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Electrochemical, spectroscopic and spectroelectrochemical studies of tantalum, niobium, tungsten and rhenium were conducted in molten alkali haloaluminate melts. The melts were in most cases treated with CCl_4 to remove oxide. Evidence was found for the formation of metallic tantalum, niobium and tungsten during controlled potential electrolysis in these melts. No conclusive evidence was found for rhenium plating. Reaction sequences, based on experimental data, were proposed for the four metals. Organic studies involved the chemistry and electrochemistry of tetrachloro-p-benzoquinone in molten chloroaluminates and the photochemical reactions of anthracene and 9-methylanthracene in EMIC/$AlCl_3$ melts.

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Final Technical Report
AFOSR Grant F49620-93-1-0129

Department of Chemistry
University of Tennessee, Knoxville

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Principal Investigators

November 8, 1995

The following is a summary of the research accomplishments and progress made during the period February 15, 1993 through September 30, 1995 under AFOSR Grant F49620-93-1-0129.

A. List of Publications Resulting from this Grant

G. S. Chen, I. W. Sun, K. D. Sienerth, A.G. Edwards, and G. Mamantov, "Removal of Oxide Impurities from Alkali Haloaluminate Melts Using Carbon TetraChloride", J. Electrochem. Soc., 140, 1523 (1993).

G. S. Chen and G. Mamantov, "Electrochemical Studies of Tantalum in Fluorochloroaluminate Melts at 200-450°C", Proceedings of the International Symposium on Molten Salt Chemistry and Technology, 1993, M. L. Saboungi and H. Kojima, eds., The Electrochemical Society, Inc., Pennington, NJ, 1993,pp. 276-283.

K. D. Sienerth and G. Mamantov, "Recent Studies of the Electrochemical Behavior of Nb(V) in $AlCl_3$-$NaCl_{sat}$ and Related Melts", Proceedings of the International Symposium on Molten Salt Chemistry and Technology, 1993, M. L. Saboungi and H. Kojima, eds., The Electrochemical Society, Inc., Pennington, NJ, 1993, pp. 365-375.

G. S. Chen, A. G. Edwards , and G. Mamantov, "Electrochemical Studies of Tantalum in Fluorochloroaluminate Melts at 200-400°C", J. Electrochem. Soc.,140, 2439 (1993).

I-W. Sun, A. G. Edwards, and G. Mamantov, Spectroscopic and Electrochemical Studies of Tungsten (VI) and Tungsten(V) Chloride and Oxychloride Complexes in

Sodium Chloride Saturated Sodium Chloroaluminate Melt", J.Electrochem. Soc., 140, 2733 (1993).

G. Hondrogiannis, C. W. Lee, R. M. Pagni, and G. Mamantov, "The Novel Photochemical Behavior of Anthracene in a Room Temperature Molten Salt", J. Am. Chem. Soc., 115, 9828 (1993).

E. M. Hondrogiannis and G. Mamantov, "Spectroelectrochemical Investigation of the Behavior of Tetra-Chloro-p-Benzoquinone in Molten Sodium Chloroaluminates", Appl. Spectrosc., 48, 406 (1994).

K. D. Sienerth, E. M. Hondrogiannis, and G. Mamantov, "A Reinvestigation of the Electrochemical Behavior of Nb(V) in $AlCl_3$-$NaCl_{sat}$ and Related Melts", J.Electrochem. Soc., 141, 1762 (1994).

E. M. Hondrogiannis and G. Mamantov, "Electrochemical and Spectroelectrochemical Investigation of K_2ReCl_6 and $[Bu_4N]Re_2Cl_6$ in the $AlCl_3$-$NaCl_{sat}$ Melt", Proceeding of the International Symposium on Molten Salt Chemistry and Technology, C. L. Hussey, D. S. Newman, G. Mamantov, and Y. Ito, eds., The Electrochemical Society, Inc., Pennington, NJ, 1994, pp. 521-524.

R. M. Pagni, G. Mamantov, C. W. Lee, and G. Hondrogiannis, " The Photochemistry of Anthracene and its Derivatives in Room Temperature Molten Salts", Proceeding of the International Symposium on Molten Salt Chemistry and Technology, C. L. Hussey, D. S. Newman, G. Mamantov, and Y. Ito, eds.,The Electrochemical Society, Inc., Pennington, NJ, 1994, pp. 638-645.

G. Mamantov, G. Guang-Sen Chen, H. Xiao, Y. Yang, E. M. Hondrogiannis, "Electrochemical and Spectroscopic Studies of Tungsten Species in the $AlCl_3$-$NaCl_{sat}$ Melt", J. Electrochem. Soc., 142, 1758 (1995).

E. M. Hondrogiannis and G. Mamantov, "Spectroscopy Electrochemistry, and Spectroelectrochemistry of Rhenium Chlorides in the $AlCl_3$-$NaCl_{sat}$ Melt", J. Electrochem. Soc., 142, 2532 (1995).

C. Lee, T. Winston, A. Unni, R. Pagni, and G. Mamantov, “The Photoinduced Electron Transfer Chemistry of 9-Methylanthracene, Substrate as Both Electron Donor and Acceptor in the Presence of the 1-Ethyl-3-methylimidizolium Ion “, submitted to J. Am. Chem. Soc., September 1995.*

1. Introduction

This program involves several aspects of the chemistry, electrochemistry, photochemistry, and spectroscopy of selected systems in molten halides. Molten halides, are used in the production of several important elements, such as aluminum, magnesium and fluorine, in some high energy battery systems, as well as in other applications.

Of particular interest to this program are haloaluminates and fluorochloroaluminates characterized by the presence of complex ions, such as $AlCl_4^-$ and $AlCl_nF_{4-n}^-$ ($n \leq 4$). This results in solute chemistry quite different from that observed in pure chlorides or fluorides. The most significant example of these differences concerns the stability of different oxidation states of refractory metals in the various media.

Due to the high sensitivity of the melts and of the solute species to atmospheric contaminants, care must be taken in the interpretation of the results. Of particular concern is oxide contamination which may result from the interaction of some melts with Pyrex glass.

