tungsten counterelectrodes were used.

Results and Discussion

Figure 2 shows the emf data obtained in four separate runs with various electrodes and solvent combinations. Within experimental error, the cell potential varied linearly with temperature. When all 85 data points are included, the least-squares fit (with marginal standard deviation estimates of error given) yields $\Delta H°_1 = -33.5 \pm 0.7$ kJ mol^{-1} and $\Delta S°_1 = -88 \pm 3$ J mol^{-1} K^{-1} with an overall standard deviation of 3.0 mV. However, a better measure of the reproducibility of the data and accuracy of the thermodynamic quantities is obtained by fitting the data from each experiment separately and then evaluating weighted-average values of $\Delta H°_1$ and $\Delta S°_1$. This procedure gives $\Delta H°_1 = -34 \pm 2$ kJ mol^{-1} and $\Delta S°_1 = -90 \pm 8$ J mol^{-1} K^{-1}, which leads to $\Delta G°_{298} = -7.1 \pm 0.6$ kJ mol^{-1}.

These results show that crystalline $Na^+C222{\cdot}Na^-$ is thermodynamically stable but only marginally so. They predict that the compound should become unstable with respect to free C222(s) and pure solid sodium between 90 and 120 °C (95% confidence limits). It is interesting that $Na^+C222{\cdot}Na^-$ actually decomposes at 83 °C into liquid C222 and sodium.[2] Because the decomposition temperature is above the melting point of pure C222 (71 °C) and because metallic sodium could be somewhat soluble in the molten cryptand, we would expect the observed decomposition temperature to be below that calculated. Of course, the ever present *irreversible* decomposition which leads to decomposition of the cryptand is thermodynamically favored at all temperatures. The modified Born-Haber cycle described in the Introduction clearly gives incorrect results because it predicts $\Delta G° > 0$. The predicted value of $\Delta H°_1$ (−35 kJ mol^{-1}) is close to that observed (−34 kJ mol^{-1}) so the major error is in the predicted value of $\Delta S°_1$ which is 100 J mol^{-1} K^{-1} more negative than the observed value. There are two major sources of error in the calculated entropy change: (1) The entropy change for the reaction $Na^+C222(g) + Na^-(g) \rightarrow Na^+C222{\cdot}Na^-(s)$ was obtained by comparison with the values for simple salts.[7] Changes in the configurational entropy of the cryptand upon packing might be important. (2) The entropy of solvation of $Na^+C222(g)$ in water was calculated by using the simple Born equation. Entropy effects caused by structure making or breaking are probably important. More realistic calculations are in progress[15] which attempt to compare $Na^+C222{\cdot}Na^-(s)$ with $Na^+C222{\cdot}I^-(s)$ in order to remove some of the approximations. The assumptions made in calculating the thermodynamics of reaction 1 are *much* less severe when comparing similar compounds since the errors tend to cancel out. Therefore, the present experimental data for $Na^+C222{\cdot}Na^-$ should permit reliable predictions to be made about the thermodynamics of formation of other alkalide salts.

Acknowledgment. We gratefully acknowledge support from NSF Grant No. DMR 79-21979 (J. L. Dye) and the Deutsche Forschungs Gemeinschaft (U. Schindewolf). We are grateful to R. Winter for independent verification of the experimental procedures used in this work and to BBC Heidelberg for providing the β-alumina.

A Radical Ion/Triplet Mechanism for Sensitized Valence Photoisomerization of a Norbornadiene

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Quenching of the fluorescence of a series of electron donor aromatic hydrocarbons in acetonitrile by dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate results in isomerization of the norbornadiene with varying efficiency. Quantum yield, CIDNP, and flash photolysis results are consistent with a rearrangement mechanism involving electron transfer from the sensitizer, intersystem crossing of resultant radical-ion pairs, and ion recombination to give norbornadiene triplets followed by rearrangement to the valence isomer. Where energetic factors are favorable, the isomerization quantum yield is as high as 0.39 and the efficiency of formation of norbornadiene triplets via ion recombination as high as 65%.

