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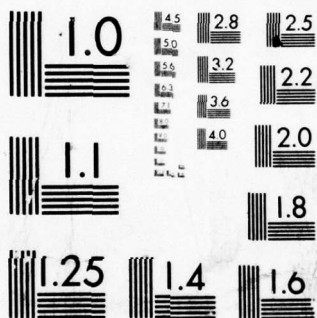
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BASIC STUDIES OF THE LITHIUM SECONDARY ELECTRODE

Technical Report
for Period 01 February 1977 — 31 January 1978

Contract No. N00014-77-C-0155
Task No. NR 359-638

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Prepared for
OFFICE OF NAVAL RESEARCH
Arlington, Virginia 22217

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20. Abstract (Cont.)

products were observed to form irrespective of electrolyte purification procedure. In fact, highly purified media reacted most readily with Li presumably due to the absence of protective film-forming gases such as O₂ and N₂. Extended pre-electrolysis of LiClO₄/THF electrolytes formed large amounts of basic material, as expected. The same experiment performed on LiAsF₆/THF electrolyte revealed essentially no change in the medium's pH. Apparently, the AsF₃ from AsF₆⁻ and the basic material from THF degradation effectively neutralize each other. A mechanism which accounts for Li-cyclic ether reactivity is proposed.

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I. INTRODUCTION

The development of a practical Li secondary battery ultimately depends on the proper management of the Li electrode. This means that all electrodeposited Li must be eventually resolubilized as Li^+ . It has been established that Li can be plated with 100% efficiency (1,2). Electrodeposition, however, invariably results in <100% efficiency. The difference represents that Li isolated from the electrode by an insulating film of Li-electrolyte reaction products. Indeed, the reactivity of as-plated Li with a variety of aprotic organic solvents is widely documented (3-6).

This program is focused on gaining an understanding of the chemistry associated with Li-electrolyte reactivity. Specifically, we wish to determine if electrolyte impurities initiate the reaction, or if the electrolyte itself is intrinsically reactive toward Li. It is known that impurities grossly mediate Li-electrolyte reactions in methyl acetate (MA) (7) and propylene carbonate (PC) (8). By scrupulously purifying solvent and salt, we hope to exclude impurities as a potential source of electrolyte degradation.

Tetrahydrofuran (THF) was chosen initially for study in this work because it embodies a wide variety of physical and chemical properties which favor its use in a secondary Li battery. It has, for example, a wide liquid range (-108 to +65°C at 1 atm), and low viscosity (0.461 cp at 25°C). It forms conductive solutions with Li salts, and THF itself is expected to manifest low chemical reactivity to reducing environments. With respect to the Li electrode, this last feature is of critical importance.

Aliphatic cyclic ethers like THF are very resistant to ring opening. The energy of the C-O bond is on the order of 85-91 kcal/mol, similar to that of an sp^3 C-C bond (9). While THF is routinely used as an inert solvent for dissolving metal reductions employing Li or Na (10) and reductions with LiAlH_4 (11), electrolytes prepared from it are known to anodically polymerize (12) and react with Li foil at elevated temperatures (3). In the latter instance, it is suggested that electrolyte reactions with Li were initiated by impurities.

In this report the effects of scrupulous solvent purification on the rate of Li/THF reactivity are investigated. Reaction products from Li/THF and Li/ LiAsF_6 /THF media were collected and identified. Finally, a mechanism is proposed to account for Li-cyclic ether reactivity.

II. REACTIONS OF TETRAHYDROFURAN AND LITHIUM HEXAFLUOROARSENATE AND WITH LITHIUM

A. Introduction

In an earlier publication (13), we found that electrolytes incorporating tetrahydrofuran (THF) as the solvent reacted with Li irregardless of salt and purification procedure. Since an understanding of Li-electrolyte reactivity is necessary for the development of a practical secondary Li electrode, this work focuses on the analysis of the kinds and distribution of these reaction products. We tacitly assume that an appreciation of Li-THF chemistry will enable us to design electrolytes in which the Li electrode is stable.