*Copy included as Appendix V

2. Recent Progress

A. Purification of Alkali Haloaluminate Melts

Oxide impurities in molten chloroaluminates have pronounced effects on the chemical and electrochemical behavior of solute species. Basic alkali chloroaluminates ($AlCl_3$/NaCl mole ratio $<$ 1) pose really serious problems in this respect as the oxide content can be very high and greatly affect the chemistry and electrochemistry of metal solute species such as Nb(V), Ta(V), and W(V). Removal of oxide impurities from alkali chloroaluminates using phosgene (1) has been previously reported. The highly poisonous nature of phosgene, and the fact that the oxide conversion into chlorides is not complete in acidic chloroaluminate melts ($AlCl_3$/NaCl mole ratio $>$ 1), has led to the search for equally effective alternatives. A method which completely converts the oxide impurities to chlorides by treatment of the melt with carbon tetrachloride has been developed (2).

Basic chloroaluminate melts containing oxides (either aluminum oxychloride or $NbOCl_5^{2-}$, added as $NbOCl_3$) were treated with the appropriate amount of CCl_4 at temperatures of the order of 200°C. The progress of the reaction was monitored by observing the decrease of the aluminum oxychloride infrared bands at 680 and 800 cm^{-1} (3). The reaction was much faster than with phosgene resulting in the complete removal of oxide in two hours.

The reaction products were chloride ions and CO_2. The latter can be removed from the melt, together with the excess carbon tetrachloride, by evacuation. The same treatment may be used to convert refractory metal oxychlorides into the corresponding chlorides. This was proved by following the decrease of the UV-visible bands at 220 and 270 nm of $NbOCl_5^{2-}$ during the treatment of a melt containing $NbOCl_3$.

The method proved to be equally effective in removing oxide impurities from acidic chloroaluminate melts ($AlCl_3$-NaCl 63-37 *m/o*) where the progress of the reaction was followed by monitoring the spectral changes due to the transformation of $WOCl_4$ into WCl_6.

Carbon tetrachloride was also used to remove oxide impurities from fluorochloroaluminates at temperatures of the order of 400°C , for $NaAlCl_4$-NaF (90-10 m/o), by adding an excess of CCl_4, and allowing it to react for ca. 30 min. The excess tetrachloride and CO_2 were removed at lower temperature under vacuum.

B. Electrochemical and Spectroscopic Studies of Refractory Metal Species in Basic Alkali Haloaluminates.

The electrochemistry and metallurgy of refractory metals has received much attention in the last decades due to their increasing technological importance. Mellors and Senderoff (4-9) published a series of papers dealing with a general method for obtaining pure, coherent deposits of refractory metals by electrolytic reduction from the ternary eutectic LiF-NaF-KF (45.5-11.5-45.0 mole percent, FLINAK). Since then additional research has been devoted to studies of refractory metal reduction in molten fluorides (10-20).

Previous activity by this group in the chemistry and electrochemistry of refractory metals has been limited to molten alkali chloroaluminates which have liquidus temperatures below 200 °C (melt composition in the range 48.9 to 100 mole percent $AlCl_3$), much lower than the 454°C of the eutectic point of FLINAK. Refractory metal deposition in the latter melt requires, in addition, temperatures in excess of 750 °C with all the material problems connected with the highly aggressive nature of fluoride melts. Chloroaluminates, on the contrary, may be conveniently handled using simple Pyrex cells and , most important, the Lewis melt acidity of chloroaluminates can be varied over a broad range by changing the $AlCl_3$ to NaCl ratio. This results in a great change of the chemical properties of the solvent that affects`the nature of the species dissolved in the melt and their electrochemical behavior.

Previous attempts to obtain coherent deposits of tantalum (22), niobium (23) and tungsten (24) in acidic chloroaluminates have shown that highly stable and/or insoluble low oxidation state cluster species are formed preventing further reduction to metal. The use of NaCl saturated $AlCl_2$-NaCl melt and of fluoride-containing chloroaluminate melts treated with $COCl_2$ or CCl_4 to remove oxide impurities was viewed as a possible solution to the problem. Fluorine containing melts may be a possible compromise between the use of fluoride melts under severe experimental conditions and low-temperature chloroaluminate melts where the stability of cluster species prevents reduction to the metal. Chloroaluminate melts containing varying amounts of fluorine have been studied by Raman spectroscopy (25) and the phase diagram of the pseudo-binary system $NaAlCl_4$-NaF has been determined using differential thermal analysis (26).

The following summarizes the results obtained on the different systems.

B. 1. Tantalum

The electrochemistry of tantalum (29, 28) was investigated in $NaAlCl_4$-NaF (90-10 mole %) purified with CCl_4 in the temperature range 200-450°C using a variety of electrochemical techniques , including cyclic voltammetry, normal pulse, square wave voltammetry, and exhaustive controlled potential coulometry. Spectroscopic techniques, such as Raman and UV-visible, together with X-ray diffraction, have been used to characterize the solvent and the products of the electrochemical reactions. Previous work (22, 27) in $AlCl_3$-NaCl melts [51-49 mole percent (m/o)] at 175°C], has shown that the reduction of Ta(V) follows the sequence: $Ta^{5+} + e = Ta^{4+}$, $2\,Ta^{4+} = Ta_2^{8+}$, $Ta_2^{8+} + 2e = Ta_2^{6+}$, $5\,Ta_2^{6+} = Ta_6^{14+} + 4\,Ta^{4+}$. Hence, in acidic chloroaluminates the reduction led to the formation of a tantalum cluster. In basic chloroaluminates (27) the study of the reduction of tantalum(V) as a function of the oxide concentration has resulted in a voltammetric method to determine the amount of dissolved oxide impurities.

Tantalum has been introduced into the fluorochloroaluminate melt as $TaCl_5$, which, given the high concentration of chloride ions present in the solvent, was believed to be present as $TaCl_6^-$. The electrochemical behavior is strongly dependent on temperature. At temperatures higher than 300°C, three main reduction and four re-oxidation waves were observed. The first and second reduction waves merge at lower temperatures. The combination of the data obtained using the different electrochemical techniques indicated the following electrochemical reaction sequence:

$Ta^{5+} + e = Ta^{4+}$ (1)

followed by the dimerization process

$2\ Ta^{4+} = Ta_2^{8+}$ (2)

Reaction (2) occurs very slowly at temperatures lower than 300°C. This accounts for the temperature dependence of the second reduction process which is believed to be a two electron process leading to an unstable tantalum(III) species that decomposes to give the cluster $Ta_6\,Cl_{12}^{3+}$; i.e.

