

cosity effects, similar to those observed in ^{27}Al spectra of aluminum alkyl derivatives.¹¹ The concentration dependence can also be attributed to viscosity effects and, in any case, would imply that no more than 10% of the 1:1 complex is present as separated ion pairs at low concentrations (10^{-3} M or greater). The concentration and temperature dependence of the ^1H NMR spectra of the 1:1 complex, which will be reported in detail elsewhere,¹² are consistent with this interpretation also.

Excess tetraethylammonium bromide (TEABr) added to a methylene chloride solution of the 1:1 complex gave, immediately after preparation, a three-line ^{27}Al spectrum: chemical shifts, 92.1, 97.5, and 101.4 ppm; line widths, 25, 25, and 15 Hz; relative intensities, 0.4, 1, and 1. These lines can be assigned to the ions dibromodichloroaluminate, bromotrichloroaluminate, and tetrachloroaluminate,¹³ respectively. The ^1H NMR spectrum for the bromide addition showed lines for both acetyl chloride (δ 2.62) and acetyl bromide (2.76) with relative intensities of 1:2. Immediately after excess TEABr was added to a methylene chloride solution of tetraethylammonium tetrachloroaluminate, no change was observed in the narrow line at 102.4 ppm assigned to tetrachloroaluminate ion. In this latter experiment, the bromotrichloroaluminate line at 97.5 ppm did not appear until 1 week after the addition of bromide; the dibromodichloroaluminate line was not observed. The same ^{27}Al spectrum appeared 1 week after addition of bromide to the 1:1 complex.¹⁴ Addition of TEACl to the 1:1 complex, acetyl bromide-aluminum chloride, gave spectra like that for the addition of TEABr to the 1:1 complex, acetyl chloride-aluminum chloride. These results suggest that the 1:1 complex is not *exclusively* an ion pair, where halide would add at the carboxonium carbon of the acylium ion, rather than to the tetrachloroaluminate. We note also that our results show that rapid exchange of halide between tetrahaloaluminate and acetyl halide does not occur in the absence of complex.

Since the temperature and concentration dependence of the 1:1 complex ^{27}Al spectra can be accounted for by viscosity effects, one can conclude that an equilibrium between separated and "tight" ion pairs or between "tight" ion pairs and donor-acceptor favors one form almost exclusively.¹⁶ Since the halide addition results eliminate the ion pair as this predominant form, we can conclude that the donor-acceptor is the principal species in methylene chloride. Additional evidence for a donor-acceptor structure is the close similarity of the ^{27}Al NMR parameters for the 1:1 acetyl chloride-aluminum chloride complex and the 1:1 complex between 3,3-dimethyl-2-butanone (pinacolone) and aluminum chloride. This latter complex, which must necessarily have a donor-acceptor structure, gives a single ^{27}Al line at 92.8 ppm, with line width 296 Hz.¹²

Acknowledgments. We acknowledge gratefully a grant by the National Science Foundation to the Chemistry Department at S.U.N.Y. at Buffalo for some of the instrumentation used in this work.