Because THF incorporating LiAsF₆ gave better cycling and storage behavior than media containing LiClO₄ or LiBF₄ (13), LiAsF₆ was employed in the present study. We also noted (13) that the presence of the AsF₆ anion initiated the formation of a brown film which uniformly coated the Li surface. It is therefore of interest to determine whether there is any connection between the superior inertness to Li of electrolytes containing LiAsF₆ and the brown film.

Reactive impurities are known to either accelerate or retard the rate of Li-electrolyte reactivity, presumably through the intervention of films (13-17). To avoid this ambiguity we sought to generate solvent free of H₂O and reactive gases. To this end, THF was distilled off benzophenone ketyl ($\phi_2\text{CO}^{\cdot-}$, Na⁺) in the glove box and sealed with Li in a Pyrex ampoule.

Reaction products were generated by incubating THF and THF/LiAsF₆ electrolytes with Li foil at 71°C; by cycling the Li electrode in a half-cell configuration; and by galvanostatic pre-electrolysis between two Li electrodes. Soluble organic products as well as solid corrosion products on Li were collected and spectroscopically characterized. On the basis of these products, a reaction scheme accounting for their generation is proposed.

B. Experimental

1. General

All purification procedures and the electrochemical experiments themselves were conducted at room temperature under an Ar atmosphere in a Vacuum-Atmospheres Corporation dry box equipped with a Model HE-493 Dri-Train. The dry box atmosphere was continuously recirculated through a

column containing molecular sieves and an activated Cu gettering material (BASF catalyst R3-11) which scavenged moisture and oxygen.

UV spectra were recorded on a Perkin-Elmer 124D Spectrophotometer. Structural elucidations were accomplished with a Varian T-60 pmr instrument (Northeastern U.) and a Beckman Acculab 5 ir Spectrophotometer. Glc analyses were performed on a Varian Model 920 gas chromatograph employing a 5' x 0.25" 10% OV-101 on Chromosorb-W column. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN). ESCA scans were run by Surface Science Laboratories (Palo Alto, CA). pH determinations were made with a Corning Digital 110 Expanded Scale meter.

2. Materials

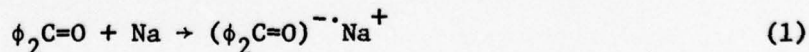
Tetrahydrofuran (THF) (Burdick & Jackson, distilled-in-glass), lithium hexafluoroarsenate (LiAsF_6) (U.S. Steel Agri-Chemicals, electrochemical grade), lithium perchlorate (LiClO_4) (Anderson Physics highest purity), and arsenic trifluoride (AsF_3) (Alfa-Ventron) were used as-received. Lithium foil (15 mil) was obtained from Foote Mineral Co. sealed under Ar.

Activated neutral alumina (Fisher, Brockman Activity 1) and molecular sieves (Linde, 4A) were used as-received, and exposed only to the dry box atmosphere. Approximately 1 g desiccant per 5 ml of electrolyte was used in a given purification procedure. The first 10% eluting through a column was always discarded.

3. Electrolyte Preparation and Purification

All electrolytes were prepared with cooling to minimize potential decomposition. The following abbreviations are used to represent purification procedures: A, solvent through alumina, then the Li salt added in the cold; S, solvent through molecular sieves, then the Li salt added in the cold; APA, A followed by pre-electrolysis, then passage through a thin plug of alumina to remove Li fines.

