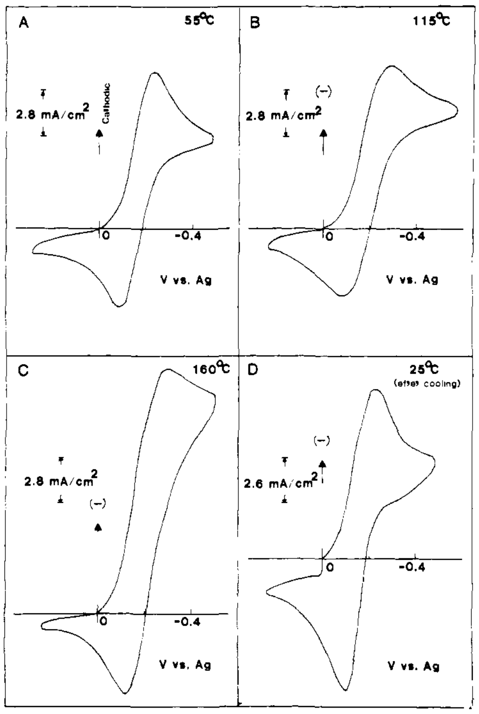

**Figure 2.** Cyclic voltammograms for reduction of *m*-chloronitrobenzene (MCNB) in $NH_3$. (A) 55 °C, 10 atm, 8 mM MCNB, 0.2 M KI ($\Delta E_p$ = 130 mV); (B) 115 °C, 82 atm, 6 mM MCNB, 0.2 M KI ($\Delta E_p$ = 180 mV); (C) 160 °C, 265 atm, 5 mM MCNB, 0.1 M KI ($\Delta E_p$ = 160 mV); (D) 25 °C (after cooling from 160 °C), 10 atm, 8 mM MCNB, 0.2 M KI ($\Delta E_p$ = 120 mV). Scan rate, 500 mV $s^{-1}$.

(between curves A and D) is probably caused by a change in potential of the silver wire (QRE).

To study changes in reversibility and diffusion coefficient ($D$) with $T$ and $P$, the reduction of *m*-chloronitrobenzene[6] (MCNB) was investigated; typical voltammograms are shown in Figure 2. The behavior remains essentially Nernstian as $T$ is raised; for example, at 160 °C a $\Delta E_p$ value[7] of 90 mV was found with a fresh solution (compared to the Nernstian value of 85 mV). However, replicate experiments at 160 °C sometimes showed $\Delta E_p$ values up to 160 mV, perhaps because of some, yet undefined, electrode surface effect. As the critical temperature is approached, the voltammograms show convective features such as an unusually shallow drop off of current past the cathodic peak current. The onset of natural convection is promoted by the low viscosity of the solution (0.024 cp at 160 °C). These convective effects probably also account for the $i_{pa}/i_{pc}$ ratio being 0.7 (rather than 1). However, normal and nearly reversible behavior is restored upon decrease in $T$ and condensation of the solvent. Chronocoulometric experiments[8] involving potential steps and acquisition of data at short times (50 to 250 ms) to avoid convective problems were used to determine $D$ as a function of $T$ and $P$. The value found at 160 °C and 272 atm (density, 0.40 g $cm^{-3}$) was $3 \times 10^{-4}$ $cm^2$ $s^{-1}$. This value can be compared with that calculated from the $D$ value at −40 °C ($2.8 \times 10^{-5}$ $cm^2$ $s^{-1}$) and the change in viscosity via the Stokes–Einstein equation ($6 \times 10^{-4}$ $cm^2$ $s^{-1}$) and appears to be consistent with values of aromatic hydrocarbons in $CO_2$ at similar viscosities.[9] The results demonstrate the stability of the MCNB radical anion and the enhanced mass transport under supercritical conditions. Further investigations of electrochemistry of $NH_3$, water, and other fluids at near-critical and supercritical conditions are in progress.[10]

**Registry No.** MCNB, 121-73-3; MCNB radical anion, 34467-54-4; $NH_3$, 7664-41-7; KI, 7681-11-0; W, 7440-33-7.

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(7) $\Delta E_p$ is the difference between the anodic and cathodic peak potentials and equals about $2.3RT/F$ for a Nernstian process. Cathodic and anodic peak currents are $i_{pc}$ and $i_{pa}$, respectively.