References and Notes

- G. A. Olah, Ed., "Friedel Crafts and Related Reactions", Vol. I-IV, Interscience, New York, N.Y., 1963-1965.
- D. Cook, Chapter 9 in ref 1, Vol. 1.
- B. Chevlier and R. Weiss, *Agnew. Chem., Int. Ed. Engl.*, **13**, 1 (1974).
- J. M. LeCarpentier and R. Weiss, *Acta Crystallogr., Sect. B*, **28**, 1421 (1972).
- (a) B. P. Susz and J. J. Wuhrmann, *Helv. Chim. Acta*, **40**, 971 (1957); (b) D. Cook, *Can. J. Chem.*, **37**, 48 (1959); (c) J. S. Shirk and J. L. Wood, *U.S. Gov. Res. Dev. Rep.*, **69**, (12), 66 (1969); (d) D. Cassimatis, J. P. Bonnin, and T. Theophanides, *Can. J. Chem.*, **48**, 3860 (1970); (e) A. Germain, A. Commeyras, and A. Casadevall, *J. Chem. Soc. D*, 633 (1971).
- (a) G. A. Olah, M. E. Moffat, S. J. Kuhn, and B. A. Hardie, *J. Am. Chem. Soc.*, **86**, 2198 (1964); (b) G. A. Olah, S. J. Kuhn, W. G. Tolgyesi, and E. B. Baker, *ibid.*, **84**, 2733 (1962); (c) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *ibid.*, **86**, 2203 (1964); (d) G. A. Olah and M. B. Comisarow, *ibid.*, **88**, 4442 (1966); (e) G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967); (f) G. A. Olah and A. M. White, *ibid.*, **89**, 7072 (1967).
- H. Haraguchi and S. Fujiwara, *J. Phys. Chem.*, **73**, 3467 (1969). In excess acetyl chloride the 1:1 complex undergoes self-acetylation, so that the species giving rise to the ^{27}Al NMR spectrum in this reference is presumably diacetylacetyl tetrachloroaluminate.
- The 1:1 complex was prepared by addition of acetyl chloride to an equimolar amount of aluminum chloride (as a suspension of AlCl_3 in methylene chloride); the product gave IR and ^1H NMR (in D_2O) spectra similar to those reported in ref 4e.
- Chemical shifts are relative to an external hexaquoaluminum standard; downfield shifts are positive. An external, water proton field-frequency lock was used. The hexaquoaluminum line was monitored (before and after the accumulation of free induction decays) to ensure that shift or resolution changes were negligible. Field homogeneity limited line widths were of the order of 10 Hz for the 10-mm nonspinning samples. The "true" line width for tetrachloroaluminate ions (as tetraethylammonium tetrachloroaluminate) in methylene chloride was ~ 3.9 Hz at 28°C , as determined by a Carr-Purcell, Meiboom-Gill pulse sequence.
- We assume here that the shift and line width for the solvent separated ion pair are the same as those for tetraethylammonium tetrachloroaluminate in methylene chloride.
- L. Petrakis, *J. Phys. Chem.*, **72**, 4182 (1968).
- J. Willinski, Ph.D. Thesis, S.U.N.Y. at Buffalo, 1977.
- R. J. Kidd and D. R. Truax, *J. Am. Chem. Soc.*, **90**, 6867 (1968).
- Since the ^1H NMR spectrum of the addition product remained unchanged 1 week after the addition of bromide, one can conclude that, as reported in ref 12, halide slowly exchanges between tetrahaloaluminate and halogenated solvent, in our case methylene chloride.
- T. W. Phillips and K. P. Murphy, *J. Chem. Eng. Data*, **15**, 304 (1970).
- We assume here that the enthalpy difference between tight ion pair and donor-acceptor is not zero, and that the differences in chemical shifts and line widths are comparable with those for appropriate model compounds, diacetylacetyl tetrachloroaluminate for a tight ion pair (ref 7 and 12) and the 1:1 complex between aluminum chloride and 3,3-dimethyl-2-butanone (pinacolone) for the donor-acceptor form (see below and ref 12).

John Willinski, R. J. Kurland*

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

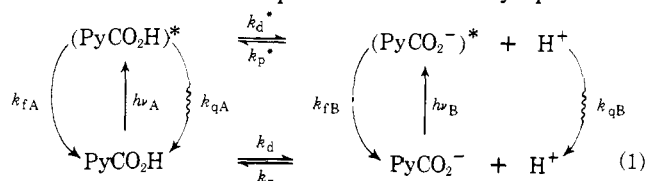
Received November 18, 1977

Ultrafast Excited-State Proton Transfer in Reversed Micelles

Sir:

Charge and proton relay through hydrogen bonds have been proposed to contribute to the catalytic efficiency of enzymes.¹⁻³ Proton inventory, taken by measuring kinetic isotope effects in mixtures of protium and deuterium oxides, has provided evidence for the coupled motions of protons.⁴ An additional factor in enhancing reaction rates is the reduction in dimensionality.⁵⁻⁸ Determinations of proton transfer or translocation rates would yield direct information on the processes involved. Experimental difficulties have precluded to date the kinetic investigations of ultrafast proton-transfer rates at enzyme-active sites. Reversed micelles^{9,10} have been used in the present work to mimic enzyme active sites. Taking advantage of nanosecond time resolved fluorescence, the present communication reports, we believe, the fastest proton transfer is far observed in a solution.

