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Metal Ion Initiated Charge-Transfer Photopolymerization of Tetrahydrofuran. A Mechanistic Investigation

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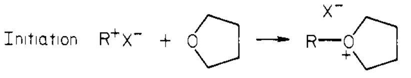
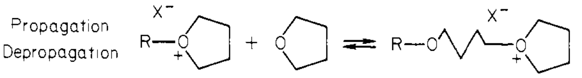
Abstract: Irradiation of dilute solutions of salts of Ag(I), Cu(II), Cu(I), and Tl(I) having suitable noncoordinating anions in tetrahydrofuran results in the formation of polytetrahydrofuran in yields comparable to those for acid-catalyzed (dark) polymerization. The yield of polymer is dependent upon the identity and concentration of metal ion, the anion, the duration of irradiation, and the dark time following irradiation. The observed polymer-yield dependencies upon metal ion and anion at low conversions are Cu(II) > Ag(I) > Cu(I) ≫ Tl(I) and PF_6^- > SbF_6^- ≫ OTf^- > BF_4^-. Both the counterion dependence and increase in polymer yield with dark time following photoinitiation are indicative of a cationic ring-opening polymerization process. Initiation of polymerization is proposed to occur via ligand-to-metal charge-transfer excitation of the metal ion–ether complex to generate oxidized ether and reduced metal, which precipitates from solution. The ether cation radical reacts further to form reactive intermediates known to initiate the cationic ring-opening polymerization of tetrahydrofuran. Evidence in support of the proposed mechanism of initiation and polymerization is presented. The initiation of thermal and photochemical ring-opening polymerization of several other ethers by metal salts is also described.

The thermal polymerization of cyclic ethers such as epoxides, oxetanes, tetrahydrofuran (THF), dioxolane, and trioxane has been extensively studied,[1,2] and it is known that the initiating step involves the generation of a cationic species. Typical initiators are strong Brønsted or Lewis acids, and considerable evidence indicates that the propagating species is a tertiary oxonium ion. As illustrated for THF in eq 1, nucleophilic attack by a noncoordinated monomer leads to ring opening (and in some cases, ring expansion) of the cyclic oxonium ion. The range of acceptors with sufficient activity to thermally initiate such polymerizations is, however, relatively narrow, and it would also be desirable to achieve greater temporal control over the initiation process. One approach to this problem would be to utilize the enhanced reactivity of many donor–acceptor pairs when in electronically excited states.[3-5] Thus, it has been demonstrated that photochemical activation of electron transfer to *organic* acceptors such as tetracyanoethylene, tetracyanobenzene, and pyromellitic dianhydride can be used to initiate the ionic polymerization of α-methylstyrene,[5a] *N*-vinylcarbazole,[5b] isobutyl vinyl ether,[5c] and cyclohexene oxide.[5a]



(1a)



(1b)

An intriguing related concept that has not been explored is the use of metal ions as electron acceptors in ionic photopolymerization reactions.[6] The intrisic coordinative preferences of the metal ion might be expected to impart significant chemoselectivity both in terms of organic substrate binding (type, number, and relative orientation of the ligands) as well as the optical/photochemical characteristics of the donor–acceptor complex. We recently communicated that thermally unreactive mixtures of THF and various metal ion salts may be photochemically activated to initiate the efficient cationic polymerization of THF.[7] This result constitutes the first example of a metal ion initiated cationic photopolymerization[8] and also the first report of a photoinitiated charge-transfer polymerization of THF. In the present contribution, we present a full account of our mechanistic studies of the initiation process for THF as well as a brief account of our investigations with other polymerizable ethers. From these, considerable information on the nature of the photoinitiation process as well as guidelines for suitable metal ion acceptors and donor/monomers are derived.

Experimental Section

Tetrahydrofuran (Aldrich, 99.5%) and benzene (Aldrich, 99.5%) were stored over sodium and Davison 4A molecular sieves and then distilled under N_2 (Matheson, prepurified) from sodium–potassium alloy and the purple benzophenone radical dianion immediately prior to use. Dioxane (Aldrich, 98%) was purified by reflux for 12 h with HCl and water[9] (3 L of dioxane, 300 mL of H_2O, and 40 mL of concentrated HCl) under a steady flow of N_2. The solution was cooled, and KOH was added until two layers separated. The upper layer (dioxane) was separated, dried over KOH, and then distilled from sodium and benzophenone. Cyclohexene oxide (Aldrich, 98%), oxetane (Aldrich, 97%), and 1,2-epoxybutane (Aldrich, 97%) were distilled, freeze–thaw degassed, and stored over sodium metal. 7-Oxabicyclo[2.2.1]heptane (Aldrich, 96%) was distilled at reduced pressure (487 mm, 103 °C). 1,3-Dioxolane (Aldrich, 96%) was distilled from sodium–potassium alloy and the purple benzophenone radical dianion. Trioxane (Aldrich, 98%) was purifed by vacuum sublimation. Since it is a solid, all polymerizations of trioxane were conducted in toluene solution (~1.5 M). A prepared toluene solution was stored over sodium and transferred via syringe into the reaction tube.

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[2] Dreyfuss, P.; Dreyfuss, M. P. *Comp. Chem. Kinet.* **1976**, *75*.

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All ethers were stored in the dark and then redistilled immediately prior to use.

Irradiation tubes were 12-mm o.d. quartz tubes equipped with Teflon needle valves. Metal salts used as polymerization initiators were handled only in a nitrogen-filled Vacuum Atmospheres glove box with a Dri-Train atmosphere purification system. Standard Schlenk techniques were used for handling air-sensitive materials. All glassware was flamed under vacuum before use. Irradiation sources were either a Hanovia X1500-061 low-pressure Hg vapor or a Hanovia 679A36 450-watt medium-pressure lamp. According to the manufacturer's specifications, the radiated energy in the ultraviolet region (200–350 nm) is approximately 50 times greater for the medium- vs. the low-pressure lamp. A water-cooled quartz lamp well was used. Absorption spectra were recorded on a GCA/McPhearson EU-700 or a Cary 17-D spectrophotometer on samples contained in quartz cuvettes fitted with Teflon needle valves. Infrared spectra were taken with Perkin-Elmer Model 267 or 283 spectrophotometers. A Nicolet 7199 instrument was used for Fourier transform infrared spectroscopy. Elemental analyses of the polymers and osmometric molecular weights were determined by H. Beck, Northwestern Analytical Services Laboratory. Elemental analyses of the silver salts were performed by Galbraith Microanalytical Laboratory. Proton and ^{13}C NMR spectra were obtained with a Varian CFT-20 spectrometer.

Synthesis of Metal Triflates.[10] Silver(I) triflate (AgOTf) was prepared[11] from Ag_2O and trifluoromethanesulfonic anhydride (Aldrich, vacuum distilled). Copper(II) triflate was synthesized[12] from $CuCO_3 \cdot Cu(OH)_2$ and trifluoromethanesulfonic acid (Aldrich, vacuum distilled in greaseless glassware). Copper(I) triflate–0.5-benzene was prepared[13] from Cu_2O and trifluoromethanesulfonic anhydride in dry benzene. Thallium(I) triflate was prepared from thallium(I) carbonate (Alfa, used as received) and trifluoromethanesulfonic acid. To 5.68 g of Tl_2CO_3 (12.1 mmol) was added 100 mL of acetonitrile (Aldrich, distilled from P_2O_5), followed by addition of 2.75 mL (31 mmol) of the acid to the stirred slurry. The solution became clear as the solid dissolved with the evolution of carbon dioxide. The solution was filtered and cooled to -20 °C, followed by addition of 25 mL of diethyl ether. The resulting white crystalline solid was dried in vacuo for 5 h to yield 5.50 g of TlOTf (15.5 mmol, 65%). The infrared spectrum of this material (Nujol mull, cm^{-1}) exhibited prominent absorptions at 2250 w, 1600 w, 1300–1150 s, 1025 s, 770 m, 720 m, 630 s and is identical with that of TlOTf prepared via an alternative procedure.[14]

The silver and thallium triflates absorb water if left exposed to the atmosphere. Copper(I) triflate–0.5-benzene is extremely air and moisture sensitive, decomposing in seconds if exposed to air. Copper(II) triflate rapidly absorbs atmospheric water, forming a blue hydrated complex in minutes.

Preparation of Anhydrous Silver Salts. The silver salts $AgBF_4$, $AgPF_6$, and $AgSbF_6$ (Alfa, "anhydrous") were found by infrared spectroscopy to contain large amounts of water and other impurities that could not be removed by drying under vacuum. It was, however, possible to prepare anhydrous 1,4-dioxane complexes of each salt.[15] Approximately 5 g of each salt was weighed into a flask under nitrogen. Then 60 mL of freshly distilled dioxane was added with stirring (the salts did not dissolve). For $AgPF_6$ and $AgSbF_6$, there was an immediate increase in the volume of the solid and heat was evolved. For $AgBF_4$, the reaction mixture was stirred for several hours. The solids were isolated by filtration under nitrogen and vacuum dried overnight, leaving microcrystalline, colorless salts. A sample of each salt was analyzed for silver content.

