enzyme, it is possible that both the real and artificial acyl-enzymes would have the same rate of deacylation.

Thus we have synthesized an organic chemical model of an acyl-enzyme intermediate of MW 428 whose hydrolysis rate is approximately equivalent to a real acyl-enzyme intermediate of MW 25 100 (Table I). This achievement indicates that out initial assumptions of a three amino acid active site and the intermediacy of an acyl-enzyme are correct for the chymotrypsin structure and mechanism.

The molecular weight ratio of 58.25 for the real over the artificial acyl-enzyme, which we have achieved, can be explained in part by the fact that we do not utilize any amino acids in our synthesis, which immediately makes it nonutilizable for biosynthesis including transmission through the genetic chain from one generation to the next and also reduces the water solubility greatly. Since all life takes place in water, it reduces the utility of the artificial acyl-enzyme to nonlife processes.

The mechanism by which this large rate acceleration occurs will be discussed in the full paper.

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Exciplex Ionic Dissociation in Nonpolar Solvent Induced by Multipolar Salt Complexes

Barbara E. Goodson and Gary B. Schuster*

Department of Chemistry, Roger Adams Laboratory
University of Illinois, Urbana, Illinois 61801

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Exciplex intermediates play a pervasive role in organic photochemistry.[1] In relatively nonpolar solvents, radiative relaxation of the exciplex often occurs in competition with chemical reactions. In more polar solvents, dissociation of the exciplex to radical ions is the dominant reaction when it is permitted energetically. Salt effects are often used to control or probe organic reactions.[2] However, only quite recently have salts been employed in the investigation of exciplexes.[3,4] Herein we report the results of a study of the interactions between tetra-*n*-butylammonium tetrafluoroborate (R_4NBF_4) and the exciplex formed from singlet excited pyrene and 1,4-dicyanobenzene, (Py–DCNB)^{*1}, in dimethoxyethane (DME) solution. The findings reveal that (Py–DCNB)^{*1} is quenched by monomeric, dipolar R_4NBF_4 without formation of ions but that reaction of the exciplex with higher aggregates $(R_4NBF_4)_n$ leads to efficient formation of pyrene radical cation (Py^{+}·) and dicyanobenzene radical anion (DCNB^{-}·). This phenomenon is useful both for controlling the chemical reactions of exciplexes and for analyzing putative electron-transfer reactions.

The fluorescence of pyrene in DME is rapidly and irreversibly quenched by addition of DCNB, and simultaneously a new, broad emission centered at 450 nm due to (Py–DCNB)^{*1} appears in the spectrum.[5] The fluorescence of pyrene is unaffected by addition of R_4NBF_4, but the emission of the exciplex is quenched by this salt. The maximum of the exciplex emission spectrum is not changed noticeably by the salt. In contrast to observations reported for related systems,[3] Stern-Volmer analysis of the exciplex quenching by the salt reveals a distinctly nonlinear relationship.[6] In effect, the salt is a less effective quencher at higher concentrations than it is at the lower concentrations. Precisely the same nonlinear behavior is observed when the lifetime of the exciplex is monitored. These results are displayed on Figure 1.

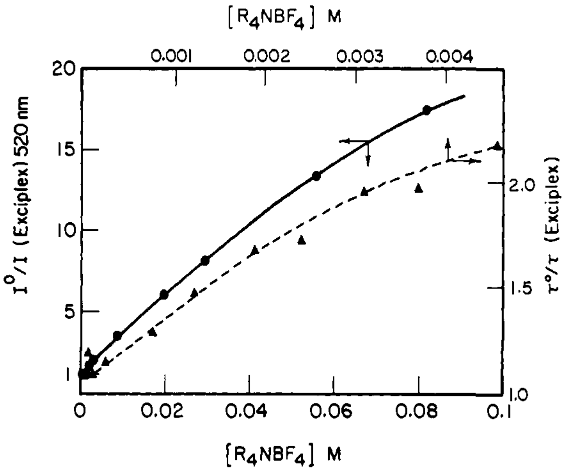

Figure 1. Stern–Volmer analysis of the quenching of the pyrene–dicyanobenzene exciplex in dimethoxyethane by tetra-*n*-butylammonium tetrafluoroborate. Circles are for intensity quenching and are plotted according to the scales shown on the left and bottom axes. Triangles are for lifetime quenching and are plotted according to scales shown on the right and top axes.

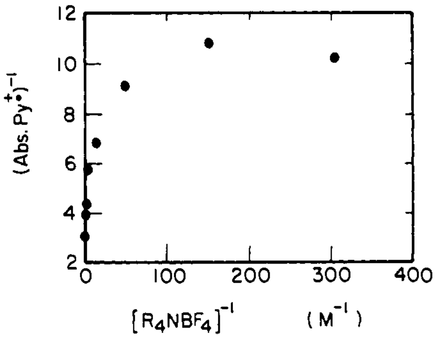

Figure 2. Double-reciprocal plot of the relative yield of pyrene radical cation against the concentration of tetra-*n*-butylammonium tetrafluoroborate in dimethoxyethane.

