that with sodium. Addition of tetraethylammonium chloride had no effect on either the absorption or fluorescence spectra of 3-aminophthalate.

The sharp difference in the effects of sodium and potassium is consistent with the proposed scheme. The metal–oxygen bonds in the sodium salts have more covalent character than in the potassium or cesium salts;[15] consequently in the present case, sodium is expected to more effectively reduce the negative charge on the carboxylate group than potassium, thus more effectively inhibiting intramolecular proton transfer. As expected, the strongly coordinating calcium ion shifts aminophthalate fluorescence entirely to the short wavelength emission, while the noncoordinating tetrabutylammonium ion has no effect. A similar cation dependence has been observed in certain reactions

(12) The influence of base ion pairing on ground state reactions has been reported: M. Svoboda, J. Hapala, and J. Zavada, *Tetrahedron Lett.*, 265 (1972), and references therein.

(13) L. Brand and M. Loken, unpublished results.

(14) Aminophthalate (5×10^{-5} *M*) in 2 mol % water–98 mol % DMSO containing 0.004 *M* TBH excited at 300 nm gave exclusively long wavelength fluorescence (λ_{max} 510 nm).[5] Addition of sodium chloride to 0.006 *M* shifted the fluorescence entirely to the band at 410 nm. Subsequent addition of TBH to a total hydroxide ion concentration of 0.01 *M* shifted the fluorescence back to exclusively the 510-nm band.

(15) P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry," Wiley, New York, N. Y., 1962, p 408.

carried out in DMSO.[16,17] For example, in the base-catalyzed isomerization of olefins, a change from a sodium alkoxide to a potassium alkoxide caused a 100-fold rate acceleration, while changing from potassium to cesium caused a further threefold rate increase.[17]

Effect of Solvent on the Ion-Pair Interaction. In the presence of sodium ion in DMSO–water mixtures, 3-aminophthalate fluorescence (excited at 300 nm) shifts in favor of the longer wavelength band with increasing water in the medium until the concentration of water reaches about 30 mol %. With more water in the medium, the spectrum then shifts back in favor of the shorter wavelength band (Figure 6a). In contrast, with potassium ion in the medium a continuous shift to the shorter wavelength band is observed with increasing amounts of water (Figure 6b and text). Increasing the concentration of water up to 30 mol % presumably increases the polarity of the medium; a decrease in the association of aminophthalate with sodium ion results, which leads to a shifting of the emission in favor of the longer wavelength band. Above *ca.* 30 mol % water, however, the effect of intermolecular hydrogen bonding dominates and shifts the emission back in favor of the shorter wavelength band (see eq 2 and the section on phototautomerism).

In a less polar solvent, such as acetonitrile, even potassium is effective in shifting the fluorescence of 3-aminophthalate to the shorter wavelength emission. In 99 mol % acetonitrile–1% water with 0.004 *M* TBH, 3-aminophthalate gives only the 510-nm fluorescence band, but with 0.004 *M* potassium hydroxide instead of TBH in the same solvent the fluorescence consists of largely the 410-nm band. Lee and Seliger[4a] also reported unusually intense short wavelength emission from 3-aminophthalate ion in relatively nonpolar, aprotic solvents such as acetonitrile and tetrahydrofuran containing potassium *tert*-butoxide. These authors suggested that the short wavelength emission might have been due to traces of water in the solvents. Ion pairing with potassium seems a more likely explanation, however, since we have found that even measurable amounts of water (*ca.* 1–2%) in acetonitrile produce no detectable short wavelength emission from 3-aminophthalate when the base used is TBH.

Fluorescence of Other Aminophthalates and Aminobenzoates. In a series of aminophthalates and aminobenzoates in 30 mol % water–70 mol % DMSO made basic with 0.02 *M* TBH, the ratio of long wavelength to short wavelength fluorescence from the ions increases in the order aminoterephthalate < 2-aminoisophthalate < 3-aminophthalate ≪ 2-aminobenzoate < *N*-methyl-2-aminobenzoate (Table II). The emission wavelengths and bandwidths are similar for all the aminophthalate and aminobenzoate ions. The markedly greater intensity of short wavelength fluorescence from the aminophthalate ions compared to the aminobenzoates suggests some participation by the second carboxyl group, possibly as a site for additional hydrogen bonding to water. The fluorescence of the aminophthalate ions is also more noticeably shifted by sodium ion than is the fluorescence of aminobenzoate (Table II).