$Ta_2^{8+} + 2e = Ta_2^{6+}$ (3)

$9\ Ta_2^{6+} = 6Ta^{4+}$ (or $3\ Ta_2^{8+}$) + $2\ Ta_6^{15+}$ (4)

At temperatures lower than 300°C, the first and second reduction processes merged into one wave indicating that the reaction sequence was an ECEC process consisting of reactions 1 to 4. Reaction (1) is the main reaction, owing to the slowness of the following chemical reactions 2 and 4.

The third reduction, although present at any temperature, became more prominent with increasing temperature and was ascribed to the electrode reaction

$Ta_2^{6+} + 2e = Ta_2^{4+}$ (5)

Limited formation of Ta_2^{6+} accounted for the ill-defined voltammetric wave at low temperature (〉 300°C). The product of reaction 5 was unstable and decomposed quickly to form the tantalum cluster Ta_6^{14+} (or Ta_6^{12+}) and metallic tantalum. The following chemical reaction was proposed

$7\ Ta_2^{4+} = 2Ta_6^{14+} + 2\ Ta^0$ (8)

The work has demonstrated that, contrary to what happens in molten chloroaluminates, metallic tantalum may be obtained from fluorochloroaluminate at temperatures much lower than in FLINAK.

B. 2. Niobium

The electrochemistry of niobium(V) (30) was reinvestigated in oxide-free $AlCl_3$-$NaCl_{sat}$ and in fluorochloroaluminates. Previous studies in non-oxide free molten chloroaluminates (23) indicated that Nb(V) was first reduced to Nb(IV) in a one-electron step. The first reduction was followed by three additional reduction steps resulting in a subvalent niobium chloride cluster species which was quite unstable. This prevented further reduction to niobium metal. As the possible existence of niobium oxide species was not known, the previously proposed reaction involving only niobium chloride species was erroneous.

Nb(V), added to an oxide-free NaCl saturated $NaAlCl_4$ melt at 178 °C as $NbCl_5$, was present in the melt as such together with some $NbCl_6^-$ as demonstrated by the UV-visible spectra. The spectral changes induced by the addition of oxide to the melt clearly demonstrated formation of a moiety niobium oxychlorides. The same type of evidence was obtained by cyclic voltammetry in the presence or absence of oxide. Four main oxidation waves were observed in both cases. The presence of oxide affected mainly the first cathodic process, which occurred at more negative potentials than in the absence of oxide.

Based on the results obtained using cyclic voltammetry, Normal pulse, square wave voltammetry, controlled potential electrolysis, and UV-visible spectroscopy, the following reaction sequence was proposed

$Nb^{5+} + e = Nb^{4+}$ (E1)

$3\ Nb^{4+} + 4e = Nb_3^{8+}$ (E2)

$2\ Nb_3^{8+} + e = Nb_6^{15+}$ (E3)

$Nb_6^{15+} + n\ e = Nb_6^{(15-n)+}$ (E4)

At long times and high concentration some of the experimental results suggested that a chemical step involving disproportionation of Nb^{4+} into Nb^{3+} and Nb^{5+} followed the first reduction step. Under these conditions the following steps may occur between E1 and E2

$2\ Nb^{4+} = Nb^{3+} + Nb^{5+}$ (C)

$3\ Nb^{3+} + e = Nb_3^{8+}$ (E2').

Although electrode filming was observed at the level of the third and forth reduction steps, formation of metallic niobium at this temperature was excluded due to the high stability of the niobium cluster moieties.

The electrochemistry of Nb(V) was also studied in $AlCl_3$-$NaCl_{sat}$ and $AlCl_3$-$NaCl_{sat}$-NaF at different temperatures. As inferred from cyclic voltammetric data, the overall electrochemical behavior, which was strongly dependent on the temperature, was similar in the two melts. As the temperature was increased from 200 to 500°C, the first reduction wave became progressively broader until it resembled a plateau at high temperature. At the same time, the other three reduction waves merged into a single large wave. At temperatures higher than 350°C, a new wave was observed close to the cathodic limit. No sufficient data were available to explain this temperature dependence.

Some evidence for the formation of thin coatings of niobium metal on nickel and tungsten electrodes was obtained during constant current electrolysis at low current densities in $AlCl_3$-$NaCl_{sat}$ and $AlCl_3$-$NaCl_{sat}$-NaF melts at temperatures of the order of 500 °C or higher.

B. 3. Tungsten.

Tungsten is known to exhibit a wide variety of oxidation states ranging from + 6 to 0; some of the lower oxidation states involve the cluster $W_6Cl_{12.}$ In previous studies of W(VI) in acidic chloroaluminates of different composition (24, 31) oxide contamination could not be completely avoided. The electrochemistry of W(VI) has been, therefore, reexamined in oxide free $AlCl_3$-NaCl melts saturated with NaCl (32, 33).

Raman and UV-visible absorption spectroscopies indicated that the addition of WCl_6 or $KWCl_6$ to a sodium chloride saturated sodium chloroaluminate melt at 175 °C produced $[WCl_6]^-$ resulting from the probable chemical reduction of W(VI) to W(V) by the free chloride ions in the melt. The electrochemical behavior was strongly dependent on the scan rate. At low scan rates $[WCl_6]^-$ was either oxidized to WCl_6 or reduced to $[WCl_6]^{2-}$ in one-electron reversible steps. At low scan rates, the latter reduction was followed by four additional steps indicating very complex electrochemistry. The overall shape of the cyclic voltammograms depended on the switching potential. The analysis of the data indicated that W(IV) underwent a chemical reaction leading to a product that was either adsorbed or deposited on the electrode causing the appearance of a stripping peak on the anodic scan. The same product was further reduced at more cathodic potentials.

The overall picture was somewhat simpler at scan rates higher than 10 V/s. Only four reduction and four oxidation processes were observed in the cyclic voltammograms. The first two reductions were the same as those found at the lower scan rates. Because of the decreased time window, the chemical reaction, which followed formation of W(VI) at low scan rates, did not have time to occurs and $[WCl_6]^{2-}$ was further reduced to $[WCl_6]^{3-}$. The shape of the last reduction wave was quite similar to that obtained for the reduction of WCl_{12} in acidic chloroaluminates.