Distillation of THF off benzophenone ketyl ($\phi_2\text{CO}^-$, Na^+) was accomplished as follows: A 250 ml round bottom flask containing 100 ml THF, 1 g benzophenone, and ~5 g Na was fitted with a 500 ml Dewar condenser. Cu shot, which had been cooled to dry ice temperature in the glove box antechamber, served as the coolant. The contents of the flask were heated to boiling after which a deep blue color (indicative of the benzophenone radical-anion) pervaded the solution (Eq. 1). After 1 hr at reflux,



a 250 ml evaporator trap was interposed between the flask and condenser (Fig. 1), and distillation commenced. The condenser was replenished with

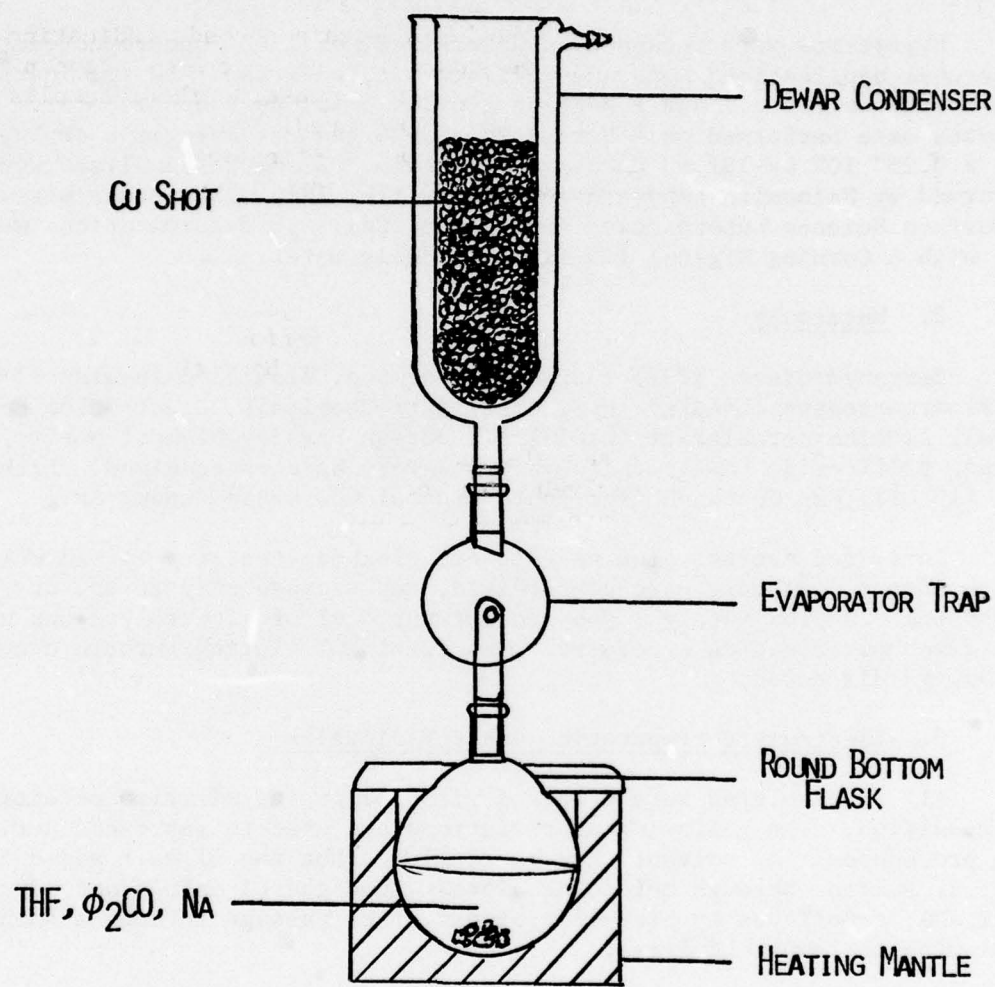


Fig. 1. Apparatus used to distill THF off benzophenone ketyl inside an Ar filled glove box.

cold shot as required. The first few 25 ml portions of THF which collected in the trap were returned to the pot. Subsequent cuts were tested with small portions (~5 ml) of ink-blue benzophenone ketyl solution. Initially, freshly distilled THF decolorized the ketyl within seconds indicating that trace amounts of H₂O and/or reactive gases were present -- perhaps picked up by the THF from the walls of the trap or condenser. These samples were returned to the pot and the distillation continued. The sixth 25 ml cut was observed to sustain the blue ketyl color indefinitely. This solvent, deemed free of H₂O and reactive gases, was subsequently sealed in a Pyrex ampoule with Li for storage at 71°C.