Anal. Calcd for $AgPF_6 \cdot 2C_4H_8O_2$: Ag, 25.14. Found: Ag, 25.53. Calcd for $AgBF_4 \cdot 0.5C_4H_8O_2$: Ag, 45.18. Found: Ag, 44.71. Calcd for $AgSbF_6 \cdot 3C_5H_8O_2$: Ag, 17.74. Found: Ag, 17.21.

Complete infrared spectra follow (Nujol mull, prepared in glove box, cm^{-1}).

$AgPF_6 \cdot 2C_4H_8O_2$: 1300 m, 1260 s, 1240 m, 1225 w, 1150 w, 1120 s, 1085 s, 1055 m, 940 w, 920 w, 900 w, 870 s, 840 s, 630 w, 620 m.

$AgBF_4 \cdot 0.5C_4H_8O_2$: 1305 m, 1290 w, 1270 m, 1260 m, 1110–1030 s, 900 m, 890 m, 870 s, 630 w, 615 w.

$AgSbF_6 \cdot 3C_4H_7O_2$: 1298 s, 1265 s, 1115 s, 1085 s, 1150 m, 900 m, 865 s, 725 w, 660 s, 620 m.

There is no evidence of water present in the infrared spectra, but upon exposure to air, water is rapidly absorbed.

Preparative Photolyses and Characterization of Polytetrahydrofuran (PTHF). In a typical preparation, 0.50 g of AgOTf (1.9 mmol) was weighed into an irradiation tube under nitrogen. Then 20 mL of freshly distilled THF was added via syringe. The colorless solution (0.095 M) was photolyzed with the medium-pressure lamp for 9 h. The solution became viscous, and a black powdery precipitate and silver mirror on the walls of the tube were formed. The contents were emptied into 50 mL of a THF solution of LiBr (0.03 M) and left to stir overnight. The bromide ion is known[1,2] to terminate cationic THF polymerizations. The solution was next filtered through Celite, and solvent was removed in vacuo, leaving a mass of brown-gold polymer. The polymer was redissolved in dichloromethane, filtered again, and, after evaporation of solvent, dried in vacuo. The infrared spectrum of a film of the polymer exhibits absorptions at 3430 s, 2950 s, 2860 s, 2797 s, 2740 m, 2079 w, 1730 m, 1635 m, 1447 s (multiplet), 1370 s, 1305 s, 1260 s, 1210 m, 1175 w, 1140–1000 s, 805 s, and 645 cm^{-1}. The ^{13}C NMR spectrum of the polymer dissolved in C_6D_6 showed only two resonances (δ 27 and 71). The ^1H NMR of a similarly prepared polymer showed two types of protons (δ 1.71 and 3.34). In another preparation, a THF solution of AgOTf (0.12 M) was irradiated for 12 h, and then polymerization was terminated by addition of water. The white polymer was purified as described above and analyzed for carbon and hydrogen content.

Anal. Calcd for $(C_4H_8O)_n$: C, 66.63: H, 11.18. Found: C, 67.14; H, 11.37.

A sample of the black precipitate that formed during photolysis was isolated by centrifugation, washed with THF, dried in vacuo, and analyzed for Ag content.

Anal. Calcd for Ag: Ag, 100.00. Found: Ag, 99.20.

The use of initiators other than AgOTf led to a polymer that was identical with that described above. A THF solution of $CuOTF \cdot 0.5C_6H_6$ [0.13 M in Cu(I)] was irradiated for 23 h with the low-pressure lamp, leading to a dramatic increase in solution viscosity and the plating out of copper metal on the walls of the irradiation tube. The polymerization was terminated by addition of water, yielding a white polymer mass that was vacuum dried. The yield, based on THF initially present, was 9.0%.

Similarly, irradiation of a THF solution of $Cu(OTf)_2$ (0.011 M) for 17 h caused the solution to become very viscous and copper metal to precipitate from solution. The polymer yield after aqueous workup was 8.9%. Photoinitiation of polymerization with TlOTf (0.028 M) led to the formation of gray thallium metal and a 5.8% yield of PTHF. In all these cases, the solutions were colorless until irradiation was begun. Photolysis was accompanied by a very large increase in viscosity and formation of metal that precipitated from solution. Because of the dramatic viscosity increase, polymerizations were generally terminated at low conversion to polymer. However, one attempt was made to measure the yield of PTHF obtainable in a typical preparative reaction. Irradiation of an $AgPF_6$ solution (0.095 M) for 13.5 h with a low-pressure lamp, followed by 11.5 h in the dark, resulted in a 50% yield of dry polymer. Yields for thermal THF polymerization are generally in the range of 30–80%.[1,2]

Photopolymerization can be inhibited by typical cationic polymerization inhibitors such as triethylamine. A THF solution of AgOTf (0.068 M) and Et_3N (0.07 M) was irradiated for 24 h, causing the formation of silver metal, but no polymer was formed. Also, addition of excess norbornene (Aldrich, sublimed) to a THF solution of $CuOTf \cdot 0.5C_6H_6$ prevented the formation of copper metal and PTHF.[16]

Molecular Weight Determination of PTHF. A THF solution of $CuOTf \cdot 0.5C_6H_6$ (0.13 M in Cu^+) was photolyzed with a low-pressure lamp for 23 h. The polymer isolated by aqueous workup and vacuum drying was analyzed for purity.

Anal. Calcd for $(C_4H_8O)_n$: C, 66.63; H, 11.18. Found: C, 66.62; H, 11.05.

The molecular weight was determined in benzene with a Mechrolab Model 302 vapor-phase osmometer. The observed number-average molecular weight ($\bar{M}_n$) was found to be ca. 18 000, equivalent to an average chain length of 250 monomer units.

Thermal Reaction of Metal Initiators in THF. A solution of AgOTf (0.031 M) was freeze–thaw degassed three times in an irradiation tube and then left sealed under vacuum. The solution, wrapped in aluminum foil to exclude light, was heated to 80 °C for 17 h and then left in the dark for 3 weeks. No formation of silver metal or increase in solution viscosity was noted. A portion of the solution was added to water without precipitation of PTHF. The remainder of the solution was next photolyzed for 12 h, causing the formation of silver metal and PTHF. Similarly, TlOTf and $Cu(OTf)_2$ did not yield metal or PTHF under similar thermal conditions. In the case of $CuOTf \cdot 0.5C_6H_6$, there was formation of copper metal in the dark, but no polymer formation occurred. The copper metal formation was especially noticeable when warm, freshly

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[10] Triflate = trifluoromethanesulfonate, $CF_3SO_3^-$, OTf^-.

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distilled THF was added to the copper(I) salt.

Effect of Anion on PTHF Yield. Solutions of THF and $AgBF_4 \cdot 0.5C_4H_8O_2$, $AgSbF_6 \cdot 3C_4H_8O_2$, $AgPF_6 \cdot 2C_4H_8O_2$, and AgOTf were prepared under nitrogen (2.2×10^{-2} M). Two 10-mL samples of each of the four salts were irradiated with the medium-pressure lamp while in a Rayonet "merry-go-round" apparatus immersed in a water bath at room temperature (22–25 °C). The light source had been turned on 30 min previously to reach constant output and was located 1 cm from the outside of the merry-go-round. One 10-mL portion of each solution was left in the dark but otherwise treated identically to the irradiated samples. After 2 h, the $AgPF_6$- and $AgSbF_6$-initiated reactions were terminated by addition of 4 mL of a THF solution of LiBr (1.1×10^{-2} M). Termination of the AgOTf- and $AgBF_4$-initiated reactions was carried out after 6 h. After thorough mixing, the solutions were emptied into preweighed round-bottom flasks, THF being used to wash out the final traces of polymer and solid inorganic material. Solvent was removed under reduced pressure, followed by overnight drying of the residue in a vacuum desiccator. Yields of PTHF were found by weighing. The yield of isolated solids for the unirradiated samples was found to correspond to the expected mass of initiator and LiBr present. This quantity was subtracted from the isolated residue obtained from the irradiated samples in order to determine the mass of PTHF formed.

PTHF Yield—Dependence on Irradiation and Dark Time. Five irradiation tubes, each with 10 mL of a THF solution of AgOTf (0.036 M), were placed in a merry-go-round apparatus immersed in a water bath at room temperature. The low-pressure Hg vapor lamp, which had been turned on 30 min previously to reach constant output, was located 1 cm from the outside of the merry-go-round. The tubes were irradiated for 4.75 h. After photolysis, the samples were placed in the dark. At various times from 0 to 126 h after photolysis, a sample was terminated by addition of 10 mL of methanol. The contents of each tube were emptied into preweighed round-bottom flasks, solvent was removed under reduced pressure, and finally all PTHF samples were dried under vacuum overnight. The yield of PTHF was determined by weighing and was found to increase with increasing time in the dark after irradiation.