Ground- and excited-state protonation of pyrene-1-carboxylic acid, PyCO_2H ,¹¹ was investigated in water and in 0.10 M dodecylammonium propionate (DAP)¹² entrapped 0.55 M water in benzene.¹⁴ The equilibria is described by eq 1¹⁶ where



k_p , k_p^* and k_d , k_d^* are rate constants for ground- and the first singlet excited-state protonation and deprotonation; K_a and K_a^* are the corresponding ground- and excited-state equilibrium constants ($K_a = k_d/k_p$, $K_a^* = k_d^*/k_p^*$); k_{fA} and k_{fB} are rate constants for the fluorescence decay of the acid and base; and k_{qA} and k_{qB} represent all competing deactivation processes. The ground-state dissociation constant of PyCO_2H was found to be identical in bulk and surfactant entrapped water

Table I. Ground- and Excited-State Protonation of Pyrene 1-Carboxylate in H₂O and in DAP Entrapped Water in Benzene at 25.0 °C

	H ₂ O	0.10 M DAP in benzene ^a
pK _a ^b	3.1 ± 0.3	3.2 ± 0.3
pK _a ^{*c}	4.2 ± 0.4	5.0 ± 0.5
ΔpK ^d	1.4 ± 0.4	2.0 ± 0.5
k _p ^{*e} , M ⁻¹ s ⁻¹	(7.7 ± 0.4)10 ¹⁰	(2.0 ± 0.2)10 ¹²
k _d ^{*f} , s ⁻¹	(5.3 ± 0.5)10 ⁵	(2.2 ± 0.3)10 ⁷
k _{fA} + k _{qA} , s ⁻¹ ^g	(2.4 ± 0.2)10 ⁷	(2.4 ± 0.2)10 ⁷

^a Containing 0.55 M H₂O. ^b Determined from changes of the absorption spectra of PyCOOH and PyCO₂⁻ as functions of added H⁺. ^c Determined from changes of the fluorescence lifetimes of PyCO₂⁻ as functions of added H⁺. ^d pK_a^{*} - pK_a, calculated from the Forster cycle. Using the absorption maxima for PyCO₂H and PyCO₂⁻ of 348 and 340 nm in water and of 355 and 346 nm in 0.10 M DAP in benzene as well as the emission maxima for (PyCO₂H)* and (PyCO₂⁻)* of 415 and 383 nm in water and of 400 and 385 nm in 0.10 M DAP in benzene. ^e Calculated from the slopes given in Figure 1. ^f Calculated from k_p^{*} and pK_a^{*} values. ^g Estimated from the intercepts of the plots in Figure 1 and k_d^{*} (see eq 2).

(Table I). Similar behavior has been observed for a number of indicators undergoing corresponding charge changes upon protonation.¹³ There was, however, an appreciable difference of pK_a^{*} values indicating an altered microenvironment of the excited-state species compared with that of their ground-state analogues.

Decreasing hydrogen ion concentrations resulted in substantial changes of fluorescence lifetimes for (PyCO₂H)* and (PyCO₂⁻)* both in bulk water and in the cavities of reversed micelles. The fluorescence rate parameters, λ values, obtained from the deconvolution of fluorescence intensities, allowed the determination of k_p^{*} values from eq 2:¹⁷

$$\lambda = k_{fA} + k_{qA} + k_d^* + k_p^*[H^+] \quad (2)$$

Slopes of the straight-line plots of λ against [H⁺], shown in Figure 1, gave k_p^{*} values. k_d^{*} values were obtained from pK_a^{*} and k_p^{*}. Table I compares the determined parameters for eq 1 in bulk and surfactant solubilized water pools.