The ampoule was fabricated from 11 mm OD thick wall Pyrex tubing. One end was sealed; to the other a $\frac{1}{8}$ 10/30 female joint was attached. The ampoule was thoroughly cleaned with detergent, rinsed, then cleaned with 10% HF. After several rinses with twice-distilled H₂O, the ampoule was baked out in a 450°C furnace and allowed to cool in the evacuated antechamber of the glove box. THF (which sustained the benzophenone ketyl) was used to twice rinse both the ampoule and a 42 cm² Li roll before a 2 ml portion of the highly purified solvent was added. The ampoule was next fitted with a $\frac{1}{8}$ 10/30 Teflon sleeve and mated to a stopcock equipped with dual $\frac{1}{8}$ 10/30 male joints. The stopcock was closed and the assemblage transferred from the glove box to a vacuum line. After cooling for 30 min in a dry ice/acetone bath, the ampoule was evacuated to 50 μ Hg and sealed off with a torch. The vapor pressure of THF at dry ice/acetone temperatures is negligible. The area to volume ratio was 21 cm⁻¹.

The sealed ampoule was then transferred to a Blue M bacteriological incubator thermostatted at 71 \pm 2°C.

Criteria for Li-THF reaction were twofold: visual signs of corrosion on the Li ribbon; coloration of the solvent noted by comparison with a tube containing fresh solvent. Purified THF stored in the absence of Li remained clear and colorless indefinitely. Other storage tests were conducted in 16 \times 100 mm culture tubes (Corning, C9826) equipped with Teflon-line screw caps. Li foil, 5.0 \times 6.35 cm was spiral wound and scratched after which 8 ml of solvent or electrolyte was added to the tube, yielding an area/volume ratio of 8 cm⁻¹.

4. Cells and Electrodes

Glass rectangular cells (10 \times 40 \times 60 mm, Vitro Dynamics) were used for the galvanostatic plating and stripping of Li, as described previously (13). The working electrode was a 5.5 cm \times 3.8 cm \times 5 mil strip cut from Ni 200 sheet (Roblinger). The counter electrode was fabricated from 15 mil Li ribbon. Details regarding cell assembly, cycling experiments and the galvanostatic pre-electrolysis technique may be found elsewhere (13).

5. Electrochemical Instrumentation

Chronopotentiometric plating and stripping was conducted with either a Wenking LT 73 potentiostat in the galvanostatic mode, or with a constant current power supply (constructed in-house). Long term experiments utilized an automatic cyler (constructed in-house) which allowed plating for a given period of time, then stripped to a preset potential (+1.0 V). Upon reaching this potential, stripping was terminated and the cell reverted to OCV until plating again commenced.

6. Product Workup and Isolation

Reaction products of Li and THF or THF-based electrolytes were recovered from both 71°C storage tests and 25°C cycling experiments. The organics were added to 100 ml H₂O which was subsequently extracted with 3 × 50 ml portions of ether. The combined organic fractions were then washed once with 50 ml H₂O to remove any remaining salts. After drying over anhydrous MgSO₄ and filtering, the ether was stripped on a rotary evaporator under aspirator vacuum. Traces of solvent were carefully evaporated with a stream of N₂ yielding a pungent yellow oil in all cases. These reaction products were weighed and then analyzed by glc. Weights of recovered products ranged from 50 to 800 mg, the higher yields corresponding to longer storage times at 71°C. Some products were collected by preparative glc and their ir and pmr spectra compared to those of authentic samples or to published spectra.

pH determinations of pre-electrolytes aliquots were accomplished by diluting 1 ml of THF-based electrolyte to 10 ml with twice distilled H₂O. The electrolyte was sampled by pipetting aliquots through a plug of glass wool. This precluded the introduction of Li fines into the sample which would have yielded anomalously high pH readings.