In a similar fashion, the dependence of PTHF yield on the length of irradiation was determined. Seven samples of a THF solution of AgOTf (0.026 M) were irradiated with a low-pressure lamp. At 15-min intervals, an irradiation tube was removed and placed in the dark until 24 h had elapsed since beginning the photolysis. Polymer was next isolated and yield determined as described above. The amount of PTHF formed increased linearly with the duration of photolysis.

Dependence of PTHF Yield on Metal Ion Employed. A solution of $Cu(OTf)_2$ in THF (0.022 M) was prepared under nitrogen. Seven 10-mL aliquots were added to quartz irradiation tubes by syringe. One sample was left in the dark, and the rest were irradiated with the medium-pressure lamp while immersed in a water bath at room temperature. At periodic intervals, a tube was removed and placed in the dark. At 18 h, the last sample was removed. To each was added 3.0 mL of $NaOC_6H_5$ in THF (0.13 M) to terminate the polymerization. Yields of PTHF were determined as described in the previous section. The yield of isolated solid from the unirradiated sample was 0.13 g, which corresponded to the expected mass of $Cu(OTf)_2$ and $NaOC_6H_5$. This was subtracted from yields from the other samples to determine the PTHF yield.

In a similar fashion, yields of PTHF as a function of irradiation time were determined for AgOTf, $CuOTf \cdot 0.5C_6H_6$, and TlOTf. All solutions were 0.022 M in metal ion, and other conditions were identical with those described above. Yields of PTHF were also determined for a solution of $CuOTf \cdot 0.5C_6H_6$ in which the metal ion concentration was doubled (0.044 M). Three samples were irradiated for 18 h. The isolated yields of PTHF were 0.85, 0.91, and 0.93 g. The PTHF yields for three $Cu(OTf)_2$ solutions (0.022 M, half as concentrated) that were irradiated simultaneously were found to be 0.93, 0.89, and 0.94 g.

In another attempt to ascertain reproducibility in these conversion studies, three separate samples of a THF solution of $Cu(OTf)_2$ (0.022 M) were irradiated for 18 h with the medium-pressure lamp located 0.5 cm from the merry-go-round. Polymer was isolated from each tube as described above. The yields of PTHF were 1.21, 1.22, and 1.14 g. This experiment was repeated for the other initiators and found to give similar results.

EPR Spectra of $Cu(OTf)_2$ and AgOTf in THF. EPR spectra were obtained with a Varian E-4 X-band spectrometer and were calibrated with Varian strong pitch ($g = 2.0026$).[17] Spectra were determined for frozen solutions (77 K) in 4-mm o.d. quartz tubes fitted with Teflon needle valves. Solutions were freeze–thaw degassed three times and left under vacuum. The spectrum of $Cu(OTf)_2$ in THF (0.02 M) was recorded. After thawing, the solution was photolyzed with the low-pressure lamp. The EPR tube was 4 cm from the light source, and the lamp had been turned on 30 min previously to warm up. At 15-min intervals, the spectrum was recorded, and the dimunition of the Cu(II) signal intensity monitored.

A solution of AgOTf in THF (0.08 M) was prepared and freeze–thaw degassed three times in an EPR sample tube. While frozen and under vacuum, no signal was detectable by EPR spectroscopy. After thawing, the solution was photolyzed with the low-pressure lamp (45 min) and then refrozen and the EPR spectrum determined. There was a strong singlet with a g value of 2.090.

Irradiation of AgOTf and Benzophenone in THF. Benzophenone (Aldrich) was recrystallized three times from ethanol. A THF solution of AgOTf (0.046 M) and benzophenone (0.011 M) was prepared under nitrogen. The irradiation source was the medium-pressure lamp equipped with Corning 0-52 and 7-54 filters to isolate the 365-nm line. The absorbance of light at this wavelength and concentration is $\sim$1.0 for benzophenone and 0 for AgOTf. After 1.5 h of irradiation, large amounts of silver metal had formed, and the solution became viscous upon standing in the dark overnight. When the solution was added to water, PTHF precipitated and was isolated and characterized. There was no formation of silver metal or polymer when AgOTf was irradiated at 365 nm in the absence of benzophenone. Photolysis of benzophenone in THF did not result in polymer formation.

Reactions of Other Cyclic Ethers. Solutions of metal salts were prepared as described for THF and either irradiated with the low-pressure mercury lamp or wrapped in foil and maintained at room temperature. The occurrence of polymerization was established either by an increase in solution viscosity or by isolation of solid polymer.

Addition of cyclohexene oxide to $Cu(OTf)_2$ resulted in formation of a dark green solution. After 2 days in the dark, the green solution (0.05 M) had become fairly viscous. There was no copper metal formed. Addition of methanol to terminate the reaction resulted in precipitation of a white polymer mass that, after drying, amounted to a 30% yield of polymer. No photochemical acceleration of polymerization was noted. In the case of Cu(I), thermal polymerization also occurred. No metal formation or photoacceleration was noted. For the other two initiators, AgOTf and TlOTf, no polymerization was noted after several days in the dark or upon photolysis.

Addition of oxetane to AgOTf, $CuOTf \cdot 0.5C_6H_6$, or $Cu(OTf)_2$ resulted in increased viscosity in the dark. No metal precipitate was observed for Ag(I) or Cu(II); however, copper metal was observed immediately upon addition of oxetane to Cu(I). Irradiation caused no apparent increase in the rate of polymerization for Ag(I) or Cu(I); however, photoacceleration was observed for Cu(II) and was accompanied by copper metal precipitation. Identical solutions (0.2 M in Cu(II)) irradiated or kept in the dark for 9 h were terminated with methanol and yielded, after drying, 100% and 30%, respectively, of a solid white polymer with infrared spectra characteristic of the polyether with hydroxide end groups.[1,2,5] Oxetane solutions of TlOTf were stable in the dark but yielded polymer and thallium metal upon irradiation.

Addition of 1,3-dioxolane to metal salts resulted in rapid thermal polymerization with AgOTf and $Cu(OTf)_2$, slower polymerization with $CuOTf \cdot 0.5C_6H_6$, and no reaction with TlOTf. Irradiation did not accelerate the reaction of Cu(I) or initiate polymerization with TlOTf.

Addition of 1,3,5-trioxane (1.6 M in toluene solution) to the triflate salts of Ag(I), Cu(I), Cu(II), and Tl(I) resulted in precipitation of white polymer but no precipitated metal after several hours in the dark. No acceleration of polymerization or metal formation was observed upon irradiation.

The triflate salts of Ag(I), Cu(I), and Cu(II) are insoluble in 7-oxabicyclo[2.2.1]heptane, whereas the Tl(I) salt is soluble. No increase in viscosity or thallium metal precipitation was observed in the dark or upon irradiation.

Irradiation of AgOTf in 1,2-dimethoxyethane solution led to precipitation of silver metal but no increase in viscosity. Irradiation of AgOTf in mixed 1,2-dimethoxyethane–THF (1:1) solution resulted in the formation of silver metal and solid white polyether. When THF was added to a previously irradiated 1,2-dimethoxyethane solution of AgOTf containing precipitated silver metal and the mixture stored in the dark overnight, no solid polymer or increase in viscosity was observed.

Results

Preliminaries. The photochemical generation of free radicals has been used extensively as a method of initiating the polymerization of monomers susceptible to free-radical polymerization.[8,18] Studies of photoinitiated cationic polymerization are not as

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[17] Poole, C. P. "Electron Spin Resonance"; Interscience: New York, 1967; pp 589–590.

