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.

---

(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.

Polyphosphazene Solid Electrolytes

Peter M. Blonsky and D. F. Shriver*

Department of Chemistry and
Materials Research Center, Northwestern University
Evanston, Illinois 60201

Paul Austin[†] and H. R. Allcock*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Received July 13, 1984

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]

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

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

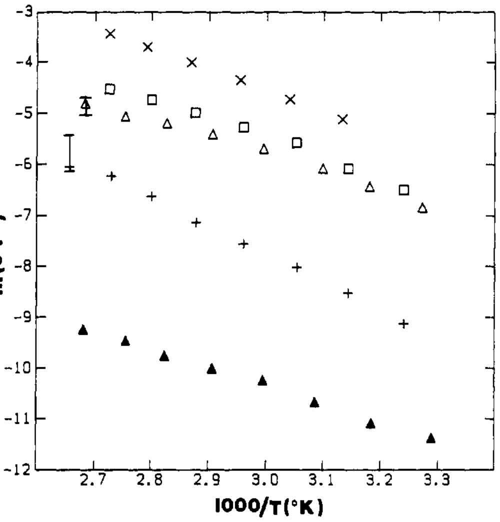


Figure 1. Temperature dependence of electrical conductivity, σ (Ω^{-1} cm^{-1}) plotted as ln ($\sigma T^{1/2}$) vs. $1/T$. (Plots of lnσ vs. $1/T$ have the same qualitative shapes.) The wide error limits for the highest temperature point of the Sr- and Na-containing samples arise from flow of the samples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

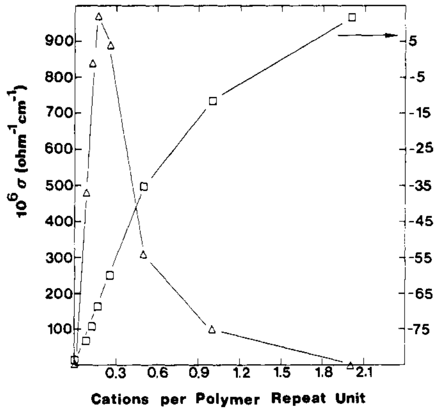


Figure 2. Left axis: △, electrical conductivity at 70 °C vs. composition of $(AgSO_3CF_3)_x$·MEEP complexes. Right axis: □, T_g (extrapolated to 0 °C/min heating rate) vs. composition of $(AgSO_3CF_3)_x$·MEEP complexes.

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 σ vs. $1/T$ (Figure 1) as expected for

---

[†] Current address: Union Carbide Corporation, Tarrytown, NY 10591.

(1) Yao, Y. Y.; Kummer, J. T. *J. Inorg. Nucl. Chem.* **1967**, *29*, 2453.

(2) Farrington, G. C.; Briant, J. L. *Science (Washington, DC)* **1979**, *204*, 1371.

(3) Sequeira, C. A. C.; Hooper, A. *Ext. Abstr., Meet. Electrochem. Soc. 163rd*, **1983**, *83*, Abstr. No. 493.

(4) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. In "Fast Ion Transport in Solids"; Vashista, P., Mundy, J. N., Shennoy, G. D., Eds.; North-Holland: New York, 1979; pp 131-136.

(5) (a) Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Phys. Chem. Solids* **1981**, *42*, 493. (b) Papke, B. L.; Dupon, R.; Ratner, M. A.; Shriver, D. F. *Solid State Ionics* **1981**, *5*, 685.

(6) Allcock, H. R. "Phosphorous-Nitrogen Compounds"; Academic Press: New York, 1972; and references therein.

(7) Austin, P. E.; Riding, G. H.; Allcock, H. R. *Macromolecules* **1983**, *16*, 719.

(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). $M_N \geq 10^6$.

(9) Tasi, Y. T.; Whitmore, D. H. *Solid State Ionics* **1982**, *7*, 129.

(10) Bauerle, J. E. *J. Phys. Chem. Solids* **1969**, *30*, 2657.

(11) MacDonald, J. R. *J. Chem. Phys.* **1974**, *61*, 3977.