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# Exciplex Isomerization in Photosensitized Cycloreversion Reactions of Cage Compounds[1]

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Most photochemical reactions occur diabatically because the electronically excited reactant tends to be converted to the ground state of product via potential energy surface crossing or touching. Some photoreactions that have a small activation energy on the excited surface, usually accompanied by a minor structural change during transformation of reactant to product, e.g., proton transfer and complex formation, are known to occassionally occur adiabatically.[2] Recently, an adiabatic exciplex isomerization of hexamethyl(Dewar benzene) to hexamethylbenzene has been demonstrated by Taylor,[3] and a method to identify the observed exciplex as that from the isomerized product was established by Jones.[4] The efficiency of this adiabatic exciplex isomerization varied with the structure of the photosensitizer (an electron acceptor) with a quantum yield which reached ca. 0.50.[4]

In connection with our recent studies on the photosensitized isomerization of cage compounds **1** to dienes **2** in polar solvents which occurs by a highly efficient radical ion chain mechanism,[5] we turned our attention to the rearrangement that can also be observed in nonpolar solvents. Herein we report an adiabatic exciplex isomerization of **1** to **2** having a quantum efficiency near unity.

Irradiation (λ > 350 nm) of a benzene solution of **1a** containing 3,9-dicyanophenanthrene (DCP)[6] or 9,10-dicyanoanthracene (DCA) resulted in isomerization to **2a**. The quantum yield extrapolated to an infinite concentration of **1a** was near 1.0 in both sensitizations. Interestingly enough, **1a** and **2a** both clearly quenched the fluorescence of DCP in benzene giving a weak,

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(6) In the case of DCP-sensitized reaction, although prolonged irradiation contaminated the reaction, any clear product other than diene **2a**, recovered cage compound **1a**, and DCP could not be isolated. Recovery of DCP was more than 95% at 55% conversion of **1a** to **2a** ([**1a**] = $3.5 \times 10^{-2}$ M, [DCP] = $2.0 \times 10^{-3}$ M).

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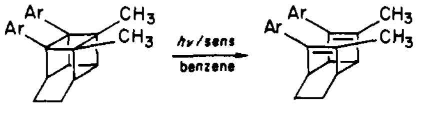
**Table I.** Fluorescence Quenching Data ($k_q\tau$, $k_q$) and Exciplex Emission Maxima ($\lambda_{max}$) of Cage Compounds and Dienes in Benzene

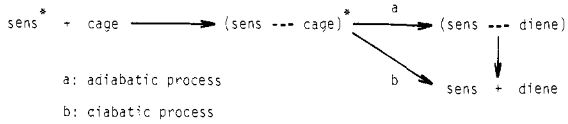


**1** (cage compound) **2** (diene)

| | | $k_q\tau$, $M^{-1}$ | | $10^{-9}k_q$,[a] $M^{-1}$ $s^{-1}$ | | $\lambda_{max}$, nm | |
|---|---|---|---|---|---|---|---|
| compd | Ar | DCP | DCA | DCP | DCA | DCP | DCA |
| **1a** | $C_6H_5$ | 73 | 94 | 7.8 | 7.6 | 450 | 542 |
| **2a** | $C_6H_5$ | 107 | 120 | 11.4 | 9.7 | 450 | 542 |
| **1b** | *p*-$MeOC_6H_4$ | 128 | 158 | 13.6 | 12.7 | 510 | no emission |
| **2b** | *p*-$MeOC_6H_4$ | 190 | 205 | 20.2 | 16.5 | 510 | no emission |
| **1c** | *p*-$MeC_6H_4$ | 92 | 123 | 9.8 | 9.9 | 468 | 568 |
| **2c** | *p*-$MeC_6H_4$ | 132 | 167 | 14.0 | 13.5 | 468 | 568 |
| **1d** | *p*-$ClC_6H_4$ | 44 | 71 | 4.7 | 5.7 | 445 | 530 |
| **2d** | *p*-$ClC_6H_4$ | 81 | 101 | 8.6 | 8.2 | 445 | 530 |

[a] Calculated from $k_q\tau$ and fluorescence lifetime ($\tau$) of sensitizer. Lifetimes are reported: $\tau$ = 9.4 ns for DCP (Caldwell, R. A.; Ghali, N. I.; Chien, C.-K.; DeMarco, D.; Smith, L. *J. Am. Chem. Soc.* **1978**, *100*, 2857); $\tau$ = 12.4 ns for DCA (Ware, W. R.; Holmes, J. D.; Arnold, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 7861).