7. Brown Film Analysis

ESCA data from scans run on transparent brown film adhering to a Ni substrate. Normalized atom % of detected elements: As, 7.5; F, 26; Li, 43; c, 17; O, 6.7.

Elemental analysis of brown film from electrolyte pre-electrolysis. Found, wt %: C, 1.74; H, 0.03; Li, 8.24; F, 22.74; As, 49.68; O, 17.30 by difference. Calculated empirical formula: Li_{1.17} F_{1.20} As_{0.66} O_{1.08}. Compound stoichiometries: LiF_{1.07}; As₂O_{3.27}.

Elemental analysis of "brown film" synthetically generated from AsF₃ and BuOLi. Found, wt %: C, 0.79; H, 0.17; Li, 18.04; F, 52.08; As, 22.60; O, 6.32 by difference. Calculated empirical formula: Li_{2.57} F_{2.74} As_{0.30} O_{0.40}. Compound stoichiometries: LiF_{1.02}; As₂O_{2.67}.

C. Results and Discussion

1. Static Reactivity of THF-Based Media with Li at 71°C

The stability of solvent or electrolyte to bulk Li can be conveniently determined by storing the system under test with Li foil at an elevated temperature. By visually monitoring the onset of Li corrosion and solvent coloration with time, a reactivity order can be compiled for a series of media.

In Table 1, data comparing solvent/electrolyte reactivity towards bulk Li is presented as a function of purification procedure. Molecular sieves (S) remove H₂O, and alumina (A) removes H₂O as well as other organic contaminants (18). Distillation of THF off benzophenone ketyl yields solvent free of H₂O and reactive gases such as O₂ and CO₂ (19), and this technique is the subject of a patent (20). Finally, the alumina-pre-electrolysis-alumina (APA) technique removes from an electrolyte protic contaminants as well as gases which react with Li, i.e., N₂, O₂, and CO₂ (13). If impurities are the source of, or initiate electrolyte degradation, one then would expect the stability of these media to increase on going to higher levels of purification.

As seen in Table 1, THF out of the bottle (no purification) began to react with Li after one day of storage. Corrosion invariably started at the scratch marks, as well as on the edge of the freshly cut Li ribbon. At the end of 14 days, the surface of the Li ribbon was uniformly corroded to a battleship-grey color. The solution began to turn pink after three days had elapsed. This color deepened to brick-red by the 14th day, after which no further change took place. The THF was clear at all times throughout the 30 day storage period. THF passed through sieves or alumina, or distilled off benzophenone ketyl manifested the same coloration/corrosion behavior, albeit over different time intervals.

The addition of LiAsF₆ to THF markedly changed the reactivity of this series of samples toward Li. Unpurified electrolyte began to take on a yellow cast after 16 days, while Li ribbon in the presence of A remained bright and shiny over 25 days. In terms of inertness, there is little to choose between APA and no purification. In this series, Li corrosion resulted in a chocolate brown film beginning at freshly cut or scratched surfaces and spreading over the Li foil. This is in contrast to the grey corrosion of Li observed in the presence of THF alone. Indeed, the brown Li corrosion product which forms during these static tests is identical in color to that observed on the Li anode during pre-electrolysis. All LiAsF₆/THF solutions eventually yellowed. There was never any hint of a red coloration, as had been observed with THF alone. These results indicate that solvent and electrolyte are initially rendered more stable to Li, and that a stability maximum is reached after treatment with alumina. But the most

Table 1

The Onset of Li Reaction with THF-Based Electrolytes at 71°C

Purification Procedure	Time, days	
	THF	1M LiAsF ₆ /THF
None	1(3) ^a	2(16)
S	1(7)	1(7)
A	4(7)	25(28)
Benzophenone Ketyl	3(2)	-
APA	-	4(7)

^aObservable Li corrosion after 1 day; observable solvent coloration after 3 days.

stringent procedures result in media which are only marginally less reactive to Li than their unpurified precursors.