[18] (a) Hutchinson, J.; Ledwith, A. *Adv. Polym. Sci.* **1974**, *14*, 49–86. (b) Pappas, S. P. *Prog. Org. Coat.* **1974**, *2*, 333.

common. Since almost all monomers have ionization potentials of at least 7 eV,[5a] direct ionization of the monomer cannot be accomplished with ultraviolet or visible light.[19] However, photoionization can be greatly facilitated by excited-state electron donor–acceptor interactions.[20] This process may occur through photoexcitation of a charge-transfer complex (eq 2) or through direct excitation of the donor molecule, D, which then reacts with the ground-state acceptor, A, or vice versa (eq 3 and 4). Formation of the polarized excited-state complex $[\mathrm{D}\cdot^{+}\mathrm{A}\cdot^{-}]^{*}$ can then lead to dissociation into ion radicals followed by initiation of cationic polymerization of the monomer.

$$\mathrm{D} + \mathrm{A} \rightleftharpoons \mathrm{DA} \xrightarrow{h\nu\mathrm{CT}} [\mathrm{D}\cdot^{+}\mathrm{A}\cdot^{-}]^{*} \qquad (2)$$

$$\mathrm{D} \xrightarrow{h\nu} \mathrm{D}^{*} \xrightarrow{\mathrm{A}} [\mathrm{D}\cdot^{+}\mathrm{A}\cdot^{-}]^{*} \qquad (3)$$

$$\mathrm{A} \xrightarrow{h\nu} \mathrm{A}^{*} \xrightarrow{\mathrm{D}} [\mathrm{D}\cdot^{+}\mathrm{A}\cdot^{-}]^{*} \qquad (4)$$

It if often difficult to distinguish between the intermediacy of a charge-transfer complex or excitation of a single component molecule (eq 2 vs. 3 or 4). The most reliable evidence for the intermediacy of a charge-transfer complex is the appearance of new, characteristically broad bands in the absorption spectrum of the mixture not attributable to either component.[21] However, the apparent absence of such features does not, a priori, rule out charge-transfer absorption since the charge-transfer bands may be masked by other absorbances or may be of intrinsically low intensity. Although usually of relatively high oscillator strength, there are cases where such transitions are weak due to poor orbital overlap or very weak complex formation.[22] At least one example of the nonintermediacy of a charge-transfer complex is known. Direct photoexcitation of the monomer *N*-vinylcarbazole leads to polymerization when electron acceptors such as acrylonitrile and carbon tetrachloride are present. However, the exciting light is absorbed by the monomer, not a charge-transfer complex.[23]

Cationic photopolymerization through charge transfer requires that the monomer be nucleophilic with respect to the electron acceptor. This nucleophilic character may be satisfied by unshared electron pairs present in the monomer, leading to complex formation. Typical n-electron donor molecules such as those possessing group 5A or 6A heteroatoms can be photoionized when complexed with suitable electron acceptors.[4b,5b,24] It is known that THF can act as an electron donor in charge-transfer complexes with some organic acceptors.[4b,24,25] In these cases, irradiation of the charge-transfer bands (all of weak intensity ($\epsilon < 400$)) leads to the formation of 1:1 adducts or polymerization of the electron acceptor.[4b,24] As already noted, cationic photopolymerization of several olefins and cyclohexene oxide can be accomplished in the presence of certain organic acceptors.[5] In all of these examples, there is evidence for the formation of a ground-state charge-transfer complex. EPR spectroscopic evidence is also available for the formation of radical ions upon irradiation; however, in the cases involving cyclic ethers, only the radical anions of the acceptors are detected. The absence of evidence for the presumed ether radical cation has been attributed[25] to line broadening due to charge migration and exchange with the solvent.

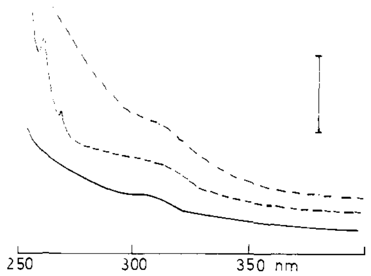

Figure 1. Optical spectra of AgOTf (---), AgBF$_4$ (—), and AgPF$_6$ (···) as solutions (3.7 × 10^{-2} M) in THF. The vertical scale marker is for an optical density of 0.1.

The present study concerns the use of metal ions as photoacceptors. Solutions of photoreducible (vide infra) metal salts [Ag(I), Cu(I), Cu(II), and Tl(I)] in anhydrous THF are indefinitely stable in the dark. For example, AgOTf in THF can be heated to 80 °C and then stored in the dark for 3 weeks without evidence of reaction. However, upon irradiation of these solutions with ultraviolet light, there is a dramatic increase in solution viscosity. Accompanying the increased viscosity is the precipitation of metal from the solution. Following suitable workup and vacuum drying, the organic product of the reaction was found to be polytetrahydrofuran (PTHF), which was characterized by elemental analysis, ^{1}H and ^{13}C NMR and infrared spectroscopy, and osmometric molecular weight ($\bar{M}_n \approx 18\,000$). Although no effort was made to optimize polymer yield or molecular weight in this study of the initiation photochemistry, yields of insoluble polymer as high as 50% were measured (reactions were usually terminated at relatively low conversions). Although THF solutions of the metal salts were colorless prior to irradiation, photolysis generates black [Ag(I)], red [Cu(I) or Cu(II)], or gray [Tl(I)] precipitates as the reaction proceeds. Relative yields of PTHF increase with the duration of photolysis and also upon standing in the dark subsequent to photolysis. The yield of polymer is a function of metal ion identity, oxidation state, concentration, and counterion. It is depressed by typical cationic inhibitors such as triethylamine[1,2] or, in the case of Cu(I), by competing olefinic ligands such as norbornene.[15] We begin our discussion by considering first the nature of the donor–acceptor pair in the ground state and then how it interacts with light.

Optical Spectroscopic Studies of Metal Ion–THF Solutions. The metal triflates were found to be insoluble in noncoordinating solvents. Therefore, optical absorption studies had to be conducted in THF solution. It should be noted that THF complexes of Ag(I) or Tl(I) have not been isolated,[26] although THF complexes of Cu(II) and several other dipositive metal ions have been isolated.[27] In these complexes, the THF molecule is loosely coordinated and readily displaced. Metal triflates are known[12,27,28] to be highly dissociated in solution. The absorption spectra of AgOTf, AgBF$_4$, and AgPF$_6$ (0.04 M) in THF are shown in Figure 1. The spectrum of AgOTf displays an intense absorption band at wavelengths shorter than 250 nm due to the free ether[29] and weaker transitions at 256 and 262 nm due to traces of benzene[30] from which the AgOTf was originally prepared. The long-wavelength absorption has a maximum at 305 nm and is rather weak, with an apparent[31] molar extinction of 3.0. Increasing the concentration of AgOTf causes the 305-nm absorption to increase in intensity. The spectra of AgBF$_4$ and AgPF$_6$ are similar to that of AgOTf, with the same absorption maximum at 305 nm. There

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[19] However, vacuum UV (below 200 nm) has been used. See: Vermeil, C.; Matheson, M.; Leach, S.; Müller, F. *J. Chem. Phys.* **1964**, *61*, 596–604.

[20] Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978.

[21] Reference 20, Chapter 5.

[22] (a) Torres, A.; Castaño, F.; Alvarino, J. M. *Makromol. Chem.* **1978**, *179*, 2653–2661. (b) Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5961–5972. (c) Trogler, W. C. *Ibid.* **1979**, *101*, 6459–6460.

[23] Tazuke, S. *J. Phys. Chem.* **1970**, *74*, 2390–2397.

[24] Irie, M.; Tomimoto, S.; Hayashi, K. *J. Polym. Sci., Part B* **1972**, *10*, 699–701.

[25] (a) Ilten, D. F.; Calvin, M. *J. Chem. Phys.* **1965**, *42*, 3760–3766. (b) Achiba, Y.; Kimura, K. *Chem. Phys. Lett.* **1976**, *39*, 515–518. (c) Spectra of ether radical cations can be observed under special circumstances: Symons, M. C. R.; Wren, B. W. *J. Chem. Soc., Chem. Commun.* **1982**, 817–818 and references therein.

[26] (a) Lee, A. G. "The Chemistry of Thallium"; Elsevier: Amsterdam, 1971; pp 284–290. (b) Thompson, N. R. In "Comprehensive Inorganic Chemistry"; Bailar, J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973, Vol III, pp 114–115. (c) Tuck, D. G. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two 1974–1975* **1975**, *1*, 331–333.

[27] Dreissen, W. L.; den Heijer, M. *Inorg. Chim. Acta* **1979**, *33*, 261–264.

[28] Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, 69–92.

[29] "DMS UV Atlas of Organic Compounds"; Butterworths: London, 1966; Vol. I.

[30] Friedel, R. A.; Orchin, M. "Ultraviolet Spectra of Aromatic Compounds"; Wiley: New York, 1951.

[31] The concentration of metal salt may not be the same as the concentration of a metal–ether complex.

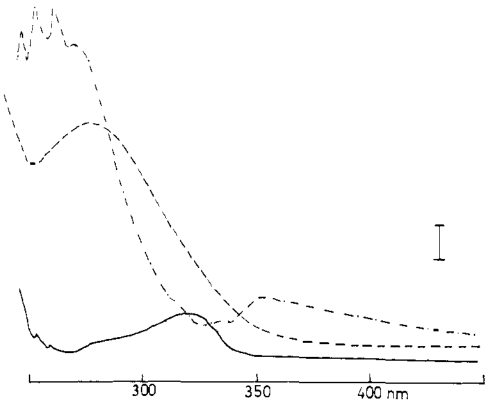

Figure 2. Optical spectra of $Cu(OTf)_2$ (---, 8.0×10^{-4} M), Cu(OTf)·$0.5C_6H_6$ (-··-, 1.8×10^{-3} M), and TlOTf (—), 1.3×10^{-3} M) as solutions in THF. The vertical scale marker is for an optical density of 0.1.