**Scheme I**



broad, and structureless emission at 450 nm with isoemissive point at 435 nm. To avoid a possibility of accidental coincidence of the exciplex maxima between **1a** and **2a**, a variety of cage compounds and sensitizers were investigated (Table I). In all cases the emission maximum from cage compounds **1a**, **1b**, **1c**, or **1d** was clearly superimposed with that from dienes **2a**, **2b**, **2c**, or **2d**, respectively. The coincidence of the exciplex emission between **1a** and **2a** was independent on solvent polarity; however, an increase of solvent polarity resulted in a red shift of the exciplex emission maximum: $\lambda_{max}$ = 420 (DCP), 513 nm (DCA) in cyclohexane; 451 (DCP), 545 nm (DCA) in ether; 468 (DCP), 575 nm (DCA) in ethyl acetate; 472 (DCP), 575 nm (DCA) in chloroform; 478 (DCP), 585 nm (DCA) in methylene chloride.[7] It is particularly important to note that the intensity of exciplex emission from **1a** reaches nearly the same value of the exciplex emission from **2a** at the same intensity of the monomer fluorescence of sensitizer, suggesting the occurrence of highly efficient adiabatic exciplex isomerization.

In order to get definitive experimental supports to prove that the emissive exciplex derived from **1a** and sensitizer is not a precursor to the isomerization of **1a** to **2a**, quenching experiments were carried out. Thus, it was found that dimethyl acetylenedicarboxylate (DMA) quenched the exciplex emission of **1a** and **2a** with nearly same efficiency for DCP ($k_q\tau$ = 4.93 $M^{-1}$ for **1a** and 4.96 $M^{-1}$ for **2a**) and for DCA ($k_q\tau$ = 1.01 $M^{-1}$ for **1a** and 1.07 $M^{-1}$ for **2a**). In the concentration range of DMA used, quenching of monomer fluorescence was negligible for DCA and was inefficient ($k_q\tau \simeq 0.15$ $M^{-1}$) for DCP. DMA quenched the isomerization reaction of **1a** to **2a** with low efficiency ($k_q\tau$ = 1.1 $M^{-1}$) for DCP, but almost no quenching was observed for DCA. The observations that the nearly same efficiencies were obtained in the exciplex emission quenching both for **1a** and **2a** but the efficiency of the reaction quenching was lower than that of the emission quenching, are clearly consistent with the proposal that the observed exciplex is that of **2a** with sensitizer generated after an adiabatic isomerization of a short-lived exciplex of **1a** with sensitizer (Scheme I).

The efficiencies of the adiabatic process (adiabatic percent, $A_p$) of cage compounds **1a**, **1b**, **1c**, and **1d**, calculated by Jones' method,[4] are shown in Figure 1. It is important to note that a higher yield for the adiabatic process was obtained as the oxidation potential[8] of the cage compound becomes lower and that DCA ($E_{1/2}^{red}$ = –0.82 V vs. SCE)[9a] was more efficient than DCP ($E_{1/2}^{red}$ = –1.51 V vs. SCE).[9b] The suggestion that charge transfer (CT) interaction between cage compound and excited sensitizer is a crucial factor for an efficient adiabatic process is supported by an observed solvent effect. As solvent becomes more polar, the $A_p$ value for the case of **1a** and DCP increases as follows: in cyclohexane ($E_T^{10}$ = 31.2, $A_p$ = 71%); in ethyl acetate (38.1, 81%); in methylene chloride (41.1, 94%); but $A_p$ for **1a** and DCA are higher than 90% in all of the solvents.

