

inset on different time scales). The sign of the photovoltage, porphyrin side positive, proves that the direction of electron transfer is from the surface-bound porphyrins to ground-state C_{60} molecules inside the lipid bilayer. The formation of porphyrin cation¹⁴ and C_{60}^- anion¹⁵ from the excited state is highly favored ($\Delta G \sim -0.7$ eV) over the formation of porphyrin anion^{14b} and C_{60}^+ cation^{15b} ($\Delta G \geq +0.6$ eV). The photovoltage¹⁶ rise (Figure 1b) consists of two components: a fast component with the same half rise time (18 ns, data now shown) and magnitude as that in Figure 1a, and is thus assigned to the inter-porphyrin electron transfer, and a slow component fit by a single exponential with $\tau = 6.0 \mu\text{s}$. The latter is assigned to the electron transfer from the interfacial porphyrin radical anion to C_{60} in the lipid core. The photovoltage decay (the middle trace of the inset in Figure 1) is fit by second-order kinetics; the observed half decay time decreases in photovoltages of higher amplitudes (obtained by increasing the laser power), confirming second-order kinetics.¹⁷ Similar photovoltage rise and decay kinetics (Figure 1c and the lower trace of the inset) were observed from a porphyrin- C_{70} system.¹⁸

The contribution of the porphyrin absorption to the photovoltage far exceeds that of C_{60} on the basis of excitation wavelength. When the excitation wavelength is changed to 355 nm with a comparable photon flux, the observed photovoltage is 0.9 of that at 532 nm. This is close to the ratio (1.1) of the absorption coefficients of the zinc deuteroporphyrin at 355 nm to that at 532 nm and is far different from the corresponding ratio (17)^{15a} of C_{60} . For C_{70} , the ratio of photovoltage at these wavelengths is 1.2 versus 3.2^{15a} for absorption.

When a ground-state aqueous electron donor, ascorbate, replaced the porphyrin in the C_{60} bilayer system, a small photovoltage (Figure 2a) was observed. The free energy difference, $\Delta G \sim -1.3$ eV, between ascorbate and $^3C_{60}^-$ highly favors the formation of C_{60}^- anion. The rise time of the photovoltage is essentially a single exponential and is consistent with slow electron transfer at the interface ($\tau = 74 \mu\text{s}$) producing a small voltage and a much faster ($\sim 1 \mu\text{s}$) escape of negative charges deeper into the bilayer, thus producing a large voltage. The order of magnitude slower rise time as compared to that with amphoteric porphyrin may reflect the increased average distance between the reactants. The photovoltage decay (Figure 2c) is fit with a single exponential decay with a surprisingly long τ of 400 ms.¹⁹ The first-order decay is probably due to a small amount of oxidized ascorbate since the rate varies with the freshness of the ascorbate solution. The ascorbate- C_{70} system (Figure 2b,d) produces larger photovoltages than those in the C_{60} system, but with the same rate constants. The larger photovoltages of the ascorbate- C_{70} system are consistent with an 8-fold-higher absorption coefficient of C_{70} than of C_{60} at 532 nm.^{15a} These results, in agreement with previous work,^{5,6} show that photoexcited triplet C_{60} and C_{70} can serve as electron acceptors. The slow photovoltage rises in Figure 2a,b must be caused by the triplet state, since the lifetime, τ , of $^1C_{60}$

is 1.2 ns and of $^1C_{70}$ is 0.67 ns,^{20a} while $\tau(^3C_{60}) = 410 \mu\text{s}$ and $\tau(^3C_{70}) = 51 \text{ms}$.^{20b}

In summary, we report unambiguous electrical evidence showing that both the ground-state and triplet C_{60} and C_{70} can serve as interfacial electron acceptors in a self-organized lipid bilayer system.

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Energy Dependence and Dynamics of Gas-Phase Ion-Molecule Reactions

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We report here the generation and unimolecular dissociation of reaction intermediates for two classes of gas-phase ion-molecule reactions: proton transfer and S_N2 displacement. The intermediates are generated in two distinct and widely separated internal energy regimes, with both high and low angular momentum. Thus we are able to initiate chemical reactions starting from energized reactive intermediates and examine directly the effects of large changes of energy and angular momentum on the product branching for both proton-transfer and S_N2 reactions. The chemical sequence which relates the two reactions is shown in Scheme I.