0002-7863/84/1506-6854$01.50/0

amorphous polymer electrolytes.[4,12,13]

The conductivity of a polymer electrolyte, as given by a configuration entropy model, follows eq 2, where the A term is

$$\sigma = AT^{-1/2}\exp(-B/(T - T_0)) \qquad (2)$$

proportional to the number of charge carriers, and the T_0 term, in the exponential, is closely related to the glass transition of the sample.[4,13] The conductivity of $(AgSO_3CF_3)_x$·MEEP complexes increased with increasing salt concentration as expected ($0 < x < 0.17$), however, further increases in salt concentration resulted in diminished conductivities (Figure 2). The progressive immobilization of polymer chains resulting in restricted segmental motion of the polymer and increased rigidity would account for the rising T_g values and decreasing conductivities observed.[12-14]

Complexes of poly(ethylene oxide), and $LiSO_3CF_3$ or $LiClO_4$ (0.125:1), are useful battery electrolytes above 100 °C.[15-17] Between room temperature and 100 °C, the conductivity of $(LiSO_3CF_3)_{0.25}$·MEEP is 1–3 orders of magnitude larger than that of the poly(ethylene oxide) systems. Thus in contrast with the poly ether-based electrolytes the new polyphosphazene electrolyte is a good candidate for a room-temperature thin-film battery. Concentration dependence of the ion mobility and T_g for the new phosphazene electrolytes substantiate current models for the influence of charge carrier concentration and fluididity on the ion transport in solvent-free polymer-salt complexes.

Acknowledgment. This research was supported by the Office of Naval Research and the NSF Materials Research Laboratory Program through the Northwestern University Materials Research Center. P.M.B. appreciates useful discussions with Shaun Clancy.

---

(12) Dupon, R.; Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Electrochem. Soc.* **1984**, *131*, 586.

(13) Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Electrochem. Soc.* **1982**, *129*, 1694.

(14) Cheradame, H. In IUPAC Macromolecules"; Benoit, H., Rempp, P., Eds.; Pergamon Press: New York, **1982**; p 251.

(15) Sorensen, P. R. *Solid State Ionics* **1983**, *9*, 1147.

(16) Weston, J. E.; Steele, B. C. H. *Solid State Ionics* **1981**, *2*, 347.

(17) Weston, J. E. Steele, B. C. H. *Solid State Ionics* **1982**, *7*, 81.

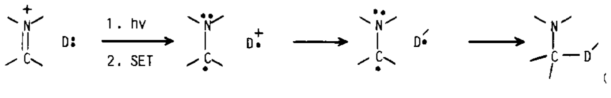
A Novel Method for Heteroatom-Substituted Free Radical Generation by Photochemical Electron-Transfer-Induced Desilylation of $RXCH_2Me_3Si$ Systems

Martha A. Brumfield, Suzanne L. Quillen, Ung Chan Yoon,[1] and Patrick S. Mariano*

Department of Chemistry, University of Maryland
College Park, Maryland 20742

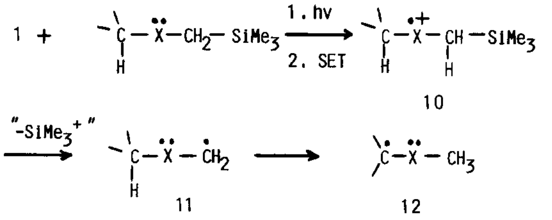
Received June 4, 1984

Our recent investigations in the area of electron-transfer photochemistry have led to the development of preparatively useful photoaddition and -cyclization reactions initiated by electron transfer from donors to iminium salt systems.[2] In general, the key, product-nature-determining step in the mechanistic pathways followed in these processes involves conversion of initially formed, cation radical pair or diradical intermediates to neutral, radical precursors of products (eq 1).