Table I. Yield of PTHF as a Function of Anion

initiator	length of photolysis, h	isolated solids, g	PTHF yield, g[b]
$AgPF_6 \cdot 2C_4H_8O_2$	0	0.15[a]	0
$AgPF_6 \cdot 2C_4H_8O_2$	2	1.40	1.25
$AgPF_6 \cdot 2C_4H_8O_2$	2	1.61	1.46
$AgSbF_6 \cdot 3C_4H_8O_2$	0	0.13[a]	0
$AgSbF_6 \cdot 3C_4H_8O_2$	2	1.10	0.97
$AgSbF_6 \cdot 3C_4H_8O_2$	2	1.13	1.00
AgOTf	0	0.09[a]	0
AgOTf	6	0.29	0.20
AgOTf	6	0.28	0.19
$AgBF_4 \cdot 0.5C_4H_8O_2$	0	0.07[a]	0
$AgBF_4 \cdot 0.5C_4H_8O_2$	6	0.11	0.04
$AgBF_4 \cdot 0.5C_4H_8O_2$	6	0.13	0.06

[a] This mass is equivalent to amounts of initiator present and LiBr added to terminate reaction. [b] Yield of PTHF after subtracting initiator and LiBr added. All samples were 10 mL of a 0.022 M AgX solution.

is no absorption at wavelengths longer than 260 nm when only pure THF is present, and the spectrum of AgOTf in other solvents such as acetonitrile does not exhibit this transition. Due to the differing structures and ionization potentials of the anions, charge transfer from the anion to the metal should reasonably result in different absorption energies for the three salts. The spectral similarities, coupled with the photoreduction of silver ion and the cationic polymerization of THF, strongly suggest that electron transfer from THF to Ag(I) can be correlated with the optical feature at 305 nm.

The optical spectra of $Cu(OTf)_2$, $CuOTf \cdot 0.5C_6H_6$, and TlOTf in THF are shown in Figure 2. For $Cu(OTf)_2$, there is a broad feature centered at 280 nm (ϵ 800); the d–d transitions are expected to be weaker and at considerably longer wavelengths.[32] For the Cu(I) salt, only a weak, broad transition is detected in the visible; it peaks at 350 nm and is noticeably asymmetric, extending to 500 nm. From the known optical properties of d^{10} ions[32a,33] and optical electronegativity considerations (vide infra), this feature is unlikely to be THF-to-Cu(I) charge transfer in origin. Rather, it appears to be associated with the disproportionation of the Cu(I) in THF[34] and subsequent formation of finely divided copper metal.[35] Warming the solution slightly or allowing it to stand for several hours at room temperature increases the amount of copper metal formed. (This does not, however, lead to polymerization of the THF.) Further examination of the Cu(I) absorption spectrum shows that there is also absorption due to benzene (present in the metal salt) and possibly a contribution from Cu(II) ion (formed in the disproportionation reaction). The presence of a Cu(I)–THF complex is thus not evident in the UV spectrum. If present, it must absorb at wavelengths shorter than 280 nm and is not detected due to the absorbance of other species present in solution. Finally, TlOTf in THF exhibits an absorption maximum at 320 nm (ϵ 200) (Figure 2). This transition can be assigned to THF-to-Tl(I) charge transfer. The free ion has transitions at considerably higher energy.[33]

Further support for the above assignments is derived from optical electronegativity considerations. By using the empirical approach of Jørgensen, we can express ligand-to-metal charge-transfer (LMCT) transition energies as in eq 5.[36-40] Here the

$$\nu'_{\mathrm{CT}} = 30000(\chi_{\mathrm{ligand}} - \chi_{\mathrm{metal}})\mathrm{cm}^{-1} \qquad (5)$$

χ parameters are tabulated optical electronegativities.[37-40] It is thus possible with the appropriate parameters to predict charge-transfer transition energies with reasonable accuracy. Unfortunately, χ parameters have not been determined for THF or for the majority of the metal ions under investigation. Nevertheless, it is possible to advance arguments for the assignment of LMCT in the present case on the basis of how χ_L and χ_M are expected to depend upon relative ligand ionization potential and metal ion reduction potential/oxidation-state characteristics. Thus, for Tl(I), charge-transfer transitions are not observed for oxetane (IP = 9.9 eV[41]) or 1,3-dioxolane (IP = 10.1 eV[41]) at energies lower than 260 nm (the onset of solvent absorption), while the corresponding transition for water (IP = 12.6 eV[42a]) as a ligand is believed to be at 220 nm.[30] On the other hand, the lower ionization potential of *p*-dioxane is comparable to that of THF (9.43 vs. 9.57 eV[41]), and an optical transition (reasonably ascribed to LMCT) is identified at 325 nm for TlOTf–*p*-dioxane solutions (vs. 320 nm for THF). For Cu(II), LMCT has been assigned in the hexaquo complex at ca. 200 nm.[38] The 12.6-eV ionization potential of water suggests that the energy of analogous transitions will be at considerably lower energy for THF, as observed (λ = 280 nm). Likewise, the lower reduction potential and positive charge of Cu(I) vs. Cu(II) argue that LMCT for the former should be at considerably higher energies, as is commonly observed.[42b,c]

Due to the insolubility of the metal triflates in noncoordinating solvents,[43] values for the complex formation constant and the extinction coefficient could not be determined by the Benesi–Hildebrand method.[44] For the cases of Tl(I), Ag(I), and Cu(I), where no stable metal ion–THF complexes have been reported, it would be difficult to rigorously determine whether the charge-transfer absorption is due to a genuine metal–ether complex or to a loosely associated variable solvation shell.[45] It is interesting

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(32) (a) Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, 1968; Chapter 4. (b) Hathaway, B. J.; Tomlinson, A. G. *Coord. Chem. Rev.* **1970**, *5*, 1–43. (c) Hathaway, B. J. *Struc. Bonding (Berlin)* **1973**, *14*, 49–67.

(33) Rabinowitch, E. *Rev. Mod. Phys.* **1942**, *14*, 112–131.

(34) 2Cu(I) → Cu(0) + Cu(II). See: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Interscience: New York, 1980; Chapter 21-H.

(35) (a) Photoaggregated Cu_n clusters absorb at wavelengths as long as 500 nm in cryogenic rare gas matrices: Ozin, G. A.; Huber, H.; McIntosh, D.; Mitchell, S.; Norman, J. G., Jr.; Noodleman, L. *J. Am. Chem. Soc.* **1979**, *101*, 3504–3511. (b) Alternatively, these features may arise from benzene → Cu(I) charge transfer.

(36) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970; Chapters 13 and 19.

(37) Endicott, J. F. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; Chapter 3.

(38) Jørgensen, C. K. *Prog. Inorg. Chem.* **1970**, *12*, 101–158.

(39) Jørgensen, C. K. *Mol. Phys.* **1963**, *6*, 43–47.

(40) Reference 32a, Chapter 8.

(41) (a) Sweigart, D. A.; Turner, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 5599–5603. (b) Bain, A. D.; Bünzli, J. C.; Frost, D. C.; Weiler, L. *Ibid.* **1973**, *95*, 291–292. (c) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*.

(42) (a) "Handbook of Chemistry and Physics", 50th ed.; Chemical Rubber Publishing Co.: Cleveland, OH, 1969; p E-82. (b) Thompson, J. S.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4180–4192, and references therein. (c) Thompson, J. S.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *Ibid.* **1979**, *101*, 4193–4200 and references therein.

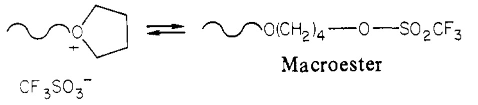
(43) They are soluble in THF, alcohols, acetonitrile, dimethylformamide, and ketones, but not chlorinated solvents and alkanes. The Cu(I) and Ag(I) triflates are slightly soluble in aromatic solvents.

(44) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.

that the Cu(II) ion, which forms an isolable THF complex,[32] has the highest extinction coefficint of the four metal triflates in THF. As already noted, the addition of strongly coordinating ligands prevents photoreduction of the metal and polymerization of THF. For example, addition of excess norbornene to a solution of copper(I) triflate in THF prevents photopolymerization and the formation of copper metal.[16] This suggests that THF coordination by the metal ion is a prerequisite for photoinitiation of the polymerization process.

Silver-Initiated Photopolymerization. Effect of Anion on PTHF Yield. The influence of anion on the propagation process (eq 1) in thermal THF polymerization is well documented,[1,2] and it was of interest to determine, for metal ion held constant, to what degree the photochemically initiated process (at low conversions) conformed to these trends, i.e., whether anion effects were evident in any component of the reaction other than propagation. The relative yield of PTHF depends upon which silver salt is used as the photoinitiator (Table I). Use of $AgPF_6$[46] resulted in the highest yield of PTHF, with the yield decreasing in the order $PF_6^- > SbF_6^- \gg OTf^- > BF_4^-$. Silver salts that were insoluble in THF (AgOAc, $AgNO_3$, AgF) did not induce polymerization upon irradiation. Another silver salt, $AgClO_4$, was found to be an effective photoinitiator, but due to the known[47] explosive nature of this salt when exposed to heat or shock, extensive studies were not conducted.