The dissolution of $WOCl_4$ in $AlCl_3$-NaCl melts saturated with NaCl gave rise to a reddish orange solution. The UV-visible spectrum was similar to that of gaseous $WOCl_4$ indicating that the oxychloride was stable in the melt and was, not chemically reduced as was the case for the corresponding hexachloride. W(V), in the form of $[WOCl_5]^{2-}$, was obtained through a reversible one-electron reduction. The electrochemical data indicated that tungsten oxychorides with oxidation states lower than 3+ were chemically converted into the corresponding chlorides in the melt. No evidence for tungsten metal formation in these melts was obtained.

Further studies on the electrochemistry of W(V), introduced into in $AlCl_3$-NaCl melts saturated with NaCl as $KWCl_6$, were performed using a variety of electrochemical and spectroscopic techniques (33). The following sequence for the six electrochemical steps involved in the reduction of W(V) was proposed

First step	$W^{5+} + e = W^{4+}$
	$2\ W^{4+} = W_2^{8+}$ (slow reaction)
Second Step	$W_2^{8+} + e = W_2^{7+}$
Third step	$W^{4+} + e = W^{3+}$
	$W^{3+} \rightarrow$ rapid decomposition
Fourth step	$W_2^{7+} + 2\ e = W_2^{5+}$
	$W_2^{5+} \rightarrow$ rapid decomposition
Fifth step	$W_6^{12+} + e = W_6^{11+}$
	$12\ W_6^{11+} = 6\ W + 11\ W_6^{12+}$
Sixth step	$1/6\ W_6^{12+} + 2\ e = W$

Identification of the different oxidation states was performed either by spectroscopic means or by addition of the appropriate compounds to the melt. X-ray diffraction was used to identify metallic tungsten, which was identified among the products of exhaustive electrolysis at potentials close to the cathodic limit of the solvent.

B. 4. Rhenium

Rhenium(IV), added as K_2ReCl_6, and the metal-metal bonded rhenium(III) complexes, $[Bu_4N]_2Re_2Cl_8$ and Re_3Cl_9, were studied in the $AlCl_3$-$NaCl_{sat}$ melt at 175 °C using a variety of electrochemical and spectroelectrochemical techniques (34). Dissolution of K_2ReCl_6 resulted in a yellow-green solution containing, as shown by UV-visible spectra, the complex ion $[ReCl_6]^{2-}$. The cyclic voltammogram of a fresh solution of K_2ReCl_6 changed shape with an increasing number of scans to reach a steady-state shape consisting of three reduction and two oxidation waves. The initial cyclic voltammograms showed only two reduction and two oxidation processes. In order to propose a reaction sequence the three reduction waves were analyzed as a function of the scan rate. Identification of the products of each electrochemical process was performed using the UV-visible spectra obtained in thin-layer cells polarized at different potentials and by comparison of the electrochemical curves and spectra obtained by directly dissolving into the melt the metal-metal bonded compounds $[Bu_4N]_2Re_2Cl_8$ and Re_3Cl_9.

Based on the spectroscopic, electrochemical, and spectroelectrochemical studies of the three compounds the following reaction sequence was proposed:

First reduction wave $[ReCl_6]^{2-} + e \rightarrow [ReCl_6]^{3-}$

$$[ReCl_6]^{3-} \rightarrow [ReCl_6]^{2-} + [Re_2Cl_8]^{2-} + Re^0 + X$$

$$[ReCl_6]^{3-} + [ReCl_6]^{2-} \rightarrow [Re_2Cl_9]^{2-} + 3Cl^-$$

where X represents other products. Co-existence of $[ReCl_6]^{2-}$, $[Re_2Cl_8]^{2-}$ and $[Re_2Cl_9]^{2-}$ was indicated by UV-visible spectra and by comparison with data obtained in $AlCl_3$-MEIC melts (35).

Second reduction wave $[ReCl_6]^{2-} + e \rightarrow [ReCl_6]^{3-}$

$$[Re_2Cl_8]^{2-} + e \rightarrow [Re_2Cl_8]^{3-}$$

Again, evidence for the formation of $[Re_2Cl_8]^{3-}$ was obtained from spectroscopic data in melts containing $[ReCl_6]^{2-}$ in the presence of aluminum metal. Other spectroscopic data pointed out the possible existence at this potential of the species $[Re_3Cl_{(12-x)}]^{(4-x)-}$ that may result from decomposition or dispropotionation of one of the rhenium(III) species.

The electrochemical parameters of the third reduction wave , and the corresponding oxidation process, were those expected for adsorption and stripping waves. Attempts to characterize the precipitate formed during bulk electrolysis of the third wave failed.

C. Organic Solute Studies in Molten Sodium Chloroaluminates.

A variety of spectroelectrochemical techniques, including Raman, UV-visible and ESR, was used to study the chemistry and electrochemistry of Tetra-chloro-p-benzoquinone in molten chloroaluminates of different composition (36). Previous electrochemical and spectroscopic studies in acidic $AlCl_3$-NaCl melts (37-39) showed that in acidic melts chloranil is complexed with $AlCl_3$ (or $Al_2Cl_7^-$) at one of the carbonyl oxygens and at the carbon-carbon double bonds. The IR spectroelectrochemical results suggested stepwise one-electron reductions to produce complexed radical anion and dianion. No evidence for complexation was found in basic melts where one overall two-electron reduction was observed. Reinvestigation of the system in basic melt using either UV-visible , Raman and ESR spectroelectrochemical cells, revealed transient absorption bands consistent with a previously not identified radical anion intermediate.

D. Photochemistry in Room Temperature Melts

The course of the photochemistry of organic compounds in room temperature molten salts is dictated by the redox properties of the substrate and molten salt. When the electron transfer from the excited state of the substrate to the acceptor, usually an imidazolium or pyridinium cation, is exothermic, the photochemistry is dominated by the electron transfer. When the electron transfer is endothermic, however, the photochemistry occurs through the excited state of the substrate instead. *cis*- and *trans*-Stilbene, for example, underwent cis- trans isomerization from their respective singlet excited states in basic 1-ethyl-3-methylimidazolium chloride (EMIC; 55 mol %)/$AlCl_3$ (40). In basic *N*-butylpyridinium chloride (BPC; 55 mol %)/$AlCl_3$, on the other hand, cis-trans isomerization occured via the respective radical cations of the two stilbenes (40) . The butylpyridinium ion, which is a much better oxidant than is the imidazolium ion, favored the electron transfer pathway.