On the basis of these observations and earlier work (13), we believe that dissolved gases (particularly N₂ and O₂) react with Li to form protective films. These films then retard the rate of reaction between Li and THF itself.

2. Spectroscopic Evaluation of Solvent and Electrolyte Reaction Products

The use of ultraviolet and infrared spectroscopy was essential in following the appearance of electrolyte/Li degradation products, and in establishing their structure. UV analysis was conducted on samples of electrolyte during purification, after storage with Li at 71°C, and after cycling experiments had been completed. Infrared spectra were run on isolated organic product mixtures extracted from electrolytes involved in both storage and cycling experiments.

Table 2 presents the UV absorbance at certain wavelengths of solvent and electrolyte during each stage of an APA purification procedure. THF and out of the bottle is transparent in the UV from 400-210 nm where solvent cutoff occurs. No change in the UV spectrum was noted after passing the solvent through an alumina column. The addition of LiAsF₆ to the solvent altered the spectrum slightly. Although the cutoff remained unchanged, a shoulder at λ_{\max} 253 nm appeared. This band may be due to the $n \rightarrow \sigma^*$ transition of the AsF₆⁻ non-bonding electrons. Anions are known to manifest weak absorptions in the near UV which often appear as a shoulder (21). Alternatively, the species absorbing at 253 nm may be an impurity introduced by the LiAsF₆. In this regard, we note that its intensity marginally decreased after pre-electrolysis and remained unchanged after filtration through a small plug of alumina. The effect of pre-electrolysis time on the UV spectra of electrolytes has been considered by us previously (13).

Having established that APA electrolyte is essentially clean to its 210 nm solvent cutoff, changes undergone in the UV spectrum after contact with Li were investigated subsequently. In Table 3, absorptions due to degradation products from bulk storage and cycling experiments are tabulated. The UV spectra of THF and LiAsF₆/THF are quite similar. Both manifested absorption bands at ~318 and ~267 nm, and the presence of LiAsF₆ seems to have little, if any, effect on the kinds of products formed. Although these samples were stored with Li for approximately the same time interval, the intensity of the degradation products from THF/Li is an order of magnitude larger than those from THF/LiAsF₆/Li. This is in consonance with the visual observations regarding media coloration with time noted previously in Table 1: unpurified THF reacts with Li more rapidly than APA electrolyte. The UV spectrum of electrolyte stored at 71°C in the absence of Li was

Table 2

UV Absorptions of Solvent and Electrolyte at Various Stages of Purification

Medium	λ_{max} , nm	Absorbance
<u>THF</u>		
A) B & J "Distilled in Glass"	210 cutoff	-
B) Through Alumina (A)	210 cutoff	-
<u>1M LiAsF₆/THF</u>		
C) Salt Added	253, 210 cutoff	0.10
D) Pre-Electrolysis (AP)	253, 210 cutoff	0.04
E) Through Alumina (APA)	253, 210 cutoff	0.04