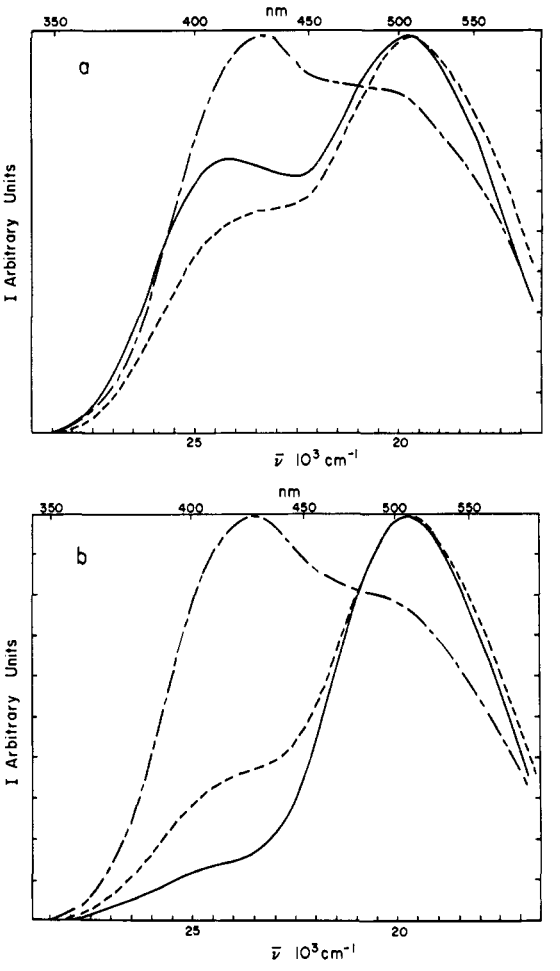


Figure 6. Corrected[5] fluorescence of 3-aminophthalate (5×10^{-5} *M*), $\lambda_{excitation}$ 300 nm in 17 mol % water–83 mol % DMSO (——), 30 mol % water–70 mol % DMSO (-------), and 50 mol % water–50 mol % DMSO (—— · ——) containing (a) 0.004 *M* sodium hydroxide and (b) 0.004 *M* potassium hydroxide.

Temperature Effects. The fluorescence of 3-aminophthalate in 30 mol % water–70 mol % DMSO 0.02 *M* in sodium hydroxide is temperature dependent; the longer wavelength emission increases with increasing temperature in the range 0–50° (Figure 7). The fluorescence of a similar solution containing TBH instead of sodium hydroxide is independent of temperature in the range 0–50°. Presumably, increased temperature shifts the equilibrium in eq 3 in favor of the dissociated ions. The luminol chemiluminescence spectrum measured in 30 mol % water–70 mol % DMSO with 0.02 *M* sodium hydroxide does not vary with temperature (0–50°) although the rate of the reaction is markedly slower at low temperature.

Luminol Chemiluminescence. In mixtures of DMSO and water containing sodium ion, the luminol chemiluminescence and 3-aminophthalate fluorescence spectra differ (Figure 1) despite the fact that the aminophthalate ion is clearly the emitting species in the chemiluminescent reaction. The chemiluminescence spectrum has a much higher ratio of long wavelength to short wavelength emission than the 3-aminophthalate fluorescence. The 3-aminophthalate fluorescence spec-

(16) See ref 15, p 54.

(17) (a) D. J. Cram, J. L. Matios, F. Hanck, A. Langemann, K. R. Kopecky, W. D. Nielsen, and J. Allinger, *J. Amer. Chem. Soc.*, **81**, 5774 (1959); (b) D. J. Cram, B. Rickborn, and G. R. Knox, *ibid.*, **82**, 6412 (1960); (c) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *ibid.*, **83**, 3678 (1961); (d) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *ibid.*, **83**, 3688 (1961); (e) S. Bank, A. Schriesheim, and C. A. Rose, *ibid.*, **87**, 3244 (1965).