Introduction

The conversion of norbornadiene and its derivatives to their valence isomers has served admirably as a prototype for the photochemical formation of highly strained organic compounds.[1] Interest has been renewed in systems of this sort in view of the possibilities for reversible photochemical energy storage.[2] The means for driving the norbornadiene reaction have included direct photolysis,[3] triplet sensitization,[4] sensitization by complexation with a metal,[5] and radiation chemical techniques.[6]

A novel mechanism of sensitization, which is of current interest, involves electron transfer to or from a singlet sensitizer, intersystem crossing and recombination of resultant radical-ion pairs, and rearrangement of the substrate thus generated in the triplet state.[7] One version

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0022-3654/82/2086-2286$01.25/0

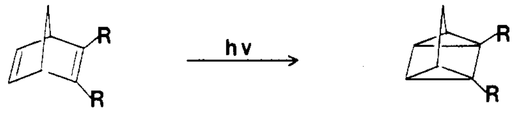
TABLE I: Energetic Parameters, Quenching Constants, and Quantum Yield Data for Donor Sensitizers and 1

	$E_{ox} - E_{red}$[a]	E_T,[b] kcal/mol	$k_q\tau$,[c] M^{-1}	$10^{10}k_q$, M^{-1} s^{-1}	ϕ_{12}([1])[d]	% quench
triphenylene	76	66	211	1.9	0.39 (0.02)	94
phenanthrene	74	62	50.4	0.21	0.16 (0.10)	93
pyrene	64	48	117[e]	1.6[e]	<0.005 (0.08)[e]	98
anthracene	64	43	36.7	0.96	<0.005 (0.25)	92

[a] Ion pair energies (excluding coulombic and entropy terms, ref 10) estimated from half-wave oxidation potentials of sensitizers (ref 12) and the reduction potential for 1 ($E_{1/2} = -1.67$ V vs. SCE, acetonitrile, TBAP) measured by cyclic voltammetry. [b] Sensitizer triplet energies (ref 9). [c] Stern-Volmer constants for quenching of sensitizer fluorescence by 1. [d] Quantum yields of 1 → 2 (concentration of 1 and extent of sensitizer quenching indicated); sensitizer concentration generally 0.01 M except phenanthrene (0.32 M); irradiation of argon-purged samples with a monochromator apparatus at 334 nm (triphenylene and phenanthrene) and using a merry-go-round chamber reactor with filter solution (340-370 nm) (pyrene and anthracene) as described previously (ref 23). [e] Pyrene excimer quenching; [pyrene] = 0.01 M.

of this mechanism[7b] employs norbornadiene as an electron donor along with an acceptor sensitizer (1-cyanonaphthalene). Although valence isomerization proceeds with low efficiency in this case ($\phi = 0.01$), the radical ion/triplet mechanism is clearly indicated by nuclear polarization (CIDNP) effects which accompany rearrangement.[7b] A similar mechanism involving radical ions and triplets appears to be important for photoreactions involving stilbene and styrene derivatives.[7a,8]

In this paper we report the sensitized isomerization of a norbornadiene derivative (1 → 2) operating with relatively high efficiency in an electron acceptor mode. Fluorescence quenching, flash photolysis, and CIDNP results support an isomerization mechanism involving electron transfer. The data provide an example of singlet sensitization (as opposed to the more conventional triplet sensitization) of a highly endoergic valence isomerization.[2c] An advantage in driving force is gained with this mechanism, since the depletion of excitation energy which normally accompanies intersystem crossing of a sensitizer is avoided.



R = CO_2CH_3

1 2

Results

Fluorescence Quenching. A series of aromatic hydrocarbons which were candidates for electron transfer to 1 were selected for a quenching study. The fluorescence of the donor sensitizers was indeed diminished by 1 in aerated acetonitrile solutions; the Stern-Volmer constants, $k_q\tau$, are shown in Table I. A correction factor obtained from fluorescence intensities for degassed and undegassed samples and literature values[9] for fluorescence lifetimes for the sensitizers in the absence of quencher were employed to compute rate constants for bimolecular quenching, k_q. The values obtained range upward of 10^9 M^{-1} s^{-1}, some approaching the diffusion-controlled limit, as expected for efficient (exothermic) electron transfer.[10,11] For the case in which pyrene acted as donor, quenching of either the pyrene singlet monomer or the pyrene excimer[13] was possible depending on the regime of sensitizer concentration.