Anthracene underwent a 4+4 cycloaddition reaction in deoxygenated basic EMIC/$AlCl_3$ from its singlet excited state (41). In the presence of O_2, however, the dimerization was suppressed and anthraquinone became the major product. This chemistry was likely initiated by electron transfer from the singlet excited state of anthracene to O_2 (42).

In deoxygenated acidic EMIC/$AlCl_3$ (55 mol % $AlCl_3$), anthracene yielded a complex mixture of oxidized, neutral and reduced monomeric and dimeric products (41). This chemistry was initiated by electron transfer from the singlet exited state of anthracene to protonated anthracene, formed by the reaction of the hydrocarbon with traces of HCl, a strong acid in the medium (43). Anthracene served as both electron donor and, through its conjugate acid, as electron acceptor as well. This had never been observed previously. It was possible to mimic this unusual behavior by photolyzing anthracene in CF_3COOH containing 2% CF_3SO_3H, a medium in which anthracene and protonated anthracene coexist (44).

9-Methylanthracene (46), a substrate more easily oxidized than anthracene, underwent photoinduced electron transfer in deoxygenated basic EMIC/$AlCl_3$ and BPC/$AlCl_3$, with EMI^+ and BP^+ serving, respectively, as electron acceptors. The products of the two photoreactions were somewhat different, however. In EMIC/$AlCl_3$ not only was the radical cation of 9-methylanthracene generated in the photoreaction but also its radical anion, generated by electron transfer from the imidazolium radical to 9-methylanthracene. This did not occur in BPC/$AlCl_3$ because the relevant electron transfer is endothermic. The formation of a radical cation and radical anion of a substrate during a photochemical reaction had not been observed previously.

These studies have demonstrated that, under appropriate conditions, many species including melt components, may serve as electron acceptors in photoinduced electron transfer reactions.

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45. C. Lee, T. Winston, A. Unni, R. M. Pagni, and G. Mamantov, to be submitted to *J. Am. Chem. Soc.*

Appendix I

Personnel Involved in This work

1. Professor Gleb Mamantov,* principal investigator.
2. Professor Richard Pagni, coprincipal investigator.
3. Dr. Guang-Sen Chen, postdoctoral research associate supported by this program during the period 2/15/93-7/20/93.
4. Dr. Haiming Xiao, postdoctoral research associate, supported by this program during the period 11/10/93-9/30/95.
5. Dr. Yvette Yang, part-time postdoctoral research associate, supported by this program during the period 2/15/93-7/31/95.
6. Dr. Anna Edwards, part-time postdoctoral research associate, not supported by this program.
7. Karl D. Sienerth, Ph.D. student, not supported by this program.
8. Ellen Hondrogiannis, Ph. D. Student, not supported by this program.
9. Carlos Lee, Ph.D. student, not supported by this program.
10. Sven Eklund, Ph.D. student, not supported by this program.
11. George Hondrogiannis, Ph.D. Student, partially supported by this program.
12. Dr. James Chambers and Dr. Charmaine Mamantov were both partially supported by the program from 3/15/95-9/30/95.

*Deceased March 12, 1995

Appendix II

Dissertations Resulting From This work*

E. M. Hondrogiannis, Spectroscopic, Electrochemical and Spectroelectrochemical Investigations of Several Solute Species in Molten Sodium Chloroaluminates, The University of Tennessee, 1994.

C. Lee, The Photochemistry of Anthracene and 9-Methylanthracene in the Room-Temperature Molten Salts, The University of Tennessee, 1995.

*Both dissertations are available from The University of Tennessee.

Appendix III

Participation and Presentations at Meetings

International Symposium on Molten Salt Chemistry and Technology*, Honolulu, HI, May, 1993.

(1) Electrochemical Studies of Tantalum in Fluorochloroaluminate Melts at 200-450°C.

(2) Recent Studies of the Electrochemical Behavior of Nb(V) in $AlCl_3$ - $NaCl_{sat}$ and Related Melts

Gordon Research Conference, Tilton, NH, August, 1993.
The Na/B" Alumina/S(IV) Molten Chloroaluminate Cell: Recent Developments

Spring Meeting of The Electrochemical Society, May, 1994.
Participated in the student poster session.

*Session Chairman

Appendix IV

A. Honors and Awards During Contract Period

Max Bredig Award, The Elecrochemical Society, May, 1993.

Named Fellow of the Electrochemical Society, February, 1995, presented posthumously October, 1995.

B. Cumulative Awards

Phi Kappa Phi, Omicron Delta Kappa, NSF Travel Award to International Congress on Polarography, 1964 and to the Institute of Inorganic Chemistry, Kiev, 1974; two NSF awards to support attendance at short courses on electronics for scientists (1963) and small digital computers (1969); NATO Senior Postdoctoral Fellowship for studies in inorganic chemistry at the University of Heidelberg - 2 months in 1972; Chancellor's Research Scholar, 1977; Fellow, American Association for the Advancement of Science, 1980; University of Tennessee Macebearer, 1980-81; Fellow, American Institute of Chemists, 1980; Phi Beta Kappa, 1980; Meggers Award (Society for Applied Spectroscopy), 1983; Who's Who in the South and Southwest, 1984; Distinguished Professor, 1986; Who's Who in America, 1988; Participant in the National Academy of Sciences Exchange Program with the Soviet Union, 1989; Charles H. Stone Award of the ACS Carolina-Piedmont Section, 1989; UTK Chapter Phi Kappa Phi Scholar Award, 1990; Foreign member, Latvian Academy of Sciences, 1991.