Table II. Fluorescence of Aminobenzoates and Aminophthalates in DMSO–Water Mixtures

Compd	Mol % water	Base (concn, *M*)	$I_{\lambda_1}/I_{\lambda_2}$[a]	λ_1,λ_2 (nm)
2-Aminobenzoate	3	NaOH (0.003)	*b*	(465, –)
	30	NaOH (0.02)	5.4	(470, 385)
	30	TBH (0.02)	9.2	(470, 385)
	50	NaOH (0.02)	1.4	(470, 385)
	50	TBH (0.02)	1.3	(470, 385)
	95	NaOH (0.02)	*c*	(–, 395)
N-Methyl-2-aminobenzoate	3	NaOH	*d*	(490, –)
	30	NaOH (0.02)	*d*	(490, –)
	30	TBH (0.02)	*d*	(490, –)
	50	NaOH (0.02)	3.8	(495, 410)
	50	TBH (0.02)	3.8	(495, 410)
	95	NaOH	*e*	(–, 415)
3-Aminophthalate	3	TBH (0.02)	*f*	(485, –)
	3	NaOH (0.004)	~0.3[g]	(–, 405)
	30	NaOH (0.02)	0.7	(480, 410)
	30	TBH (0.02)	2.0	(480, 410)
	50	NaOH (0.02)	~0.45	(480, 415)
	50	TBH (0.02)	~0.45	(480, 415)
	95	NaOH (0.02)	~0.3[h]	(–, 425)
Aminoterephthalate	30	NaOH (0.015)	0.45	(490, 405)
	30	TBH (0.015)	0.76	(490, 405)
	17	NaOH (0.015)	1.0	(490, 400)
	17	TBH (0.015)	2.8	(490, 400)
2-Aminoisophthalate	30	TBH (0.015)	0.96	(490, 400)
	30	NaOH (0.015)	0.75	(490, 400)

[a] Ratio of intensity of longer wavelength maximum to intensity at shorter wavelength maximum from uncorrected fluorescence spectra. [b] Single band λ_{max} ≈465. [c] Single band λ_{max} ≈395. [d] Single band λ_{max} ≈490. [e] Single band λ_{max} ≈415. [f] Single band λ_{max} ≈485. [g] Single band λ_{max} ≈405. [h] Single band λ_{max} ≈425.

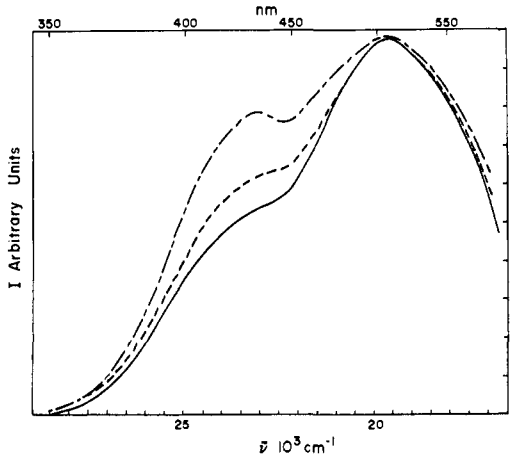


Figure 7. Corrected[6] fluorescence of 3-aminophthalate (5×10^{-5} *M*) in 30 mol % water–70 mol % DMSO containing 0.02 *M* sodium hydroxide $\lambda_{excitation}$ 300 nm, at 45° (——), 26° (--------), and 6° (—— · ——).

tra vary depending on the wavelength of exciting light (see above), but at no excitation wavelength does the fluorescence match the luminol chemiluminescence. Excess sodium ion does shift the chemiluminescence to the short wavelength band, but much more is required than to shift the aminophthalate fluorescence. For example in 30 mol % water–70 mol % DMSO containing 0.017 *M* TBH and 0.1 *M* sodium chloride, luminol chemiluminescence gives two bands of equal intensity while 3-aminophthalate fluorescence excited at 300 nm under the same conditions gives only the shorter wavelength band (uncorrected spectra). Apparently the excited 3-aminophthalate ions produced *via* the oxidation of luminol exist in the ion pair form with sodium to a lesser extent than the excited aminophthalate ions produced by light absorption.

We have shown that there exists significant ion-pair interaction between sodium ions and ground state 3-aminophthalate ions so that in the fluorescence experiments the aminophthalate ions exist to some extent as ion pairs with sodium prior to formation of the excited state. Comparable prior formation of ion pairs in the chemiluminescence pathway would require ion-pair interaction between sodium ions and some form of the oxidized luminol molecule at or near the transition state of the chemical reaction leading to the formation of excited aminophthalate ion; such interactions are apparently weak. It would appear that these effects of ion pairing could serve as a probe into the nature of the transition states leading to the chemical production of excited states.