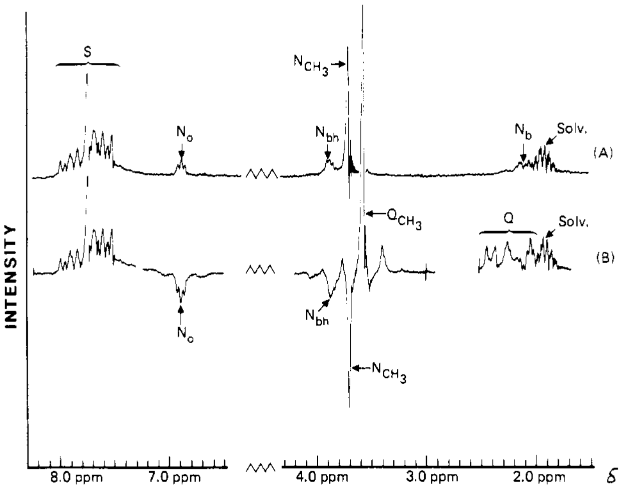


Figure 1. Proton NMR spectra (60 MHz) of phenanthrene (0.001 M) and **1** (0.02 M) in acetonitrile-d_3, (A) before irradiation, and (B) during irradiation at 290–360 nm. The resonances of **1** and **2** are designated N and Q, respectively. Lower case indices refer to olefinic (o), bridgehead (bh), bridge (b), and methyl (CH_3) positions.

Scheme I

$^1S + 1 \rightarrow {}^1[S^+ \text{-} 1^-]$	singlet quenching
$^1[S^+ \text{-} 1^-] \rightarrow S + 1$	singlet ion-pair recombination
$^1[S^+ \text{-} 1] \rightarrow {}^3[S^+ \text{-} 1^-]$	ion-pair intersystem crossing
$^3[S^+ \text{-} 1^-] \rightarrow S + {}^31$	triplet ion-pair recombination
$^3[S^+ \text{-} 1^-] \rightarrow {}^3S + 1$	
$^31(^3S) \rightarrow 1(S)$	triplet decay
$^31 \rightarrow 2$	triplet isomerization

CIDNP Experiments. Irradiation with filtered light (290–360 nm) of 0.02–0.10 M solutions of 1 in CD_3CN in the presence of the donor sensitizers in the probe of an NMR spectrometer resulted in CIDNP which could be associated with 1 and the isomeric product 2. Emission signals were assigned to the protons of the methyl ester group and to bridgehead and olefinic protons of 1 whereas enhanced absorption was associated with the corresponding protons of 2 (Figure 1). No polarization was observed for the bridge (methylene) protons of either 1 or 2 or for protons of the sensitizers. CIDNP was also not observed

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(11) Singlet energies for the sensitizers are uniformly greater than values estimated for the ion pairs (Table I) and range from 83 (triphenylene) to 75 (anthracene) kcal/mol.[9]

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on direct irradiation of 1 alone or on sensitization by conventional triplet energy transfer agents such as benzophenone (isomerization is observed under these conditions).[2b,c] Notably CIDNP signals for the singlet sensitizers, phenanthrene and triphenylene, were 300–500 times stronger than for anthracene and pyrene.[14]

The CIDNP results are consistent with a mechanism for quenching and isomerization involving electron transfer and hyperfine-induced intersystem crossing between nascent singlet and triplet radical-ion pairs.[7a,15] Spin polarization results from singlet pair recombination which favors 1 and triplet recombination which favors 2 (Scheme I). The directions of spin polarization in 1 and 2 are further in accord with the modified Kaptein rules for net effects,[16] incorporating the following features: (1) formation of ion pairs in the singlet state, (2) a larger *g* value for 1 than for the hydrocarbon radical cations, (3) positive hyperfine coupling constants for the relevant protons of 1^-,[17] and (4) a triplet exit channel which leads to 2.[14]