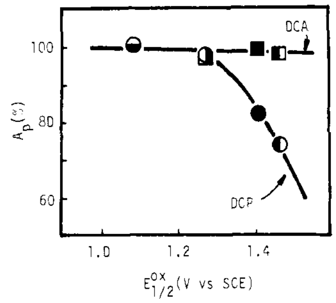


**Figure 1.** Plots of adiabatic efficiencies ($A_p$) vs. oxidation potentials ($E_{1/2}^{ox}$) of cage compounds in benzene: for DCP–**1a** (●), –**1b**, (⊖), –**1c** (◑), and –**1d** (◐); for DCA–**1a** (■), –**1c** (◨), and –**1d** (◧).

On the basis of our previous work showing that the cation radical of the cage compound has shallow energy minimum on the potential energy surface and suffers fast ring opening to diene,[11] we assume that the contribution of a canonical structure (cage compound$^{\delta+}$—sensitizer$^{\delta-}$)* to the exciplex is one of the most important factors for an efficient adiabatic process. A decrease in the oxidation potential of cage compound (high HOMO) and an increase in the reduction potential of sensitizer (low LUMO) would accelerate an adiabatic process. Raising the HOMO energy of cage compound and lowering the LUMO energy of sensitizer would decrease the excitation energy of the exciplex. Thus, this interpretation seems to be compatible with Jones' observation that the efficiency of the adiabatic process increases as an exciplex

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[7] The wavenumber of exciplex emission maximum correlates with solvent polarity ($E_T$): for DCP, $r$ = –0.965, for DCA, $r$ = –0.981. $E_T$ value is a parameter of solvent polarity: Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29.

[8] The oxidation potentials ($E_{1/2}^{ox}$ vs. SCE) of cage compounds were 1.41, 1.09, 1.28, and 1.49 for **1a**, **1b**, **1c**, and **1d**, respectively. The data are quoted from ref 5a and unpublished results by Sato, K., and Mukai, T.

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[10] See ref 7.

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emission maximum is shifted to the red region.[12]

**Registry No.** **1a**, 61377-37-5; **1b**, 66606-92-6; **1c**, 89610-95-7; **1d**, 66606-93-7; **2a**, 61109-78-2; **2b**, 66606-89-1; **2c**, 89684-74-2; **2d**, 66606-90-4; DCP, 7473-70-3; DCA, 1217-45-4; DMA, 762-42-5.

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(12) Jones has proposed that the efficiency of the adiabatic process increases according to the proximity of ground- and excited-state energy surfaces in the latter stages of the rearrangement.[4] However, the adiabatic rearrangement itself is highly exothermic and has a small activation energy. Therefore, the transition-state structure of the adiabatic process should resemble the reactant exciplex. In this context, the proximity of the potential energy surfaces in the former stages of the rearrangement must be also considered.

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## Polyphosphazene Solid Electrolytes

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Considerable attention is currently focused on inorganic ion conducting solids[1,2] from both a fundamental standpoint and for their use as electrolytes in high-energy-density batteries and sensors. Recently, a radically new battery design, based on a solvent-free thin-film polymer electrolyte, has been tested and found promising for medium-temperature (ca. 100 °C) applications.[3] In the present communication we report a new type of host polymer which forms complexes with a wide variety of metal salts having good conductivity at room temperature. The dependence of conductivity on salt concentration shows a distinct maximum which is consistent with current theory of charge transport in these materials.

Research on the ion transport in polymer-salt complex electrolytes implicates a liquidlike mechanism.[4] One criterion for the requisite polymer fluidity is a low glass transition temperature, $T_g$.[4,5] This consideration prompted us to explore salt complexes of polyphosphazenes, because some polyphosphazenes exhibit very low glass transition temperatures,[6] and the extensive chemistry of poly(dichlorophosphazene), $[-NPCl_2-]_n$, affords the opportunity for easy modification.