Experimental Section

Materials. Commercial 3-aminophthalic acid hydrochloride was recrystallized from concentrated hydrochloric acid yielding white crystals; the material gave a single spot on tlc (cellulose with ethanol, water, ammonium hydroxide 8:1:1 by volume). Luminol hydrobromide (5-amino-2,3-dihydrophthalazine-1,4-dione hydrobromide) was recrystallized from 48% hydrobromic acid. Commercial reagent grade 2-aminobenzoic acid and 2-methylaminobenzoic acid were used without further purification. All materials were pure by tlc. Sodium chloride, potassium chloride, and tetraethylammonium chloride reagent grade materials were used as received.

Aminoterephthalic acid was prepared by catalytic hydrogenation of nitroterephthalic acid. Nitroterephthalic acid (1 g, 4.7 mmol) was dissolved in 100 ml of glyme; 0.1 g of 10% palladium on carbon was added and the mixture was stirred with hydrogen at 1 atm for 12 hr. The mixture was filtered through Celite and the solvent removed by rotary vacuum evaporation. A portion (*ca.* 500 mg) of the yellow solid product was dissolved in dilute hydrochloric acid and crystallized as the hydrochloride. Several recrystallizations from dilute hydrochloric acid yielded pale yellow crystals. The hydrochloride was dissolved in water and precipitated by addition of ammonium hydroxide. The product was collected by filtration and dried 5 hr at 0.01 mm and 80°; infrared (KBr) 3490, 3380, 1680, and 1240 cm^{-1}.

Anal. Calcd for $C_8H_7NO_4$: C, 53.04; H, 3.90. Found: C, 53.06; H, 3.79.

2-Nitroisophthalic acid was prepared by the oxidation of 1,3-di-

methyl-2-nitrobenzene with potassium permanganate according to the method of Noelting and Gachot.[18]

2-Aminoisophthalic Acid. A mixture of 1 g (4.7 mmol) of 2-nitroisophthalic acid and 0.1 g of 10% palladium on carbon in 100 ml of glyme was shaken 4 hr with hydrogen at 40 psi. The catalyst was removed by filtration and the solvent by rotary vacuum evaporation. A portion of the product was recrystallized from dilute hydrochloric acid yielding off-white crystals. The hydrochloride was dissolved in water and precipitated by addition of ammonium hydroxide. The product was collected by fitration and dried 5 hr at 0.01 mm and 80°; infrared (KBr) 3450, 3340, 1690, and 1245 cm^{-1}.

Anal. Calcd for $C_8H_7NO_4$: C, 53.04; H, 3.90. Found: C, 53.34; H, 4.04.

Solvents. Dimethyl sulfoxide (reagent) was stirred over potassium hydroxide overnight, distilled under reduced pressure, then redistilled from potassium *tert*-butoxide or potassium superoxide at *ca.* 40° and 0.01 mm; the middle cut was retained and stored under nitrogen. Identical results were obtained using either DMSO prepared in this manner or Fischer spectranalyzed DMSO without purification; solvent fluorescence was negligible. Distilled water was passed through a deionizing column before use. 2-Methyl-2-propanol was distilled from potassium under dry nitrogen, then stored in a tightly stoppered bottle in a dry glove box. Acetonitrile, Eastman Spectrograde, was used without further purification.

Absorption spectra were recorded with a Cary 14 spectrophotometer. Fluorescence and chemiluminescence spectra were recorded with a Hitachi MPF-2A spectrophotofluorometer equipped with a thermostated sample cell holder. The spectra were corrected for variation in spectral sensitivity of the instrument using a computer program which has been previously described.[5b] Fluorescence spectra were also corrected for solvent fluorescence by subtracting the emission from suitable blanks identical with the sample solution except for the absence of the fluorescer. Chemiluminescence spectra were adjusted for luminol absorption below 450 nm in the following manner. The absorbance of the luminol solutions was estimated by preparing samples similar to those used for chemiluminescence measurements but with solvent which had been purged for 15 min with oxygen free nitrogen to remove dissolved oxygen. The adjustment to the initial chemiluminescence spectra was calculated assuming an effective path length of 0.5 cm.