Flash Photolysis. So that the evolution of potential radical-ion or triplet intermediates could be observed, laser flash photolysis experiments were carried out with a ruby laser system previously described[18] (excitation at the doubled frequency, corresponding to 347 nm) or a Lumonics excimer laser (XeF, emitting at 350 nm; maximum pulse energy, 60 mJ; pulse width, 13 ns) equipped with a Tektronix 466 storage oscilloscope and a xenon lamp for monitoring at 300–700 nm. Irradiation of phenanthrene alone in acetonitrile resulted in transient absorption (λ_{max} 485 nm, τ = ca. 10 μs) that could be assigned to the phenanthrene triplet.[19] On similar excitation of phenanthrene in the presence of 1 (0.21 M, a concentration sufficient to quench 91% of phenanthrene singlets) absorption at 485 nm was insignificant but a new, relatively weak, absorption was observed at 375, 400, and 430 nm (τ also, ca. 10 μs), which was assigned to the phenanthrene radical cation.[20]

A sensitizer which did not produce a strong CIDNP signal was examined as well. Flash photolysis of pyrene (347 nm) in acetonitrile resulted in relatively intense transient absorption at 412 (τ = 21 μs), 450 (τ = 27 μs), and 492 nm. These bands were presumed to arise from, respectively, pyrene triplet and the pyrene radical cation and anion generated through triplet–triplet annihilation.[21] When extinction coefficients reported for the triplet (ϵ 29 000) and the cation (ϵ 47 000)[22] were used, a ratio of transients (absorbances decaying at 10–70 μs, extrapolated to zero time) was calculated (1.0:0.33). In the presence of 0.2 M 1, a concentration sufficient to quench >90% of pyrene singlets (predominantly the monomer at 2×10^{-4} M pyrene and the excimer at 10^{-3} M pyrene), the 412- (τ = 11 μs) and 450-nm (τ = 21 μs) transients were observed (ratio 1.0:0.63) but the absorption due to the pyrene radical anion was absent. The important comparison is that on sensitizer singlet quenching the triplet of pyrene is evolved whereas under similar conditions the phenanthrene triplet is not produced in the microsecond time regime.

Quantum Yields. Quantum efficiencies were measured for formation of 2 under conditions of sensitizer singlet quenching in CH_3CN (Table I). A clear demarcation again was found between those sensitizers which were effective (phenanthrene and triphenylene) and those which gave 2 only in trace amounts (pyrene and anthracene). For sensitization by triphenylene, no more than 10% of the observed quantum yield could have been due to intersystem crossing of unquenched sensitizer singlets followed by triplet-induced rearrangement.[2b,24] If one assumes that the efficiency of isomerization is primarily associated with triplet recombination events, and since the yield of 2 from triplet 1 is approximately 0.6,[2b] then the total yield of triplet recombination of ion pairs can be computed (~65% for triphenylene and, similarly, ~27% for phenanthrene).

CIDNP and other experiments did not permit a quantitative distinction between triplet recombination of paired radical ions and back electron transfer of radical ions in bulk solution which produces triplets on a spin statistical basis.[25] Some insight into the relative importance of these steps was gained in a three-component experiment in which an electron transfer relay, tetramethyl-*p*-phenylenediamine (TMPD), was employed. At 0.015 M triphenylene, 0.02 M 1, and 0.00025 M TMPD the quantum efficiency of isomerization was 0.37. Under these conditions TMPD was not a competitive quencher of triphenylene (TRI) singlets (~1%). However, efficient interception of TRI cations which reach bulk solution was expected on the basis of oxidation potentials for the respective donors ($E_{1/2}$ = 1.63 and 0.16 V vs. SCE for TRI and TMPD, respectively)[12,26] and previously reported results for electron exchange.[27]

$$TRI^+ + TMPD \rightarrow TRI + TMPD^+$$

The important feature of this experiment is that the ion-pair energy for TMPD–1 (42 kcal/mol) is insufficient for generation of triplet 1 (E_T = 53 kcal/mol[2c]). The quantum yields for photolysis of triphenylene and 1 with and without TMPD are within experimental error. Therefore, if the TMPD relay is efficient in trapping TRI radical cations which reach bulk solution, then the majority of triplet recombination events must occur within the solvent cage.[29]