Appendix V

The Photoinduced Electron Transfer Chemistry of 9-Methylanthracene. Substrate as Both Electron Donor and Acceptor in the Presence of the 1-Ethyl-3-methylimidazolium Ion

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Abstract

Photolysis of 9-methylanthracene (**1a**; 9-MeAn) in a deoxygenated molten salt consisting of 1-ethyl-3-methylimidazolium chloride (**3**; EMIC) (55 mol %) and $AlCl_3$ at room temperature yields, in addition to the anti 4+4 dimer (**2**), six products, four of which are dimeric (two oxidized [**8** and **9**]; two neutral [**4** and **5**]) and two of which are monomeric (one reduced [**7**]; one neutral [**6**]). The same products are produced in CH_3CN containing **3**. These six products arise by initial electron transfer from 9-MeAn^{*1} to EMI^+ to form the radical cation of 9-MeAn and EMI•. The reduced product **7** arises by electron transfer from EMI• to 9-MeAn. This system thus contains both the radical cation and radical anion of 9-MeAn at various stages of the reaction.

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† Deceased March 12, 1995

Ordinarily photoinduced electron transfer (PET) reactions occur between different substrates, with one in an excited state and the other in the ground state.[1,2] The Rehm-Weller equation[3] that describes the free energy change of the process suggests, however, that electron transfer between the same species to form its radical cation and radical anion is also possible, i.e. the free energy of the reaction is negative, if the species is both relatively easy to oxidize and reduce and the reaction is carried out in a solvent with a large dielectric constant . Nonetheless, this behavior has not been observed in solution. Anthracene (An) in CH_3CN, for example, should undergo such an electron transfer, but its exciplex collapses to a 4+4 dimer instead.[4,5] We wish to report that it is possible to prepare the radical cation and radical anion of the same species via photoinduced electron transfer, not by direct electron transfer but indirectly using a second species as the electron carrier.

Photolysis of 9-methylanthracene (9-MeAn; **1a**) in CH_3CN yielded the anti 4+4 dimer (**2**) exclusively.[8] Photolysis of 9-MeAn, on the other hand, in CH_3CN which was 3.41M in 1-ethyl-3-methylimidazolium chloride (EMIC; **3**), a potential electron acceptor, or the room temperature molten salt, EMIC (55 mol %)/$AlCl_3$,[9] afforded **2** (major product) and six other products (**4-9**) (Table 1), all of which were synthesized independently. Four of the products, **2**, **4**,[10] **5**[10] and **6**,[10] have the same oxidation state as 9-MeAn (identical empirical formulas), while **7**[11] is reduced and **8**[12] and **9**[12] are oxidized. The photoreaction which is largely bimolecular was faster in the less viscous CH_3CN,[13] and more of the reaction occurred by the 4+4 pathway in CH_3CN. Those products which possess the anthracene chromophore were either formed in trace amounts or increased in yield as a function of time and then decayed.

Although the majority of the photoreaction occurred by the pathway yielding **2**, some of the reaction also occurred, as evidenced by products containing the 9-anthrylmethyl moiety (9-AnCH$_2$), by photoinduced electron transfer from **1a**^{*1}[14] to EMI$^+$ (Scheme 1).[15] In CH$_3$CN, where the electron transfer is somewhat endothermic (Table 2), only about 1% of the overall reaction occurred by PET;[16] in the molten salt, where the electron transfer is somewhat exothermic, approximately 20% of the reaction occurred in this fashion.

Scheme 1

$$\mathrm{AnCH_3} \xrightarrow{h\upsilon} \mathrm{AnCH_3}^{*1}$$

$$\mathrm{AnCH_3}^{*1} + \mathrm{AnCH_3} \longrightarrow \text{Exciplex} \longrightarrow \text{4+4 Dimer}$$

$$\mathrm{AnCH_3}^{*1} + \mathrm{EMI}^{+} \longrightarrow \mathrm{AnCH_3}^{+\bullet} + \mathrm{EMI}\bullet$$

$$\mathrm{AnCH_3}^{+\bullet} + \mathrm{Cl}^{-} \longrightarrow \mathrm{AnCH_2}\bullet + \mathrm{HCl}$$

Experiments using deuterated 9-MeAn (**1b**)[17] in the nondeuterated molten salt and **1a** in the deuterated molten salts containing 2-deuterio EMIC[18] or 2,4,5-trideuterio EMIC[18] showed that the added hydrogens in **7** and the repositioned hydrogens in **4**, **5** and **6** arose from two sources, the methyl group of **1** and the hydrogen at position 2 of **3** (See Supplementary Material for details). This is a consequence of the fact that HCl arising from methyl group and EMI$^+$, a carbon acid in water,[19] serve as proton donors. **6**, for example, arose by protonation of AnCH$_2^-$, formed by electron transfer from EMI$\bullet$ to AnCH$_2\bullet$, by HCl and EMI$^+$.[20] AnCH$_2^-$ is known to be protonated at both the methylene group and carbon 10,[21] whereas AnCH$_2\bullet$ only abstracts hydrogen at the methylene group.[22]

The reduced product **7** was generated ultimately by protonation of the radical anion of **1** which was formed by electron transfer from EMI$\bullet$ to **1**, a reaction which is exothermic in both CH_3CN and the molten salt (Table 2).[23] That this is true was demonstrated in two ways. Firstly, metal (Li/liquid NH_3) and electrochemical (bulk electrolysis in the molten salt) reduction, both of which yield $\mathbf{1}^{-\bullet}$, gave **7** exclusively. Secondly, when the photolyses were carried out in CH_3CN containing 1.2M *N*-butylpyridinium chloride (BPC), a much more readily reduced electron acceptor than EMIC (Table 2), and the molten salt BPC (55 mol %)/$AlCl_3$,[24] **8** and **9** - but no **7** - were formed.[25] In these cases the forward electron transfer is exothermic, i.e. from $\mathbf{1}^{*1}$ to BP^+, but the reverse electron transfer from $BP\bullet$ to **1** is not.[26]

Scheme 2

$$\mathrm{EMI}\bullet + \text{9-MeAn} \longrightarrow \mathrm{EMI}^{+} + \text{9-MeAn}^{-\bullet}$$

$$\text{9-MeAn}^{-\bullet} \longrightarrow \longrightarrow 7$$

The formation of both $\mathbf{1}^{+\bullet}$ and $\mathbf{1}^{-\bullet}$ is unusual but should not be unique. There should be many other pairings of donor and acceptor in which the two relevant electron transfers are exothermic, the donor radical cation has a chemical outlet, and the reduced form of the acceptor has sufficient chemical stability to serve as an electron donor.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research and the National Science Foundation. TW and AV thank the University of Tennessee Science Alliance Center of Excellence for summer support. CL thanks "The Black Graduate Opportunity Program Fellowship" for support.