The sodium salt of 2-(2-methoxyethoxy)ethanol was allowed to react with poly(dichlorophosphazene) (I) in the presence of tetra-*n*-butylammonium bromide[7] to yield the fully substituted, stable high polymer MEEP (II) (eq 1). $^{31}P$ NMR, $^{13}C$ NMR, and elemental analysis all indicate total halogen replacement has occurred.[8]

$$\underset{\text{I}}{[-N{=}PCl_2-]_n} + 2nNaOC_2H_4OC_2H_4OCH_3 \xrightarrow[THF,\ \Delta]{n\text{-}Bu_4NBr}$$

$$\underset{\text{II}}{[-N{=}P(OC_2H_4OC_2H_4OCH_3)_2-]_n} + 2nNaCl \quad (1)$$

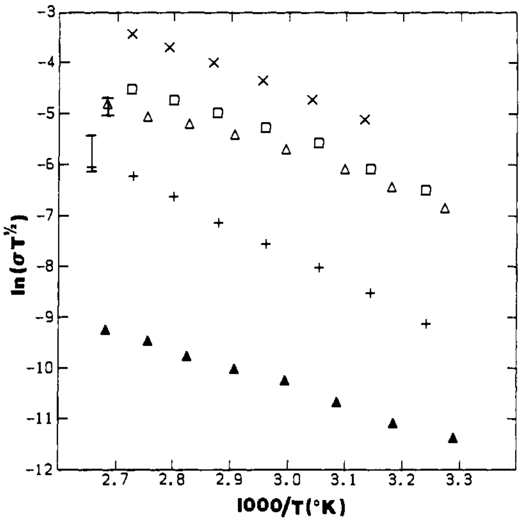

**Figure 1.** Temperature dependence of electrical conductivity, $\sigma$ ($\Omega^{-1}$ cm$^{-1}$) plotted as ln ($\sigma T^{1/2}$) vs. $1/T$. (Plots of ln$\sigma$ vs. $1/T$ have the same qualitative shapes.) The wide error limits for the highest temperature point of the Sr- and Na-containing samples arise from flow of the samples and corresponding uncertainty in its thickness. Complexes: ▲, pure polymer; +, $[Sr(SO_3CF_3)_2]_{0.25}\cdot$MEEP; △, $[NaSO_3CF_3]_{0.25}\cdot$MEEP; □, $[LiSO_3CF_3]_{0.25}\cdot$MEEP; ×, $[AgSO_3CF_3]_{0.25}\cdot$MEEP.

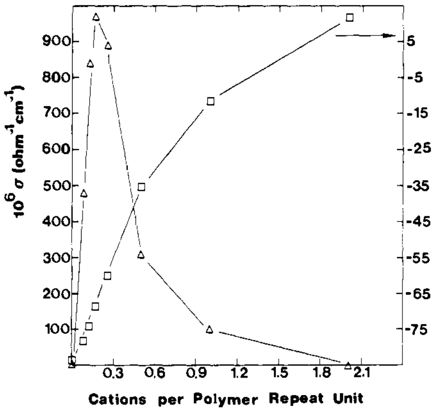

**Figure 2.** Left axis: △, electrical conductivity at 70 °C vs. composition of $(AgSO_3CF_3)_x\cdot$MEEP complexes. Right axis: □, $T_g$ (extrapolated to 0 °C/min heating rate) vs. composition of $(AgSO_3CF_3)_x\cdot$MEEP complexes.

Solvent-free complexes of $AgSO_3CF_3$ were prepared by vacuum removal of THF from a solution containing a predetermined ratio of polymer and salt. All complexes were found to be amorphous by X-ray diffraction, optical microscopy, and differential scanning calorimetry (DSC). The complexes range from a hard material at 2:1, metal cation/polymer repeat unit, concentration to a rubbery, elastic species at 0.25:1 and lower stoichiometries, and a corresponding increase in the glass transition temperature, $T_g$, was observed.

Conductivities were measured with a vector impedance meter and analyzed by complex impedance techniques between 5 and 500 000 Hz.[9-11] Polarization cell experiments, on triflate salt complexes, indicate that the transference number for $Ag^+$ is 0.03 or less at 50 °C, and for $Li^+$ it is 0.32 under the same conditions. Gentle curves are obtained, when the conductivity data are plotted as either ln ($\sigma T^{1/2}$) or ln $\sigma$ vs. $1/T$ (Figure 1) as expected for

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(8) $^{31}P$ NMR -6.3 ppm ($H_3PO_4/D_2O$). Anal. Calcd for $PNC_{10}H_{22}O_6$: P, 10.93; N, 4.94; C, 42.40; H, 7.83; O, 33.89. Found: P, 10.50; N, 5.00; C, 41.84; H, 7.73; O, 34.93 (by difference). $M_N \geq 10^6$.

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