In the purely thermal polymerization process, simple anions such as halides are not suitable counterions for polymerization because the oxonium ion, $R_3O^+X^-$, will disproportionate to form ether and alkyl halide.[1,2] Complex anions such as PF_6^- and SbF_6^- are excellent counterions since they do not form stable alkyls. With such anions, termination of polymerization by counterion does not occur, and the extent of polymerization is thermodynamically determined, dependent only on concentration and temperature (a "living" polymerization). The BF_4^- anion is not as inert a counterion as PF_6^- and SbF_6^-, and yields are correspondingly lower at room temperature. Thus, for thermal polymerizations, the yield decreases in the order $PF_6^- > SbF_6^- > BF_4^-$, as also observed in the present case of photoinitiation.[48,49] The use of triflate as counterion involves a more complex, slower polymerization due to a macroion–macroester equilibrium[1,48] (eq 6). The macroester



(6)

Macroester

Macroion

form is thought to be relatively inactive in propagation but represents a dormant concentration of potential active centers. Final yields of PTHF are also thermodynamically determined ("living"), but the approach to equilibrium is slower with OTf^- than that with the other anions. The position of the triflate anion, as determined in the photoinitiated yields of PTHF ($PF_6^- > SbF_6^- \gg OTf^-$) (Table I), likely reflects the occurrence of the macroion–macroester reaction.

Silver-Initiated Photopolymerization. Effect of Reaction Time on PTHF Yield. For relatively short periods of low intensity irradiation, the relative polymer yield was found to increase linearly with the duration of photolysis. Several aliquots of an AgOTf solution in THF (0.025 M) were irradiated with the low-pressure lamp, and at 15-min intervals a sample was removed and placed in the dark. After 24 h had elapsed from the beginning of irradiation, the solutions were appreciably viscous and yields of PTHF were determined. The yield of polymer is shown in Figure 3. As can be seen, there is a linear dependence of yield on irradiation time for short photolysis periods. There is no induction period evident, and it can be seen that there is no polymer formation without irradiation, as has been noted. Photolysis for longer periods causes the solutions to become much darker due to extensive silver metal formation, and polymer yields no longer increase in this linear fashion. Scattering of UV light from the silver metal precipitate is detected immediately after photolysis. After 5 min of irradiation in a UV cuvette, the absorption spectrum of AgOTf in THF shows broad background scattering throughout the 250–400-nm wavelength region.

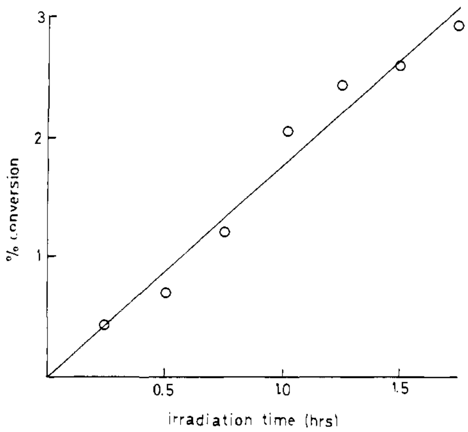


Figure 3. Yield of PTHF (0.026 M in AgOTf) as a function of short periods of irradiation time using a low-pressure lamp.

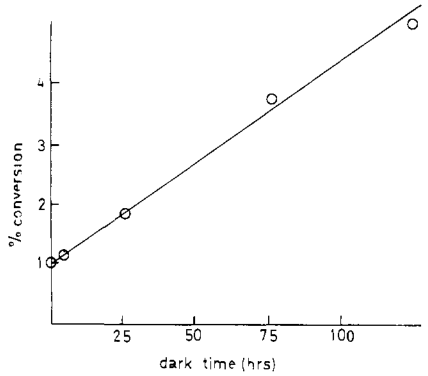


Figure 4. Yield of PTHF (0.026 M in AgOTf) as a function of total reaction time. Samples were irradiated 4.75 h with a low-pressure lamp and then stored in the dark 0–126 h prior to terminating the reaction.

It was found that the total isolated yield of PTHF depends not only upon the duration of photolysis but also upon the total reaction time. When a solution of AgOTf in THF is irradiated and then placed in the dark, the solution viscosity continues to increase. This viscosity increase was found to correspond to an increase in polymer yield as shown in Figure 4. The yield of PTHF was measured after varying the period of time the samples were left in the dark following photolysis with the low-pressure lamp. The PTHF isolated increased from approximately 1% immediately following photolysis to 6% after 130 h in darkness. This continued polymerization in the dark is especially noticeable with AgOTf as photoinitiator. The rather slow approach of AgOTf solutions to limiting polymer yield vis-à-vis the other silver salts is likely a manifestation of the aforementioned macroion–macroester equiibrium in eq 6.

Effect of Metal Photoinitiator on Relative PTHF Yield. The rate of polymer formation was found to be dependent upon the choice of metal ion initiator and concentration. Irradiation of the triflate salts of Ag(I), Cu(II), Cu(I), and Tl(I) (0.02 M) in THF with the low-pressure mercury lamp for 14 h followed by storage

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[45] Mataga, N.; Kubota, T. "Molecular Interactions and Electronic Spectra"; Marcel Dekker: New York, 1970; Chapter 8.

[46] $AgPF_6$, $AgBF_4$, and $AgSbF_6$ were used as dioxane salts (see Experimental Section). The presence of dioxane does not have any effect on the THF polymerization rate. See ref 15.

[47] Schilt, A. A. "Perchloric Acid and Perchlorates"; G. Frederick Smith Chemical Co.: Columbus, OH, 1978; Chapter 3.

[48] Dreyfuss, P.; Dreyfuss, M. P. *Adv. Chem Ser.* **1969**, *No. 91*, 335–349.

[49] These trends are not the subject of universal agreement, and there appear to be significant solvent effects: (a) Matryjaszeski, K.; Slomkowski, S.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 69–80. (b) *Ibid.* **1979**, *17*, 2413–2422.

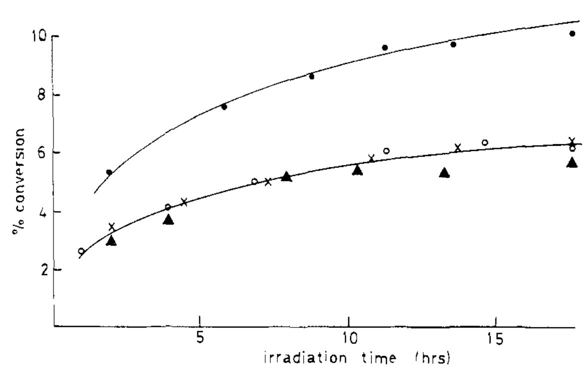

Figure 5. Yield of PTHF as a function of metal ion (all solutions are 0.022 M) with a medium-pressure lamp. See Experimental Section for methodological details. $Cu(OTf)_2$ (●), $Cu(OTf)\cdot0.5C_6H_6$ (○), AgOTf (▲), TlOTf (×).

in the dark for 36 h led to isolated polymer yields relative to Ag(I) = 1.0 (5.2% yield) of Cu(II) = 1.6, Cu(I) = 0.3, and Tl(I) < 0.05. The values for Ag(I), Cu(II), and Tl(I) roughly parallel the absorbance of the THF solutions at 254 nm (Figures 1 and 2).

Irradiation of metal triflate–THF solutions with the more intense medium-pressure mercury lamp for varying periods of up to 18 h followed by storage in the dark and isolation of PTHF after 18-h total reaction time led to different results. The Cu(I)-, Ag(I)-, and Tl(I)-initiated systems displayed essentially indistinguishable behavior during the course of reaction (Figure 5), reaching a limiting polymer conversion of approximately 6.0% after 18 h of photolysis. The first hour of irradiation causes the most rapid increase in polymer formation, followed by a gradual approach to final yield. Since 1 h of irradiation with the medium-pressure lamp is sufficient to effect the complete photoreduction of Cu(II) (vide infra), the differences in metal ion initiation efficiency due to difference in light absorbance observed for low intensity irradiation apparently are unimportant at high light intensities. For initiation with Cu(II), not only is the final polymer yield greatest but at any intermediate point there is an increase in polymer production by a factor of ca. 1.6 over the univalent ions.

Increasing the concentration of initiator also affected the yield of polymer. Irradiation with a medium-pressure lamp of a 0.022 M solution of CuOTf resulted in a polymer yield of 6.2% after 18 h. Doubling the concentration of Cu(I) produced a 10.1% polymer yield, essentially the same result as obtained with 0.022 M Cu(II). This result together with the similar behavior of the unipositive ions suggests that the yield of THF photopolymerized under these conditions is related principally to the number of electrons transferred in the metal ion photoreduction.