The most striking feature of the obtained data is the extraordinarily large rate constant for the protonation of (PyCO₂⁻)* in the surfactant solubilized water pool; k_p^{*} = (2.0 ± 0.2)10¹² M⁻¹ s⁻¹! Such ultrafast proton transfer is only feasible if the donor and acceptor are in close proximity. Indeed, protonation of (PyCO₂⁻)*, at a given acid concentration, can be regarded as a unimolecular process within an ion pair at the hydrated inner surface of reversed micelles. The reactive partners need not diffuse together—they are there all the time. An analogous situation has previously been encountered in the protonation of hydrogen bonded trifluoroacetate ions.^{18,19} The average aggregation number of 0.10 M DAP in the presence of 0.55 M water is 65.^{15,20} Such an aggregate contains a water pool whose radius is ~15 Å. More significantly, substantial amounts of water molecules are tied up in hydrating the surfactant headgroups; the radius of free water in this system is only 11 Å.¹⁵ Since the pyrene moiety of PyCO₂H is intercalated in the hydrophobic regions of DAP,¹⁵ proton transfer must occur within the hydration shell of the surfactant. Figure 2 illustrates the proposed mechanism in reversed micelles where the donor and acceptor are in close proximity. This proximity is responsible for the 26-fold enhanced proton-transfer rate compared with that in water. A similar argument can be marshalled for the 42-fold faster deprotonation rate in DAP entrapped water. Enhanced deprotonation rates of the same magnitude have been observed at the surface of aqueous micelles.²¹ The experimental value of k_p^{*} in water is (Table I) in agreement with that calculated by the Debye equation²² (k_p^{*} = 10 × 10¹⁰ M⁻¹ s⁻¹) using a Debye radius of 7.1 Å. An analogous calculation cannot be performed for k_p^{*} in the

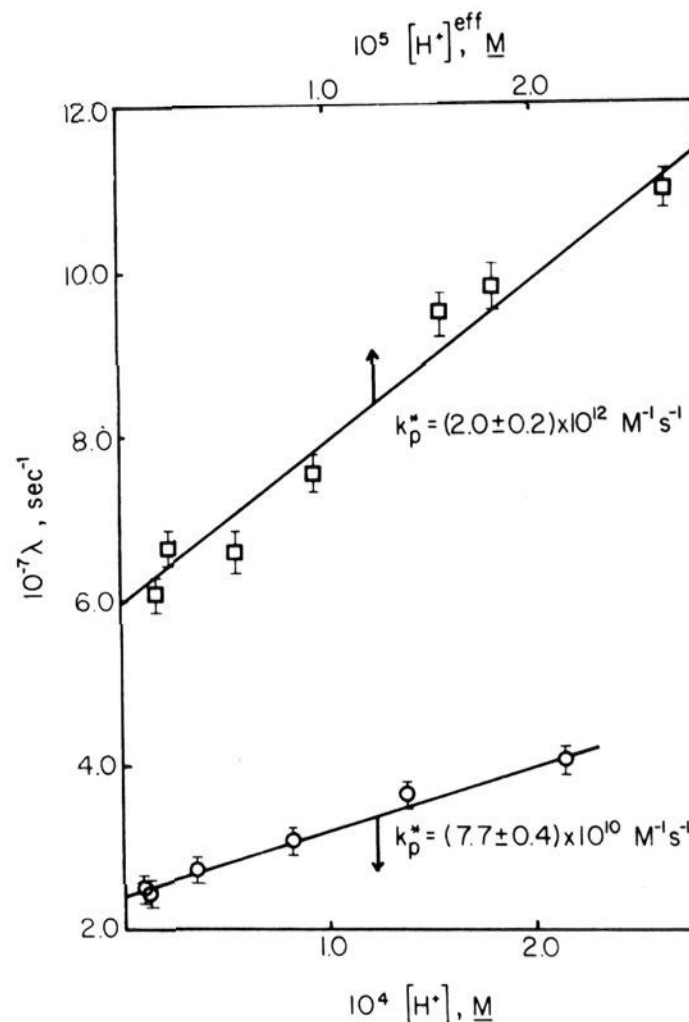


Figure 1. Plots of λ against hydrogen ion concentration for the excited-state protonation of pyrene 1-carboxylate in H₂O (O) and in 0.10 M DAP solubilized water in benzene (□) at 25.0 °C. See ref 12 for the calculation of proton concentration in the surfactant solubilized water pool, [H⁺]^{eff}.