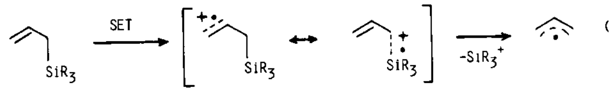


(1)

Scheme I



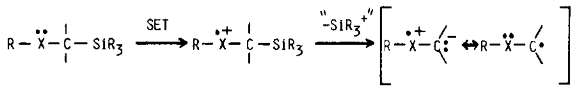
The charge-neutralizing, secondary transformations of the cation radical species include addition of nucleophiles and loss of electrofugal groups from sites adjacent to the positively charged centers.[3] The actual routes selected appear to be governed by the nature of the cation radical species, the types of electrofugal groups present in the systems, and the solvent. More recent efforts have focused on excited-state reactions of this type activated by cation radical desilylation. Examples in which allylsilane-derived cation radicals are converted to allyl radical counterparts by loss of trialkylsilyl fragments have been described (eq 2).[4]



(2)

Owing to the large rate of cation radical desilylation relative to nucleophilic addition or α-deprotonation,[5] pathways involving sequential electron transfer–desilylation serve as useful methods for site-selective radical generation.

This proposal has been successfully tested recently in explorations targeted at the development of regioselective methods for heteroatom-substituted radical generation. We envisaged that cation radicals arising from (trialkylsilyl)methyl ether, sulfide, or amine precursors would undergo rapid, nucleophile-assisted loss of the trialkylsilyl fragment to selectively generate α-alkoxy-, α-alkylthio-, or amino-substituted carbon radicals (eq 3).



(3)

The facility of this process would be a result of the good overlap existing between the filled σ_{C-Si} MO and half vacant heteroatom sp^3 AO, and the propensity for nucleophilic attack on silicon of β-silyl cations.[6] Moreover, this method for heteroatom-substituted radical formation would be superior to the more common photochemically induced, sequential electron-transfer–deprotonation route observed for a number of amine[7] and ether[2c] systems since the site of radical generation can be controlled by preselected placement of the trialkylsilyl grouping at the proper α-position. The results of our preliminary investigations concentrating on the photochemistry of 2-phenyl-1-pyrrolinium and quinolinium salt systems demonstrate that this pathway serves as a mild, regioselective method for radical generation.

Calculations[8] based upon the known singlet-excited-state reduction potential of 2-phenyl-1-pyrrolinium perchlorate (**1**) ($E_{1/2}^{S1}(-) = +2.9$ V)[2d] and the estimated oxidation potentials of

---

(1) Current address: Department of Chemistry, College of National Sciences, Busan National University, Busan, Korea 607.

(2) (a) Stavinoha, J. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 3136. (b) Stavinoha, J. L.; Mariano, P. S.; Leone-Bay, A.; Swanson, R.; Bracken, C. *J. Am. Chem. Soc.* **1981**, *103*, 3148. (c) Mariano, P. S.; Stavinoha, J. L.; Bay, E. *Tetrahedron* **1981**, *37*, 3385. (d) Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130. (e) Mariano, P. S. *Tetrahedron* **1983**, *39*, 3845.

(3) Information about the chemistry of radical cation species can be derived by inspection of mass spectrometric fragmentation and electrochemical processes.

(4) (a) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213. (b) Ullrich, J. W.; Chiu, F. T.; Harding, T.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 220. (c) Chiu, F. T.; Ullrich, J. W.; Mariano, P. S. *ibid.* **1984**, *49*, 228. (d) Chen, S. F.; Ullrich, J. W.; Mariano, P. S. *J. Am. Chem. Soc.* **1983**, *105*, 6160.

(5) (a) Recent results[5b] indicate that the desilylation rate is >7-fold larger than the rate of deprotonation from analogous benzyl cation radicals. (b) Quillen, S. L.; Lan, A.; Mariano, P. S., unpublished results.

(6) Pitt, C. G. *J. Organomet. Chem.* **1973**, *61*, 49. Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981.

(7) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048. Schaeffer, C. G.; Peters, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 7566. Lewis, F. D.; Ho, T. I.; Simpson, J. T. *J. Org. Chem.* **1981**, *46*, 1077 and references cited therein.

(8) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

0002-7863/84/1506-6855$01.50/0