A number of experimental and chemical variables render unambiguous determination of relative metal ion initiator efficiencies rather difficult. For example, immediately after photolysis begins, there is formation of precipitated metal that increases scattering and decreases the amount of light available for reaction. There is also formation of an opaque metal mirror on the walls of the reaction tube. How these processes affect the photochemistry is expected to vary with the aggregation and optical characteristics of the bulk metal. On a more microscopic scale as well, the inorganic photoproducts will be a strong function of the particular metal. Thus, generation of thallium metal in the presence of thallous ion is known[50a,b] to lead to the formation of metal ion–metal atom clusters (eq 7). Similarly, generation of silver atoms

$$Tl^+ \xrightarrow{e} Tl^0 \xrightarrow{Tl^+} Tl_2^+ \qquad (7)$$

in the presence of silver ions has been reported to lead to the formation of Ag_2^+ and higher aggregates, which have been characterized by EPR spectroscopy.[51,52] In Cu(I) triflate solutions, Cu(II) and Cu(0) are present due to thermal disproportionation of the Cu(I) salt in THF. That $CuOTf\cdot0.5C_6H_6$ is itself a photoinitiator and not merely a source of Cu(II) is demonstrated by the different reactivities of Cu(I) and Cu(II) with other cyclic ethers (vide infra). Formation of charged metal aggregates of the type known for silver and thallium is also likely, further complicating the interpretation of results.

Table II. Thermal and Photochemical Reactivity of Cyclic Ethers with Metal Triflates[a]

ether	IP, eV[b]	Ag(I)	Cu(II)	Cu(I)	Tl(I)
cyclohexene oxide	10.6	–	Δ	Δ	–
oxetane	9.9	Δ	Δ, *hν*	Δ	*hν*
tetrahydrofuran	9.6	*hν*	*hν*	*hν*	*hν*
1,3-dioxolane	10.0	Δ	Δ	Δ	–
1,3,5-trioxane	10.8	–	Δ	Δ	–

[a] Key to symbols: (–) no reaction; (Δ) thermal reaction only; (*hν*) photochemical reaction only; (Δ, *hν*) thermal reaction with acceleration by light. [b] Reference 41.

Other metal salts were examined as possible photopolymerization initiators. Perchlorate salts[53] of Ni(II) and Cr(III) were found to be ineffective as photoinitiators of THF polymerization. Uranyl salts are known[54] to photooxidize organic substrates; however, photolysis of uranyl triflate[55] in THF did not lead to polymerization. Finally, ferric salts were not effective photoinitiators.

EPR Spectroscopy of Irradiated Cu(II) and Ag(I) Solutions. Frozen (77 K) solutions of $Cu(OTf)_2$ in THF exhibit a typical,[42b,c,56] essentially axial Cu(II) EPR spectrum with spin Hamiltonian parameters $g_{\parallel} = 2.543$, $A_{\parallel} = 10.2$ mK, and $g_{\perp} \approx 2.17$. Monitoring the intensity of this signal as a function of irradiation time (medium-pressure lamp, room temperature) revealed a continuous photodepletion of cupric ion concentration to <1% of its initial value (0.02 M) within 30 min. No induction period was evident, and no new intermediate species of any significance were detected. No signal attributable to a THF radical cation was observed.

Solutions of AgOTf (d^{10}) in THF at 77 K exhibit no EPR signal prior to irradiation. Irradiation of these solutions at room temperature followed by EPR spectroscopy at 77 K revealed a relatively narrow signal at $g = 2.090$ as well as several weaker features. The spectrum of isolated Ag^0 atoms in cryogenic rare gas matrices at 4 K consists of a signal (doublet of doublets) centered at $g = 1.999$ with ^{107}Ag, ^{109}Ag ($I = {}^1/_2$, 51.35% and 48.65% abundant, respectively) hyperfine coupling of 604 and 697 mK, respectively.[57] Recent photoaggregation and annealing studies of such matrices have provided spectral parameters for higher metal aggregates (narrow signals with g values as high as 2.028 are observed for conduction electron spin resonance),[58] while ^{60}Co γ irradiation of Ag^+ complexes in a variety of glasses is reported to generate EPR-active species such as Ag_2^+, Ag_3^{2+}, and Ag_4^{3+}.[51,59] EPR data also exist for several Ag^{2+} complexes.[60] The present spectral parameters do not conform well to any of the published data, and all that can be concluded is that the types of simple Ag^0 and Ag_n^{x+} species observed previously (generated under considerably different conditions) are not evident.

Polymerization of Other Cyclic Ethers. The results of thermal and photochemical reactions of metal triflate salts with several cyclic ethers are summarized in Table II along with literature

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(52) Symons, M. C. R. "Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy"; Wiley: New York, 1978; p 61.

(53) All were used as anhydrous dioxane complexes.

(54) (a) Reference 36, Chapter 15. (b) Cauzza, G.; Gennari, G.; Giacometti, G.; Agostini, G. C.; Gambaro, A. *Inorg. Chim. Acta* **1979**, *32*, 45–52. (c) Murayama, E.; Sato, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3022–3026.

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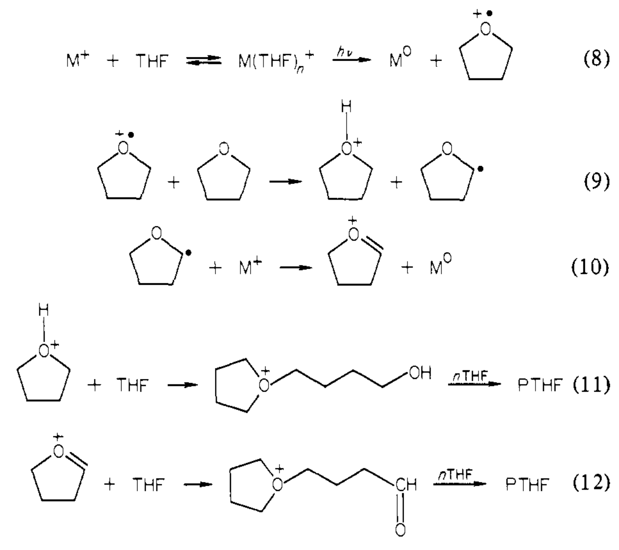
(60) Symons, M. C. R.; Eastland, G. W.; Zimmerman, D. N. *J. Chem. Soc., Dalton Trans.* **1980**, 709–711 and references therein.

Scheme I



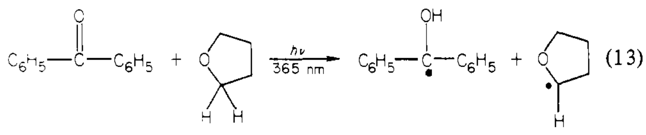
values for the gas-phase ionization potentials of the ethers. The choice of ethers was restricted by the known structural limitations on thermal ring-opening polymerization.[2] Thermal initiation of polymerization was observed for 1,3,5-trioxane with all four metal triflates, for 1,3-dioxolane and oxetane with all metal salts save TlOTf, and for cyclohexene oxide only with Cu(I) and Cu(II) triflates. Unlike photoinitiated polymerization, which yields metallic precipitates, thermally initiated polymerization did not yield reduced metal except in the case of Cu(I) in oxetane. No thermal or photoinitiated polymerization of 7-oxabicyclo-[2.2.1]heptane by metal triflates was observed. The insolubility of Ag(I), Cu(I), and Cu(II) triflates in this polymerizable ether suggests that steric hindrance of coordination may preclude initiation.

Discussion

The efficacy of transition-metal ions and their complexes in the photooxidization of organic substrates is well documented.[31,36,54,51] For example, salts of Cu(II) and Fe(III) are effective in the photooxidation of alcohols.[61,62] In another example, a transition-metal complex, VCl$_4$, has been proposed to photooxidize isoprene and isobutylene,[6b] leading to olefin polymerization. Studies of the photochemistry of ethers with metal complexes have been largely limited to the use of FeCl$_3$. Photolysis of FeCl$_3$ in diethyl ether leads to formation of FeCl$_2$ and chlorination products of the ether,[63a,b] while photolysis in epoxide/methanol mixtures results in FeCl$_2$ formation and solvolysis of the epoxide.[63c] There have been, however, no reports of photochemistry involving uncomplexed metal ions and cationically polymerizable substrates such as cyclic ethers.