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(13) The viscosity of CH_3CN at 25°C is 0.345 cp *(Handbook of Chemistry and Physics*; 63rd ed.; CRC Press: Boca Raton, FL, 1983) and that of the molten salt is 32.5 cp.[9b]

(14) Electron transfer from the triplet state of 9-MeAn to EMI^+ is far too endothermic

to contribute to the reaction.

(15) This is based on the behavior of other methyl-substituted arenes. See Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290.

(16) If back electron transfer to regenerate **1a** and EMI^+ is important, PET may be more important than is apparent from the product yields.

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(22) Treatment of 9-chloromethylanthracene with tributyltin hydride and AIBN yields **1a** exclusively.

(23) If one ignores the Coulombic term which should be small in any event, $\Delta G = -8.31$ kcal/mol (CH_3CN) and -9.2 kcal/mol ($EMIC/AlCl_3$) for $EMI\bullet + 9\text{-MeAn} \rightarrow EMI^+ + 9\text{-MeAn}^{-\bullet}$.

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(25) Other products formed include small amounts of **2**, 9-pentylanthracene, 9-methyl-10-butylanthracene and *N*-butyl-1,4-dihydropyridine

(26) $\Delta G = +10.1$ kcal/mol for $BP\cdot + 9\text{-MeAn} \rightarrow BP^{+} + 9\text{-MeAn}^{-\bullet}$ in CH_3CN if one ignores the small Coulombic term.

Table 1. Photochemistry of 9-Methylanthracene in the Presence of 1-Ethyl-3-methyl-imidazolium Chloride.[a,b]

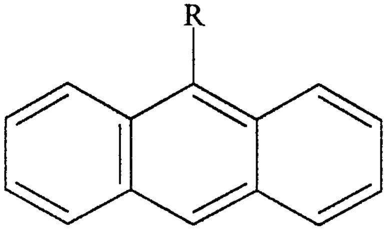
Medium	Time (h)	Product (%)[c,d]								Material Balance (%)
		1	**2**	**4**	**5**	**6**	**7**	**8**	**9**	
Molten Salt[e]	3	57.2	21.1	1.0	1.2	t	1.3	t	1.0	>82.8
Molten Salt[e]	17	25.8	49.1	1.4	2.4	t	2.2	t	5.8	>86.7
Molten Salt[e]	36	18.3	60.4	0.9	1.0	t	2.9	t	10.0	>93.5
3/CH_3CN[f]	3	8.2	76.0	t	t	0.1	0.1	t	0.5	>84.9
3/CH_3CN[f]	17	4.0	79.0	t	t	0.2	0.1	t	0.9	>84.2
3/CH_3CN[f]	36	0.4	83.0	t	t	0.2	0.2	t	0.7	>84.5

(a) Degassed solution photolyzed in a pyrex vessel on a Rayonet reactor at 350 nm. (b) At t=O, 100% **1a**. (c) Yields based on starting **1a**. (d) t = trace amount. (e) 0.065M **1** in **3** (55 mol %)/$AlCl_3$. (f) 0.065M **1** and 3.41M **3** in CH_3CN.

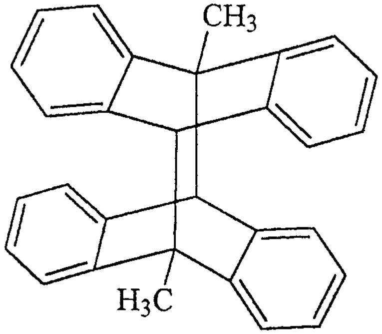
Table 2. Free Energy Changes for PET Processes.[a]

Compound	Solvent	$E_{00}(S)$ (kcal/mol)	$E_{1/2}(OX)$[b] (V)	$E_{1/2}(RED)$[b] (V)	$\Delta G(D^* + A)$[c] (kcal/mol)
9-MeAn (D)	CH_3CN	74.1	.797	-2.31	
	$EMIC/AlCl_3$	73.0	.692	-1.85	
	$BPC/AlCl_3$	73.0[d]	e	e	
EMIC (A)	CH_3CN			-2.67	+5.8
	$EMIC/AlCl_3$			-2.25[f]	-5.2
BPC (A)	CH_3CN			-1.87	-12.6
	$BPC/AlCl_3$			-1.5[f]	

(a) $\Delta G = 23.06\ [E^0(D^+/(D)-E^0(A/A^\cdot)]-E_{00}S$ when the acceptor is ionic.[1,2] (b) Reference electrodes: $Ag/AgNO_3(CH_3CN)$; Al wire in $EMIC/AlCl_3$(2:1) for $EMIC/AlCl_3$; Al wire in $BPC/AlCl_3$(2:1) for $BPC/AlCl_3$. (c) D = donor; A = acceptor). (d) Assumed to be identical to value in $EMIC/AlCl_3$. (e) 9-MeAn is not oxidized or reduced within the limits (+0.6 to -1.5V) of the molten salt. (f) Cathodic limit.



1a $R = CH_3$
1b $R = CD_3$



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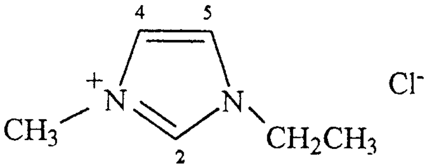

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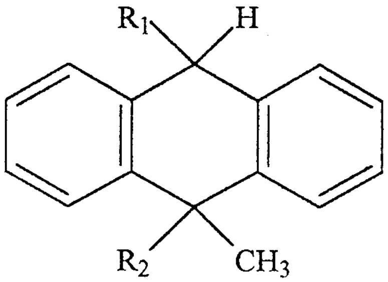
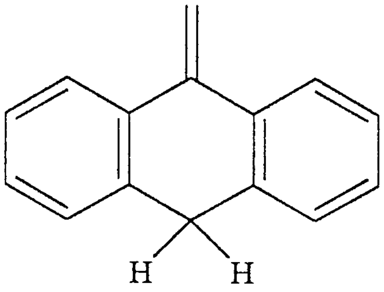
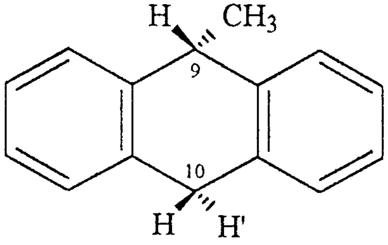