Samples for fluorescence and chemiluminescence spectral measurements were prepared in 1-cm quartz cuvettes by mixing appropriate quantities of an aqueous base solution, water, DMSO, and a DMSO solution of the fluorescer or reactant (3-aminophthalic acid, luminol, etc.) (*e.g.*, a 5×10^{-5} *M* solution of 3-aminophthalate in 30 mol % water–70 mol % DMSO 0.015 *M* in sodium hydroxide was prepared by pipeting 0.15 ml of 0.3 *M* aqueous sodium hydroxide,[19] 0.15 ml of water, 2.1 ml of DMSO, and 0.6 ml of a DMSO solution 2.5×10^{-4} *M* in 3-aminophthalic acid hydrochloride[20] into the cuvette and mixing).

The effect of added salts (sodium chloride, potassium chloride, or tetraethylammonium chloride) on the fluorescence or absorption spectra was measured by adding microliter amounts of 2 *M* or 4 *M* aqueous salt solution to the cuvette with a micropipet, mixing thoroughly, and rerecording the fluorescence or absorption after each addition.

Solutions containing 2-methyl-2-propanol were mixed in a dry glove box immediately before recording the spectra, allowing only sufficient time after mixing for the solution to reach thermal equilibrium with the surroundings.

Stock aqueous solutions of the alkali metal hydroxides were prepared by dissolving reagent grade base in deionized water and filtering; precise base concentration was determined by titration with standard hydrochloric acid solution. A stock TBH solution was prepared by stirring an aqueous solution of tetrabutylammonium bromide over silver oxide for *ca.* 2 hr at room temperature, then filtering. The filtrate was stirred with neutral activated charcoal to remove fluorescent impurities which were found in the solution; the mixture was filtered again and the base concentration determined by titration with standard hydrochloric acid. Potassium *tert*-butoxide solution was prepared by dissolving potassium metal in distilled 2-methyl-2-propanol; base concentration was determined by titration (with standard acid) of a 1-ml aliquot diluted to 10 ml with water.

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(18) E. Noelting and C. Gachot, *Ber.*, **39**, 73 (1906).

(19) The base was introduced first and then diluted with DMSO since reverse addition often results in incomplete solution of the alkali hydroxides.[3a]

(20) Neutral solutions of 3-aminophthalic acid hydrochloride in DMSO are not stable for long periods of time;[6] stock solutions were prepared within a few hours of use.

Solvolytic Studies in the 2-Bicyclo[3.1.0]hexyl System[1]

Edwin C. Friedrich* and Mahmoud A. Saleh

Contribution from the Department of Chemistry, University of California, Davis, California 95616. *Received September 21, 1972*

Abstract: A study of the kinetics and products of hydrolysis of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates (**1**-ODNB and **2**-ODNB) in 80% aqueous acetone at 100° has been carried out. Both isomeric 3,5-dinitrobenzoates reacted at similar rates and gave, within experimental error, identical product mixtures consisting of about 35% **1**-OH, 37% **2**-OH, 25% cyclohexen-4-ol, and 3% cyclohexen-3-ol. Studies of the products obtained from hydrolysis of 2-deuterio-substituted **1**-ODNB and **2**-ODNB it is felt showed the absence of any deuterium scrambling occurring *via* degenerate cyclopropylcarbinyl cation rearrangement for either isomer. Finally, it was found that introduction of a 5-methyl substituent produced a similar large acceleration of about 20 in the rates of hydrolysis of both **1**-ODNB and **2**-ODNB. These results are interpreted in terms of **1**-ODNB and **2**-ODNB both ionizing to bisected bishomoallyl type activated complexes and forming products *via* a single bisected bishomoallylic cyclopropylcarbinyl cation intermediate.

In studies of the acetolysis of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl *p*-toluenesulfonates (**1**-OTs and **2**-OTs), it was observed[2] that the rates and products of

(1) This investigation was supported by the Petroleum Research Fund, administered by the American Chemical Society, and by the Academic Senate Committee on Research of the University of California, Davis. A preliminary report of part of this work has appeared in *Tetrahedron Lett.*, 1373 (1971).

(2) E. C. Friedrich, M. A. Saleh, and S. Winstein, *J. Org. Chem.*, **38**, 860 (1973).