Excitation of a DME solution of pyrene containing 0.02 M DCNB with the output of a nitrogen laser (15 ns, 337 nm, 7 mJ, absorbed exclusively by the pyrene)[7] permits analysis of these reactions by transient absorption spectroscopy. In the absence of added salt this experiment reveals, not unexpectedly, that the radical ions are not formed in detectable amount from dissociation of the exciplex in this relatively nonpolar solvent. However, when the solution also contains 0.05 M R_4NBF_4 the absorbance of Py^{+}· is readily observed, and its yield (determined from the absorbance change at 445 nm)[8] is virtually the same as that obtained from the dissociation of this exciplex in acetonitrile solution.[5] The yield of Py^{+}· is dependent on the salt concentration in a curious, nonlinear way (Figure 2). The amount of Py^{+}· formed when the salt concentration is less than ca. 5×10^{-2} M is small even though

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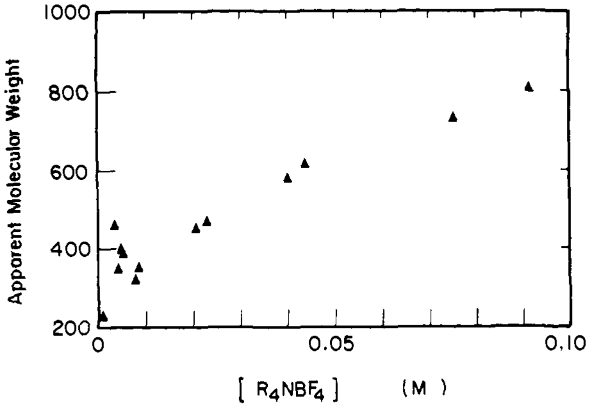
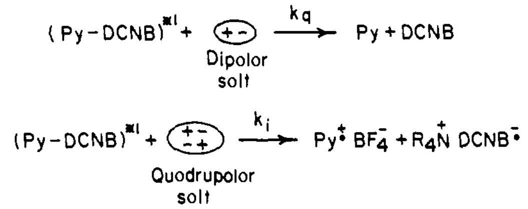


Figure 3. Plot of the apparent molecular weight of tetra-*n*-butylammonium tetrafluoroborate as a function of concentration in dimethoxyethane.

Scheme I



this concentration is sufficient to quench the exciplex emission significantly (Figure 1). However, the efficiency of $Py^{+\cdot}$ formation from quenched exciplexes increases at greater salt concentrations. This finding underscores and expands the exciplex emission quenching results; at low salt concentration the exciplex is quenched but gives $Py^{+\cdot}$ only inefficiently, while at higher salt concentration $Py^{+\cdot}$ is a major product. This nonlinear behavior may be traced to the self-association of R_4NBF_4.

The association of unionized salts to form quadrupoles and higher aggregates in nonpolar solvents is well-known.[9] Figure 3 shows a plot of the apparent molecular weight of R_4NBF_4 (determined by vapor pressure osmometry) as its concentration increases in DME solution. The molecular weight is seen to increase monotonically over the salt concentration range where nonlinear behavior is observed for the exciplex fluorescence quenching and for the yield of $Py^{+\cdot}$.

These observations are reasonably coupled and suggest that reaction of the exciplex with monomeric, dipolar salt results in quenching but not in radical ion formation and that the reaction of the exciplex with quadrupolar or aggregated salt gives radical ions in good yield, probably by an ion-pair exchange process. These concepts are illustrated for the case where the higher aggregates are represented as quadrupoles in Scheme I. This mechanism can account both qualitatively and quantitatively for the findings if $k_q > k_i$.

Finally, we confirmed that the radical ion pairs presumed to be formed from reaction of salt with the exciplex in nonpolar solvent give the same products as solvated ions formed in polar solvent, at least for one case. The electron-transfer-sensitized photooxidation of *trans*-stilbene by 9,10-dicyanoanthracene was used as a probe.[10] In acetonitrile this reaction gives benzaldehyde presumably by reaction of the stilbene radical cation. No oxidation is observed when this reaction is attempted in DME. However, addition of 0.035 M R_4NBF_4 to the DME solution leads to efficient formation of benzaldehyde. Similarly, when 1,4-dioxane is used as a solvent only a very low yield of $Py^{+\cdot}$ is detected by transient absorption spectroscopy even at high salt concentration. In this case benzaldehyde formation remains inefficient even when R_4NBF_4 is added to the reaction solution.

In sum, the quenching of exciplexes by R_4NBF_4 leads to ionic dissociation at high salt concentration where formation of quadrupoles and higher aggregates occurs. At low salt concentration, the exciplex is quenched but does not dissociate. This unusual behavior may be a useful probe for the intermediacy of ionic intermediates in photochemical processes.

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Registry No. Py, 129-00-0; DCNB, 623-26-7; Bu_4NBF_4, 429-42-5.

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Binuclear Complexes of a Covalently Linked Porphyrin–Bipyridine Ligand

Andrew D. Hamilton,* Holly-Dee Rubin, and
Andrew B. Bocarsly*

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

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In recent years there have been many attempts to devise synthetic systems capable of photochemical energy conversion analogous to photosynthesis.[1-3] Many of these have been based on the excited-state chemistry of metalloporphyrins[4] or tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$).[3-8] We present here the synthesis, electrochemical properties, and luminescence behavior of a novel binuclear complex containing a $Ru(bpy)_3^{2+}$ covalently linked across the face of a porphyrin at a distance of approximately 4 Å.[9] The fixed proximity of the two photochemically active centers results in a strong interaction which is reflected in both the luminescence and electrochemical properties of the complex.

The 5,5′-bis(3-hydroxypropyl)-2,2′-bipyridine (**1**) was prepared by the following route. Bromination of diol **2**[10] with HBr in acetic acid gave bis(bromomethyl)bipyridine **3**, which was alkylated by diethyl malonate to tetraester **4**. Decarboxylation of **4** to diester **5** in wet Me_2SO followed by $LiAlH_4$ reduction gave diol **1** in 21% overall yield from **2**. Reaction of diol **1** with the diacid chloride of mesoporphyrin II **6**[11] at high dilution in methylene chloride provided **7** (27%).[12] Reaction of **7** with $Ru(bpy)_2Cl_2$ in refluxing

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