Proton-transfer reactions are a simple and general system in which temperature or energy dependences can be studied. The temperature dependence and dynamics of proton-transfer reactions in the gas phase have been the subject of numerous investigations¹⁻¹² and have been reviewed by Magnera and Kebarle.¹³ The proton-transfer reaction shown in Scheme I has recently been studied using high-pressure mass spectrometry by Mautner.⁵ The overall enthalpy (ΔH°) and entropy¹⁴ (ΔS°) changes for the reaction $(\text{NC})_2\text{CH}^- + \text{HCl} \rightarrow (\text{NC})_2\text{CH}_2 + \text{Cl}^-$, were found to be $-2.3 \text{ kcal mol}^{-1}$ and $-8 \text{ cal deg}^{-1} \text{ mol}^{-1}$, respectively, making the free energy change (ΔG°) at room temperature very close to zero.¹⁵

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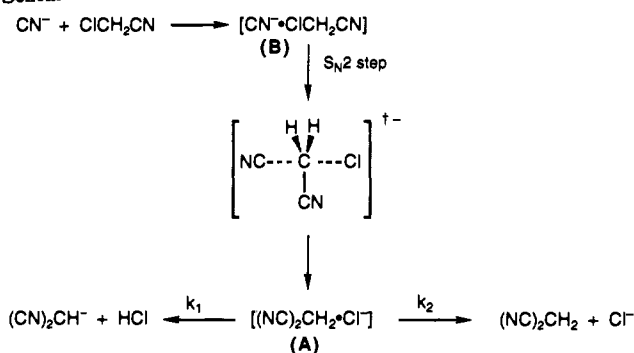
(16) The larger photovoltage of Figure 1b, as compared with that in Figure 1a, is most likely caused by the high efficiency of electron transfer and larger distance of charge separation into the low dielectric, i.e., the hydrocarbon core of the bilayer. The amphoteric charged porphyrins cannot penetrate more deeply into the bilayer, but electrons can be transported into the bilayer by C_{60}^- anion diffusion or by electron hopping among C_{60} molecules.

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(19) Since the system relaxation (RC) time is ~ 500 ms, the true decay time may be as long as 2 s, indicating that the C_{60}^- anion is very stable under our experimental conditions. The photovoltage is not saturated by the pulsed light and can be increased several fold at higher incident light intensity.

Scheme I



We have prepared the proton-transfer intermediate complex A via three different routes and observed the effects of internal energy on the branching between reactant (k_1) and product (k_2) channels. Infrared multiple-photon (IRMP) activation¹⁶ of the isolated and thermalized complex A accesses a low-energy, low angular momentum regime¹⁷ (0–3 kcal mol⁻¹ above threshold). Chemical activation (CA) via the S_N2 displacement reaction¹⁸ generates the complex in a much higher energy regime (~30–35 kcal mol⁻¹ above threshold) resulting from the exothermicity of the S_N2 reaction. This was accomplished using the bimolecular S_N2 reaction which forms A with high angular momentum and by IRMP activation¹⁹ of complex B which forms A with low angular momentum.

Experiments were performed using an IonSpec OMEGA ion cyclotron resonance (FT-ICR) spectrometer equipped with impulse excitation.^{2,20} The stable intermediates A and B were synthesized²¹ using McMahon's method.^{6,22} Photochemical activation of the intermediates to form product ions was accomplished by IRMP activation¹⁶ at many different fluences²³ (and thus intensities). In the bimolecular experiment, CN⁻ was allowed to react with ClCH₂CN to form products directly via CA without isolation of either intermediate. Cl⁻ and (CN)₂CH⁻ were the only product ions observed. To avoid problems due to differential ion loss, ion intensities were measured at the shortest time delays possible.

Table I shows the results for the proton-transfer dissociation branching ratio (BR) at low energy obtained via IRMP activation of the thermalized complex A. The BR is close to unity, consistent with the near-zero free energy change for the reaction at room temperature.⁵ At higher fluences (higher internal energy) the BR increases, producing more (CN)₂CH⁻ and less Cl⁻. Table I also shows the observed BR for dissociation of A via CA at much higher energies above threshold. The BR obtained from the bimolecular and IRMP-induced unimolecular CA experiments deviates significantly from unity and is approximately [(CN)₂CH⁻]:[Cl⁻] = 15:1 and 10:1, respectively.