4 R_1 = 9-anthrylmethyl, R_2 = H
5 R_1 = H, R_2 = 9-anthrylmethyl



6



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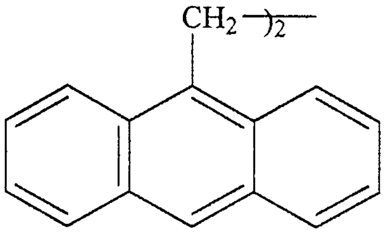

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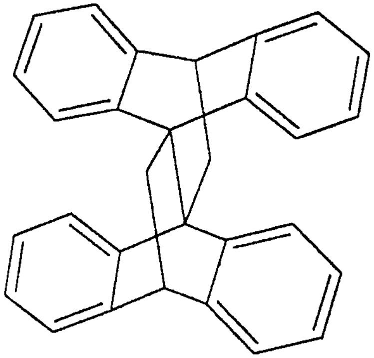

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Supplementary Material

Methods, Chemicals and Instruments. 1-Ethyl-3-methylimidazolium chloride (**3**) and $AlCl_3$ were prepared and purified as described elsewhere.[1] 9-Methylanthracene (Aldrich) (**2**) was recrystallized once from ethanol. Molten salts and solutions of 9-methylanthracene in the molten salts were prepared in a nitrogen atmosphere glove box, and manipulated by Shlenk line techniques. Photolysis was carried out in vacuum-sealed pyrex glass tubes in a Rayonet Type RS Photochemical Reactor using 3500 Å lamps. Reaction mixtures were quenched in ice water. After the aqueous phase was neutralized by 6 M sodium hydroxide, the organic products were extracted into methylene chloride. Products were isolated by column chromatography on silica gel (petroleum ether), and prep HPLC on a Varian Model 5000 HPLC, which had a programmable gradient elution capability, a variable UV wavelength detector and a Varian 4400 Integrator. A Whatman Partisil 10 ODS-3 column was used for product separation (98% CH_3CN/H_2O). Product yields and ratios were determined by a combination of ^1H NMR spectroscopy (Brucker 250 and 400 MHz instruments), GC/MS (Hewlett-Packard 5890 Gas Chromatograph and 5970 Series Mass Selective Analyzer, with a crossbonded 100% dimethyl polsiloxane column), using internal standards where appropriate, and by weight. EMIC-d_1 (**3**-d_1)[2] (4% H at C-2) EMIC-d_3 (4-5% H at C-2, C-4 and C-5), and 9-methylanthracene-d_3 (**1b**)[3] (5% H at methyl) were prepared by literature methods.

Characterization of Products.

9-Methylanthracene Photodimer (2). This compound was identical to an authentic sample of **2** prepared by photolysis of **1a** in deoxygenated CH_3CN.

9-(9-Anthrylmethyl)-10-methyl-9,10-dihydroanthracene (4). This compound was identical to a sample of **4** synthesized independently.[4]

9-(9-Anthrylmethyl)-9-methyl-9,10-dihydroanthracene (5). This compound was identical to a sample of **5** synthesized independently.[4]

9-Methylene-9,10-dihydroanthracene (6). This compound was identical to a sample of **6** synthesized independently.[4]

9-Methyl-9,10-dihydroanthracene (7). This compound was identical to a sample of **7** synthesized independently.[5]

1,2-Bis(9′-anthranyl)ethane (8). This compound was identical to a sample of **8** synthesized independently.[6]

Lepidopterene (9). This compound was identical to a sample of **9** synthesized independently.[6]

Deuterium Analyses.

Compound 6. The deuterium content was determined by mass spectrometry using the molecular ion. For reaction of **1a** in the monodeuterated molten salt after 17 hours, **6** consisted of 64% d_o, 34% d_1, and 2 % d_2. For reaction of **1b** in the nondeuterated molten salt after 17 hours, **6** consisted of 72% d_2, 26% d_3, and 2% d_4. Because **6** should not contain d_2 and d_4 when **1a** and **1b** are photolyzed, respectively, 2% represents the error limits of the analysis.

Compound 7. There are six mono- and dideuterio-analogs of 7 which can be produced in the photoreaction: no d (A), 9-d (B), 10-d (C), 10′-d (D), 9,10-d_2 (E), and 9,10′-d_2 (F) [see paper for assignments]. By a combination of MS and ^{1}H and ^{2}H NMR spectroscopy, it is possible in principle to deduce the contribution of all six components. Unfortunately, the proton-decoupled ^{2}H NMR spectra, obtained in an unlocked mode, were not well enough resolved to be useful. Thus, less than the maximum information content was obtained. For MS, the M-CH_3 peak was used. The ^{1}H resonances were assigned based on the work of Strothers.[7] The results were as follows: (1) For photolysis of **1a** in the monodeuterated molten salt for 17 hours, A = 33%, B = 9%, C+D = 48%, E+F = 10%, C+E = 37%, and D+F = 21%. The order of abundance of the six species is: A > C > D > B > E, F. The total deuterium content at each position is: 9, 19%; 10, 37%; 10′, 21%. (2) For photolysis of **1b** in the nondeuterated molten salt for 17 hours, A = 35%, B = 16%, C+D = 35%, E+F = 14%; C+E = 42%, and D+F = 7%. The order of abundance of the six species is: A $\geq$ C > B > E > F, D. The total deuterium content at each position is 9, 30%; 10, 42%; 10′, 7%.

Compounds 4 and 5. Because the compounds are only formed in trace amounts in CH_3CN, only the reaction of **1a** in the monodeuterated molten salt for hours was analyzed. Because the compounds are air sensitive and difficult to separate, the analysis was carried out by MS on a mixture of the two compounds. It was not possible to quantitate the deuterium content because the fragmentation pattern of each compound was not appropriate for such an analysis. Nonetheless, by comparing the MS of nondeuterated **4** and **5** to the test sample, it is apparent that **4** and **5** contain deuterium.

For the reaction of **1a** in the trideuterated molten salt, the products had a deuterium distribution similar to that for reactions run in the monodeuterated molten salt.

Recovered **1a** and **1b** from the photolyses showed little deuterium incorporation and loss, respectively, after photolysis in the appropriate molten salts.

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