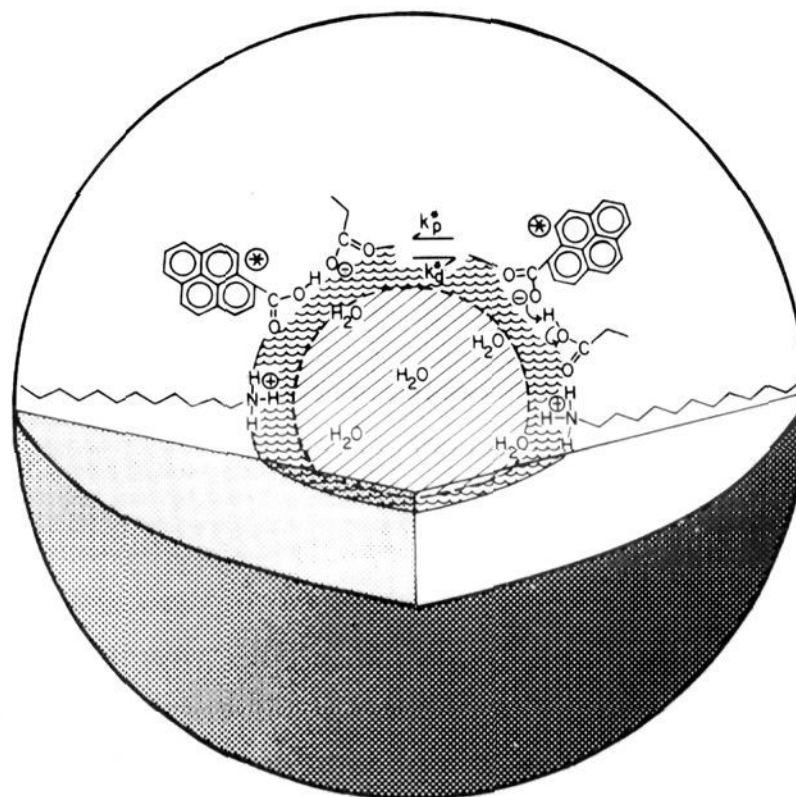


Figure 2. A proposed model for the ultrafast proton transfer at the hydration shell of the surfactant headgroups in reversed micellar DAP in benzene. Since the concentration of surfactant is in a very large excess over the probe,²⁰ proton transfer must occur from dodecylammonium propionic acid to pyrene 1-carboxylate. For the sake of clarity, two pyrene moieties are drawn in the aggregate shown. In reality, there is much less than one probe per aggregate.²⁰ The shaded area indicates the extent water which hydrates the surfactant headgroups.¹⁵

reversed micelles since neither the Debye radius nor the relative diffusion coefficient is known. In any event, the ultrafast excited-state proton transfer is likely to be a composite effect of the reacting partners having a distance of closest approach very much shorter than the Debye radius and of the changed microviscosity of the reaction medium at the hydration shell in the reversed micellar interior compared with that in water. Environments provided by reversed micelles have been sug-

gested to resemble that of ionic crystals.¹⁰ Indeed the rate constant for the ultrafast proton transfer observed in the present work (2.0 ± 0.2) ($10^{12} \text{ M}^{-1} \text{ s}^{-1}$) lies between values determined in water ($\sim 10^{11} \text{ M}^{-1}$) and derived in ice (10^{13} – $10^{14} \text{ M}^{-1} \text{ s}^{-1}$).²⁴ Excited-state proton tunneling cannot be excluded.

The present communication has demonstrated the feasibility of ultrafast proton transfer when the reactants are localized in suitable environment. Micellar surfaces provide a convenient means for the reduction in dimensionality, an important and recognized way fast reaction occurs at membrane surfaces^{6,7} and in complex biomacromolecules.

Acknowledgments. Support of this work by the National Science Foundation and the Robert A. Welch Foundation is gratefully acknowledged.