The results from both the IRMP and CA experiments demonstrate that, with increasing internal energy, decomposition of A favors channel 1 (i.e., formation of (CN)₂CH⁻), which is the endothermic but entropically favored direction. The energy dependence of the BR can be rationalized using RRKM theory.²⁴

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(18) The rate for the bimolecular S_N2 reaction is 2.2 × 10⁻¹⁰ cm³ s⁻¹ molecules⁻¹. This corresponds to an efficiency of about 4.5%.

(19) IRMP activation of the S_N2 intermediate B allows B to undergo unimolecular isomerization via crossing of the S_N2 reaction barrier. Thus, it can be considered chemically activated via a photochemically initiated reaction.

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Table I. Branching Ratio for the Proton-Transfer Reaction,^a CH₂(CN)₂ + Cl⁻ → CH(CN)₂⁻ + HCl, as a Function of Internal Energy

method	energy above threshold ^b	k ₁ /k ₂	
		experiment	statistical theory prediction ^c
chemical activation	30–35	15 ± 3	25–30
IRMP activation of S _N 2 complex	~30	~10 ^d	20
IRMP activation of PT complex ^e	0–3		0–2.1
	(2.8)	0.6	
	(3.7)	1.0	
	(5.0)	1.4	
	(5.5)	2.6	

^aΔG^o₂₉₈ ≈ 0 and ΔH^o₂₉₈ = +2.3 kcal mol⁻¹ (ref 5). ^bkcal mol⁻¹. ^cStatistical RRKM theory was used to determine the branching ratios (see text for details). ^dOnly obtained at low fluence due to poor mass balance at higher fluences. ^eLaser fluence in units of J cm⁻² given in parentheses.

Even though the dissociation threshold for channel 1 lies at a slightly higher energy relative to channel 2 by ~2.3 kcal mol⁻¹, the sum of available quantum states increases more rapidly, and within a few kcal mol⁻¹ the sums of states, and hence the unimolecular rates, become equal. By the time the system reaches 30 kcal mol⁻¹ of excess energy, dissociation strongly favors channel 1. The RRKM interpretation of the BR energy dependence provides a microscopic explanation for the observed results in terms of the relative availability of quantum states in the reactant and product channels for the proton-transfer reaction. This is directly related to the partition functions and manifests itself in the thermochemistry as a strong temperature dependence for both the enthalpy (ΔH^o) and entropy (ΔS^o) changes which ultimately contribute to the strong temperature dependence of the equilibrium constant found by Mautner.²⁵ At such high energies, however, the absolute rates predicted from RRKM theory approach 10¹⁴ s⁻¹, which raises important questions about incomplete intramolecular vibrational energy redistribution. Thus, while the RRKM results are consistent with experiment, cautious interpretation is indicated at the highest energies.

The chemical activation experiments also provide important information about the dynamics of exothermic S_N2 reactions,^{26–31} a topic of considerable current interest.^{32–40} The proton-transfer

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and S_N2 reactions share a common intermediate complex, $[(C-N)_2CH_2-Cl]^-$.⁴¹ The observation of proton transfer indicates that the lifetime of the complex is sufficiently long to allow for structural rearrangement and rules out a mechanism in which the leaving group (Cl^-) is ejected immediately following the substitution event. The lifetimes of S_N2 reaction intermediates may provide insight about the details of ion-molecule complex dissociation dynamics and energy transfer within the ion-molecule complex. Recent theoretical results of Vande Linde and Hase³⁶ and the experimental results of Graul and Bowers,³³ Viggiano and co-workers,⁴² and Buckner and co-workers³⁹ on S_N2 reactions have suggested that energy transfer between certain modes within the ion-molecule complex may be inefficient. A detailed interpretation of our results, and their relationship to inefficient energy transfer, will be the subject of a forthcoming publication.

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Registry No. $(CN)_2CH^-$, 41470-37-5; CN^- , 57-12-5; $ClCH_2CN$, 107-14-2.