The mechanism of the present metal ion initiated polymerization of THF can be rationalized in terms of the reaction sequence presented in Scheme I for the case of a monovalent metal ion. Solvation of the metal ion by THF gives rise to a complex with an accessible LMCT excited state. Evidence for this transition was presented in the discussion of the optical spectra. Excitation of this transition then activates the loosely coordinated THF for nucleophilic attack. The immediate products of electron transfer are the photoreduced metal and the THF cation radical (eq 8). Considerable evidence suggests that the aggregation of the zero-valent metal atoms should be essentially irreversible under these conditions,[35a,58,64] thus preventing thermal back-electron transfer to theradical cation, a feature that contrasts to the behavior of many organic photoacceptors.[5]

Generation of cyclic ether radical cations, although never observed spectroscopically in solution, has been proposed in a number of investigations to explain chemistry observed after photolysis of THF with organic acceptor molecules[5a,25,65] and of epoxides with FeCl$_3$.[63c] As indicated in Scheme I, the THF radical cation can react with another THF molecule and through hydrogen atom abstraction form a protonated oxonium ion and a THF radical (eq 9). Such a process has been advanced to account for radical coupling products formed during the photolysis of THF and TCNE.[25b,65] The protonated oxonium ion is, of course, the same species formed during thermal initiation of polymerization with strong Brønsted acids and will continue polymerization in the normal thermal manner (eq 11).[1,2] In the present case, it is likely that the metal salts oxidize the THF radicals to form a cyclic oxonium ion (eq 10) that can also act as a cationic initiator (eq 12); silver salts and other metal ions are known to rapidly oxidize free radicals[66,67]). An experiment to substantiate this is based upon the known[68] reaction of photoexcited benzophenone with THF to generate, via hydrogen atom abstraction, THF radicals (eq 13). We find that irradiation of a THF solution of benzophenone and AgOTf at 365 nm, where benzophenone absorbs and AgOTf does not, leads to photoreduction to silver metal and the polymerization of THF.[69] Importantly, irradiation (at the same wavelength) of only AgOTf dissolved in THF or of only benzophenone dissolved in THF does not lead to photopolymerization. Thus, generation of a THF radical in the presence of Ag(I) will lead to polymerization. The cationic species formed by thermal oxidation of the THF radical (eq 10) can also be formed by electrochemical means[70] or through hydride abstraction[1,2] from neutral THF. In both cases, polymerization leads to formation of an aldehyde end group (eq 12)[71] detectable by IR spectroscopy. The Fourier transform infrared spectrum of a film of the PTHF produced by AgOTf photoinitiation shows a weak band at 2740 cm^{-1} and a medium-intensity band at 1730 cm^{-1}. These are suggestive of an aldehyde absorption.[72] There is also an intense OH stretching absorption, suggesting that a large percentage of end groups are alcohol functionalities. The proposed mechanism (Scheme I) requires that both the photoreduction of metal ions and the polymerization initiation processes should be linearly dependent upon irradiation time, as is observed. The possibility that irradiation serves to generate an active catalyst such as colloidal metal or triflic acid is distinctly less likely. Irradiation of AgOTf in the nonpolymerizable ether dimethoxyethane yields silver metal precipitate; however, addition of THF to the irradiated mixture yields no polymer, whereas irradiation of AgOTf in THF–dimethoxyethane solution does lead to polymer formation.



Further evidence for initiation of THF polymerization by photostimulated ligand-to-metal charge transfer is provided by the variation in photopolymerization efficiency with metal ion and cylcic ether (Table II). In thermodynamic terms, the free-energy

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(61) (a) Sato, T.; Tamura, K.; Muruyama, K.; Ogawa, O.; Imamura, T. *J. Chem. Soc., Perkin Trans. 1* **1976**, 779–783. (b) Sato, T.; Yamamoto, K.; Fukui, K.; Saito, K.; Hayakawa, K.; Yoshiie, S. *Ibid.* **1976**, 783–787.

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(69) Metal ion oxidation of the diphenylhydroxymethyl radical would also be expected to generate cationic initiators.

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(72) "The Aldrich Library of Infrared Spectra", 2nd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1975.

change for THF photooxidation is given by[73] eq 14 where E_{ex} is

$$\Delta G = -E_{ex} + \mathrm{THF}_{ox} - M_{red} \tag{14}$$

the energy of the longest wavelength absorption band of the metal ion–THF complex, i.e., the energy of the photon absorbed (305 nm ~ 4.1 eV), THF_{ox} is the oxidation potential of THF, and M_{red} is the reduction potential of the metal in THF. Since the "donor numbers" of THF and water are similar,[74] it is reasonable for the purpose of discussion to consider the aqueous, one-electron reduction potentials for Ag(I), Cu(I), Cu(II), and Tl(I), which are +0.80, +0.52, +0.15, and −0.34 V, respectively.[75] While the oxidation potentials of ethers are too high to allow precise measurements, a lower limit for $\mathrm{THF}_{ox} = +3.6$ V can be estimated from the data available.[76] These values indicate that sufficient energy is available in the electronic excitation to render the one-electron oxidation processes highly exothermic for Ag(I) ($\Delta G \leq -1.3$ eV), Cu(I), and Cu(II) and approximately isothermic for Tl(I). The other cyclic ethers investigated all have higher ionization potentials than THF (Table II). Since the ionization and oxidation potentials of related molecules are directly correlated ($\mathrm{IP} = aE_{D/D^+} - b$),[77] increasing ether oxidation potential renders the photooxidation process less favorable energetically.

While the mechanism of initiation of thermal polymerization of cyclic ethers by metal salts has not been investigated in detail, the absence in the present examples of metallic precipitates argues against ligand oxidation by metal ions. The possibility that trace amounts of triflic acid formed by the reaction of metal triflates with adventitious water initiate thermal polymerization can also be excluded since THF should also undergo thermal polymerization by this mechanism. The most likely mechanism for thermal polymerization is a "coordinate" mechanism in which an electron-deficient coordinated monomer is subject to nucleophillic attack by free monomer.[1,2] The metal ion thus functions as a Lewis acid polymerization initiator. Such a mechanism is known to occur in the case of catalysis of epoxide ring opening by iron, zinc, and aluminum catalysts.[2] The necessity of ether coordination for thermal polymerization is demonstrated by the inability of the Cu(I)–norbornene complex, $\mathrm{CuOTf{\cdot}C_7H_{10}}$, to initiate ring opening polymerization of 1,3-dioxolane. The metal ion selectivity of thermal polymerization (Table II) may reflect the ability of Cu(I) and Cu(II) ions to form more stable etherate complexes than do Ag(I) or Tl(I) ions.

Conclusions

The results of this study demonstrate that photopolymerization of THF is readily initiated by certain metal ions. Ligand-to-metal charge-transfer excitation of a metal–ether complex causes photoreduction of the metal ion and cationic polymerization of THF. When an intense broad-band source is used for irradiation, the effectiveness of the metal ion used depends solely on its oxidation state, with the 2+ ion being most effective. Following the metal ion mediated photoinitiation, polymerization proceeds through the normal cationic chain mechanism. The observed effect of anion identity on yield, the continued growth of polymer in the dark, and inhibition of polymerization by triethylamine and water are all characteristic of the thermal polymerization of THF.

Metal ion initiated photopolymerization offers several unique features not available in either thermal or organic acceptor photoinitiated systems. The THF–initiator mixture is completely stable until activated by ultraviolet light. The reacted initiator (precipitated metal) can be easily separated after polymerization by filtration. The diverse thermal and photochemical behavior observed with several different metal ions and cyclic ethers indicates that coordination may allow significant fine tuning of reactivity not achievable with thermal initiators.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the generous support of this research and to PPG Industries for providing a fellowship for M.E.W. We thank the Materials Research Center of Northwestern University for access to magnetic resonance equipment supported under NSF grant DMR79-23575.

Registry No. THF, 109-99-9; $\mathrm{AgPF_6}$, 26042-63-7; $\mathrm{AgBF_4}$, 14104-20-2; $\mathrm{AgSbF_6}$, 26042-64-8; AgOTf, 2923-28-6; $\mathrm{Cu(OTf)_2}$, 34946-82-2; TlOTf, 73491-36-8; CuOTf, 42152-44-3; cyclohexene oxide, 286-20-4; oxetane, 503-30-0; 1,3-dioxolane, 646-06-0; 1,3,5-trioxane, 110-88-3.

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Orientation and Linear Dichroism of Symmetrical Aromatic Molecules Imbedded in Stretched Polyethylene

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Abstract: A general procedure for the analysis of linear dichroism of solutes partially aligned in a stretched polymer is described. Results for UV-visible dichroism of over a hundred symmetrical aromatic molecules in polyethylene are presented. Their orientation factors are dominated primarily by molecular shape, making the experimentally very simple stretched-sheet method suitable for the determination of absolute polarization directions in aromatics.

The determination of polarization directions of electronic transitions in molecules has been acquiring increasing importance,[2,3] particularly in biochemical applications. Because of its experimental simplicity, the stretched-sheet method of UV–visible[2-4] and IR[5] polarization measurement is gaining in popularity. In the method, the solute of interest is imbedded in a stretched polymer sheet, which orients it partially, and its linear dichroism is then measured and evaluated. Qualitative observations of this phenomenon were reported a hundred years ago,[6] and the several

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