Table 3
UV Absorptions of THF-Based Media after Contact with Li

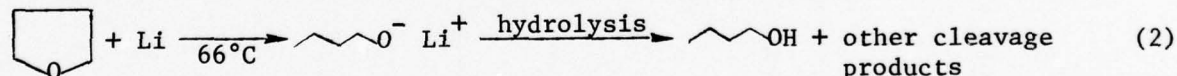
Medium	Days at 71°	Coul/cc	λ_{max} , nm	Absorbance
THF	10	-	317, 268	1.57, 4.31
1M LiAsF ₆ /THF-APA	7	-	319, 265	0.15, 0.42
1M LiAsF ₆ /THF-APA	-	4.5 (Li on Ni)	287, 253	0.26, 0.58
1M LiAsF ₆ /THF-APA	-	6.7 (Li on Li)	286, 253	0.49, 0.72

identical to that of freshly prepared electrolyte. The last two entries in Table 3 compare the UV spectra of electrolytes cycled to and from Ni and Li substrates. The similarity in degradation products generated at two diverse working electrode surfaces indicates that in these systems, Ni manifests no special catalytic properties which facilitate electrolyte reduction.

The UV spectra of media exposed to bulk Li at 71°C and to the Li electrode at 25°C are similar in their absorbance bands and relative intensities. This suggests that the kinds and distribution of soluble degradation products are not mediated by the presence of LiAsF₆ or metal substrate. More substantial evidence supporting this hypothesis was gleaned from ir and glc studies conducted on isolated organic reaction products.

Table 4 compares product distribution and ir functional group assignment for a series of reaction product mixtures isolated from solvent and electrolyte. In all cases, irregardless of purification procedure, the presence of LiAsF₆, or the mode of product generation, one major and several minor components were noted in the glc trace. In all samples, the major peak eluted at the same retention time as did four of the minor peaks. Furthermore, the ir spectra of all product mixtures were virtually identical. Absorption bands at 3350 cm⁻¹ and 1720 cm⁻¹ may be associated with hydroxy and carbonyl stretching frequencies. No C-H stretching bands above 3000 cm⁻¹ were noted indicating that the reaction mixture consisted solely of saturated C-C bonds. Although the relative intensities of all absorption bands varied from one spectrum to another, their positions were coincident within ± 10 cm⁻¹.

The major peak was collected via preparative glc, and its ir spectrum was found to be identical to that of n-butanol. This was not a particularly surprising result since Eisch previously reported on the reductive cleavage of THF with Li to yield n-butanol and other cleavage products (22)(Eq. 2).



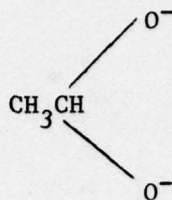
The presence of n-butanol in the reaction mixture accounts for the hydroxy stretching frequency noted at 3350 cm⁻¹, but not the carbonyl absorption at 1720 cm⁻¹.

The identification of other components observed in the glc trace was facilitated by obtaining a pmr spectrum of the reaction mixture. The key to the interpretation of this spectrum was the presence of a downfield quartet at δ5.1 coupled to a doublet at δ1.3, J = 5.5 Hz. Other resonances about δ1.3 precluded a clean integration of the doublet. Nevertheless, the observed A₃X splitting pattern is characteristic of a CH₃CHX₂ moiety, where X is an electronegative atom. Since oxygen is the most electronegative constituent of the THF molecule, we may assume a partial structure as represented by I:

Table 4

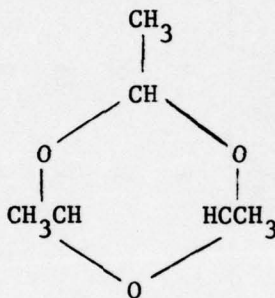
Analysis of Li-THF Reaction Product Mixtures from
71°C Storage and from Cycling Studies

Medium	Days at 71°C	Coul/cc	GLC Peaks Major Minor	Functional Groups, Infrared
THF	90	-	1 5	-OH, >=0
THF off $\phi_2\text{CO}^-$, Na^+	147	-	1 5	-OH, >=0
1M LiAsF ₆ /THF	60	-	1 11	-OH, >=0
1M LiAsF ₆ /THF-APA	34	-	1 9	-OH, >=0
1M LiAsF ₆ /THF-APA	-	6.7 (Li on Li)	1 8	-OH, >=0