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Ring-Opening Metathesis Polymerization of Substituted Bicyclo[2.2.2]octadienes: A New Precursor Route to Poly(1,4-phenylenevinylene)

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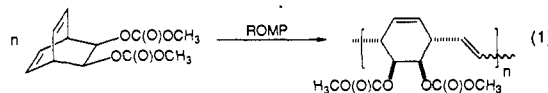
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Poly(1,4-phenylenevinylene) (PPV),¹ a perfectly alternating copolymer of *p*-phenylene and *trans*-vinylene units, possesses attractive material properties. Thin films of PPV display high electrical conductivity when doped ($\sigma = 5000$ S/cm),² a large, third-order nonlinear optical response ($\chi^{(3)} = 1.5 \times 10^{-10}$ esu),³ and photo- and electroluminescence in the visible region.⁴ However, the extended planar topology of the PPV backbone, which renders it infusible and insoluble in nonreactive media, limits the capacity for post-synthesis fabrication of the material. A convenient method to circumvent this problem consists of a two-step synthesis via a processable intermediate polymer.⁵ This precursor polymer can be fabricated into the desired form and subsequently converted to the target polymer by a clean, intramolecular chemical reaction. Wessling and Zimmerman have reported the synthesis of a processable, water-soluble poly(1,4-xylylenesulfonium salt) that undergoes a thermally-induced elimination to PPV under mild conditions.⁶ The precursor

polymer formation occurs via the generation and in situ polymerization of *p*-xylylenesulfonium chloride, a very reactive intermediate.⁷ Therefore, certain aspects of the polymer structure, for example, the degree of polymerization, polydispersity, and sequence homology of copolymers, are difficult to control in this synthetic route. We report an alternative precursor synthesis of poly(1,4-phenylenevinylene) based on the *living* ring-opening metathesis polymerization (ROMP)⁸ of bis(carboxylic ester) derivatives of bicyclo[2.2.2]octa-5,8-diene-*cis*-2,3-diol **1** and subsequent pyrolytic acid elimination from the polymer.⁹

In contrast to bicyclo[2.2.1]heptenes, few examples of the ring-opening metathesis polymerization of bicyclo[2.2.2]octenes or -octadienes have been reported¹⁰ although the calculated strain energies of the two ring systems (16.0 and 20.4 kcal/mol, respectively)¹¹ are significantly larger than cycloalkenes that undergo successful polymerization. The lack of general synthetic routes to simple bicyclo[2.2.2]octenes and -octadienes, compared to the readily available norbornenes, has hindered their utilization as ROMP substrates. The synthesis of the bicyclo[2.2.2]octadiene monomers of type **1** is depicted in Scheme I. Diels-Alder reaction between the acetonide adduct of 3,5-cyclohexadiene-*cis*-1,2-diol and ethynyl *p*-tolyl sulfone generates the anti cycloadduct as the sole product.¹² Reductive desulfonation¹³ followed by acid-catalyzed hydrolysis of the acetonide yields the bicyclic diol, which may be converted into bis(carboxylate) derivatives **1a** and **1b**.¹⁴

Ring-opening polymerization of **1a** and **1b** was attempted with the olefin metathesis catalyst $[Mo(=NAr)(=C(H)CMe_2Ph)(OCMe_2(CF_3))_2]$ **2** (Ar = 2,6-diisopropylphenyl),¹⁵ which initiates the polymerization of both monomers at ambient temperature (eq 1). However, only **1b** undergoes polymerization under these



conditions in high yield.¹⁶ A single downfield doublet (12.69 ppm), characteristic of a propagating alkylidene $C_{\alpha}H$, is observed in the ¹H NMR spectra of polymerizations in THF. This resonance increases in intensity at the expense of the initiating alkylidene as the reaction proceeds to completion. Preliminary investigations indicate that the rate of polymerization in CH_2Cl_2 is at least an order of magnitude faster than in THF and that the rate of initiation is marginally slower than the rate of propagation in both cases. Typical preparative-scale polymerizations are performed in CH_2Cl_2 , terminated by capping with benzaldehyde, and isolated by precipitation.¹⁷ Relatively narrow molecular

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