References and Notes

- (1) D. M. Blow in "The Enzymes", Vol. 3, 3rd ed, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1971.
- (2) D. M. Blow, J. J. Birkoft, and B. S. Hartley, *Nature*, **221**, 337 (1969).
- (3) G. A. Rogers and T. C. Bruice, *J. Am. Chem. Soc.*, **96**, 2473 (1974).
- (4) R. L. Schowen, *Prog. Phys. Org. Chem.*, **9**, 275 (1972); R. L. Schowen in "Isotope Effects in Enzyme Catalysis", W. W. Cleland, D. Northrup, and M. H. O'Leary, Ed., University Park Press, Baltimore, Md., 1977.
- (5) G. Adam and M. Delbruck in "Structural Chemistry and Molecular Biology", A. Rick and N. Davidson, Ed., Freeman and Co., San Francisco, Calif., 1968.
- (6) P. H. Richter and M. Eigen, *Biophys. Chem.*, **2**, 225 (1974).
- (7) M. Eigen in "Quantum Statistical Mechanics in the Natural Sciences", B. Kusenoglu, S. L. Mintz, and S. Widmayer, Ed., Plenum Press, New York, N.Y., 1974, p 37.
- (8) A. J. Frank, M. Gratzel, and J. J. Kozak, *J. Am. Chem. Soc.*, **98**, 3317 (1976).
- (9) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, N.Y., 1975.
- (10) J. H. Fendler, *Acc. Chem. Res.*, **9**, 153 (1976).
- (11) PyCO_2H has been prepared by the Ag_2O oxidation of the corresponding aldehyde in ethanol-water mixture (10:1). Subsequent to separation the product was recrystallized twice from ethanol.
- (12) Preparation, purification, and characterization of DAP have been described.^{9,10} Hydrogen ion concentrations have been adjusted by HClO_4 . Proton concentrations in the surfactant solubilized water pool have been calculated by quantitative infrared titrations of DAP in the presence of different amounts of HClO_4 . There are two assumptions: firstly, all acid is assumed to partition into the aqueous phase, and secondly, the pK_a of propionic acid is considered to be the same in the reversed micelle as in water. In view of the identical pK_a of several indicators in these two media, these assumptions are reasonable. Nevertheless, proton concentrations in the surfactant solubilized water pool is expressed as $[\text{H}^+]^{\text{eff}}$. See ref 13 for experimental details.
- (13) F. Nome, S. A. Chang, and J. H. Fendler, *J. Chem. Soc., Faraday Trans. 1*, **72**, 296 (1976).
- (14) Absorption spectra were taken by a Cary 118C recording spectrophotometer. Steady-state fluorescence spectra were determined on a SPEX Fluorog spectrofluorometer in the E/R mode. Fluorescence lifetimes were obtained on a modified Ortec 9200 single photon counting nanosecond time resolved fluorescence spectrometer, interfaced with a PDP 11-10 minicomputer. Fluorescence lifetimes were deconvoluted using the method of moments program.¹⁵ All spectral work was carried out at 25.0 °C on degassed samples. Degassing was accomplished on a high vacuum line by repeated freeze-pump-thaw cycles.
- (15) G. D. Correll, R. N. Chesser, III, F. Nome, and J. H. Fendler, *J. Am. Chem. Soc.*, **100**, 1254 (1978).
- (16) See J. H. Ireland and P. A. H. Wyatt, *Adv. Phys. Org. Chem.*, **12**, 131 (1976), for a recent review.
- (17) The treatment here is essentially the same as that given for excimer formation (J. B. Birks, D. J. Dyson, and I. H. Munro, *Proc. R. Soc. London, Ser. A*, **275**, 575 (1963)) and used subsequently for excited-state proton transfer (M. L. Loken, J. W. Hayes, J. R. Gohlke, and L. Brand, *Biochemistry*, **11**, 4779 (1972)).
- (18) M. M. Kreevoy and C. A. Mead, *J. Am. Chem. Soc.*, **84**, 4596 (1962).
- (19) M. M. Kreevoy and C. A. Mead, *Discuss. Faraday Soc.*, No. 39, 166 (1965).
- (20) Since the stoichiometric concentration of PyCO_2H was $1.0 \times 10^{-6} \text{ M}$, there is ~ 1 mol of PyCO_2H for every 1500 aggregates.
- (21) F. M. Menger and J. L. Lynn, *J. Am. Chem. Soc.*, **97**, 948 (1975).
- (22) $k_p^* = 4\pi N' D_{12} R_0 / [1 - \exp(-R_0/R_0)]$ where N' is the Avogadro's number per millimole, R_0 is the distance of closest approach (6.0 Å), D_{12} is the relative diffusion coefficient ($9.32 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$),²³ and R_0 is the Debye radius.
- (23) Th. Forster and S. Volker, *Chem. Phys. Lett.*, **34**, 1 (1975).
- (24) M. Eigen and L. DeMaeyer, *Proc. R. Soc. London, Ser. A*, **247**, 505 (1958).