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J. Phys. Chem. **1982**, *86*, 2289-2291

Conclusions

The mechanism of electron transfer sensitization for the isomerization of norbornadiene 1 has been investigated. Flash photolysis results show that radical ions are products of quenching of electron donor sensitizers, and CIDNP experiments indicate that intersystem crossing of radical ion pairs is important. A mechanism consistent with the observations is shown in Scheme I (S = sensitizer). The yield of isomerization induced by singlet quenching and electron transfer is sensitive to the triplet energy of the sensitizer. Electron donors having triplet energies (Table I) above that of 1 ($E_T \sim 53$ kcal/mol, triphenylene and phenanthrene) are relatively efficient sensitizers, whereas donors with low triplet energies (pyrene and anthracene) are ineffective. In the latter case (pyrene) it was shown that evolution of the triplet of the sensitizer is important, and CIDNP results confirm that the role of triplet recombination of radical-ion pairs yielding triplet 1 is greatly diminished. In the case of triphenylene sensitization, the yield of triplet recombination is remarkably high ($\sim$65%).[31] An agent for trapping sensitizer radical cations (secondary donor, TMPD) was used to show that the formation of triplets is primarily due to recombination of paired radical ions rather than reencounter in bulk solution.

Acknowledgment. The support of this research by the Department of Energy (Office of Basic Energy Sciences) is gratefully acknowledged. The authors also thank Professors V. Vaida and N. N. Lichten, and J. Welch for assistance with excimer laser flash photolysis measurements, Drs. J. Bargon and K.-M. Dangel for assistance and helpful discussions involving nuclear polarization experiments, and Professor M. S. Wrighton for providing cyclic voltammetry measurements.

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Approximate Quantum Differential Cross Section for the F + HD $\rightarrow$ HF + D and DF + H Reactions

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(Received: March 18, 1982)

In a previous paper we proposed a novel way to obtain approximate quantum mechanical differential cross sections. Here, we use this approximate method to study the reactions F + HD(v=0) $\rightarrow$ FH(v'=2) + D and F + DH(v=0) $\rightarrow$ DF(v'=3) + H. Backward and forward scattering are found for the first reaction and only backward scattering for the second one. These results agree qualitatively with experiment.

In a previous paper[1] we used a novel quantum theory of reactive scattering[2,3] to calculate differential cross sections for the F + H_2(v=0) $\rightarrow$ HF(v'=2) and HF(v'=3) + H reactions. In this theory a reduced number of degrees of freedom are treated quantum mechanically and the remaining ones are described by transition-state theory.[2] For reactions with a collinear transition state, e.g., F + H_2, H + H_2, etc., the quantum mechanical input to the theory is the collinear exact quantum reaction probabilities. We apply this theory here to the F + HD $\rightarrow$ HF + D and DF + H reactions.

There is considerable interest in the F + H_2, F + D_2, and F + HD systems because of the recent experimental measurements of the differential cross sections to form the products in specific final vibrational states.[4,5] In addition, j_z-conserving quantum calculations of the partial wave reaction probabilities for the F + H_2 $\rightarrow$ HF(v'=2) + H reaction revealed a resonance at particular values of the impact parameter.[6] These calculations suggested that the sidewise peaking in the measured differential cross section for this reaction was due to this resonance. Our previous calculations of both the partial wave reaction probabilities and the differential cross section are in complete accord with this conclusion and further suggested that the differential cross section should exhibit an oscillation in the vicinity of the sidewise peak. This feature has been observed experimentally.[5] Sidewise peaking in the HF(v'=2) differential cross section has also been predicted by recent infinite order sudden calculations.[7]

Here, we continue using this approximate method to study the differential cross sections of the F + HD reaction. As in our previous study,[1] we used the collinear exact quantum scattering matrices of Kaye and Kuppermann,[8] who employed the Muckerman V LEPS potential energy surface in their new quantum calculations.

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