Jose R. Escabi-Perez, Janos H. Fendler*

Department of Chemistry, Texas A&M University
College Station, Texas 77843

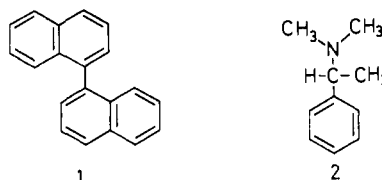
Received December 2, 1977

Steric Effect on Fluorescence Quenching of 1,1'-Binaphthyl by Chiral Amines

Sir:

Although several works have been published recently dealing with steric influence upon fluorescence quenching rates,¹ a satisfactory answer to the question of whether a specific geometry is required for charge-transfer or electron-transfer quenching processes has not yet been given.² Efforts have so far been directed to measuring the quenching rate as a function of substitution on the quenchers or the excited molecules. The conclusions deduced from these experiments have several limitations, since the introduction of substituents implies electronic, as well as steric, changes, which can affect the role of a charge-transfer interaction in the excited state.³ In addition, the imposition of bulky substituents may also produce an effect on the solvation shell and on diffusion rates, which will result in differences in the quenching rate.

In this communication we would like to present unambiguous evidence that specific geometry is required for the fluorescence quenching of 1,1'-binaphthyl (**1**) by *N,N*-dimethyl- α -phenethylamine (**2**) in less polar solvents. Both **1** and **2** are



chiral compounds. The chirality of 1,1'-binaphthyl is molecular in nature.⁴ The use of chiral compounds as excited molecules and quenchers enables one to examine pure steric effect upon the quenching rate without being disturbed by the electronic factor, since enantiomers have inherently the same electronic nature, i.e., oxidation-reduction potential or bulkiness. Chiral sensitizers or quenchers are also useful in photochemical reactions, such as asymmetric inductions⁵ or racemization reactions.^{4,6}

Photoexcited 1,1'-binaphthyl gives a fluorescence around 360 nm. The fluorescence can be quenched by adding *N,N*-dimethyl- α -phenethylamine, the quenching being similar to a typical exciplex-type quenching observed in the naphthalene-triethylamine system.⁷ Figure 1a shows Stern-Volmer plots of a fluorescence quenching of racemic mixture of 1,1'-binaphthyl by enantiomers, (*S*)-(-)- and (*R*)-(+)-*N,N*-dimethyl- α -phenethylamines in *n*-hexane. No difference was discerned in the quenching rate. On the other hand, a significant difference in the rates was observed for the quenching of (*R*)-(-)-1,1'-binaphthyl ($[\alpha]_D -190^\circ$) fluorescence by these enantiomers, as shown in Figure 1b and 1c. The ratio of the quenching rates, $k_q(R-S)/k_q(R-R)$, was determined to be 1.90. The difference in the rate clearly indicates that the quenching occurs in the contact pair of an excited molecule and a quencher, and specific orientation is required in the quenching process.

Solvent polarity is believed to alter the quenching mechanism.^{1,8,3,8,9} In nonpolar solvents, exciplex formation is dominant in the quenching process; in polar solvents, quenching by electron transfer in an encounter complex of loose structure dominates. This mechanism was examined by measuring the quenching rate with the two enantiomers as a function of the polarity of solvent. The ratio, $k_q(R-S)/k_q(R-R)$, has a tendency to decrease with increasing solvent polarity as shown in Table I. No noticeable difference was detected in acetonitrile. In 1,2-dichloroethane, however, there is still a significant difference. The Stern-Volmer constant also depends upon the polarity. It increases with increasing solvent polarity, the highest value being observed in acetonitrile. The increase is