I

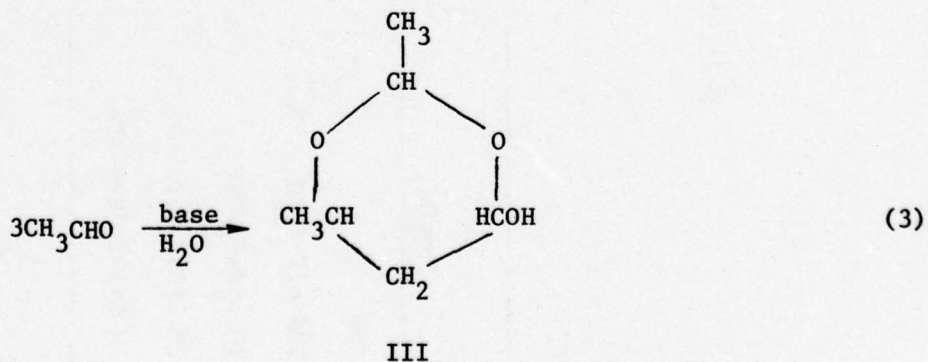
The downfield shift position of a methinyl hydrogen in this chemical environment occurs between $\delta 4.5$ - $\delta 6.3$ (23). One candidate which satisfies the splitting pattern under discussion is paraldehyde (II). Its pmr spectrum manifests a



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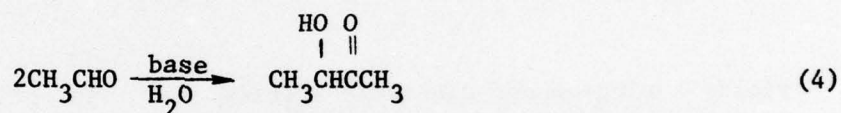
quartet at $\delta 5.05$ and a doublet at $\delta 1.4$, $J = 5.0$ Hz (24). Paraldehyde is the trimer of acetaldehyde, and acetaldehyde and ethylene have been identified as thermal decomposition products of THF (25).

Another compound which satisfies the aforementioned pmr multiplets is a methylated hydroxyacetal (III), also a trimer of acetaldehyde (26) (Eq. 3).



But these trimers alone plus *n*-butanol neither account for all of the observed absorbances in the pmr spectrum nor the carbonyl band in the ir. A mixture of these compounds along with acetaldehyde would, however.

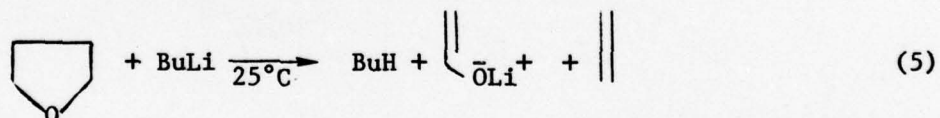
To ascertain whether the aldehydic portion of the isolated reaction product mixture could be synthetically generated, authentic acetaldehyde (Aldrich) was shaken with a dilute solution of NaOH in H₂O. Base was used in this synthetic mixture in order to mimic the alkalinity of the THF/Li product extraction's aqueous phase. After the usual workup, a colorless pungent oil was isolated. The ir of this material included the carbonyl band at 1720 cm⁻¹, as well as all of the other bands observed in the THF/Li reaction mixture. Furthermore, the glc trace of the synthetic material revealed four peaks which had the same retention time as four of the minor peaks from the THF/Li degradation product mixture. These peaks were found to superimpose when both samples were coinjected. Although the ir spectrum of aldol (IV) a dimer of acetaldehyde (Eq. 4), was quite similar to



IV

the ir of the THF/Li products, no correspondence between the respective glc traces was noted.

Besides being produced by thermal decomposition of THF (25), acetaldehyde may also be generated (after workup) by the action of a strong base on THF. Bates and coworkers demonstrated that *n*-butyllithium (BuLi) cleaves THF to give ethylene and the enolate anion of acetaldehyde (27) (Eq. 5).

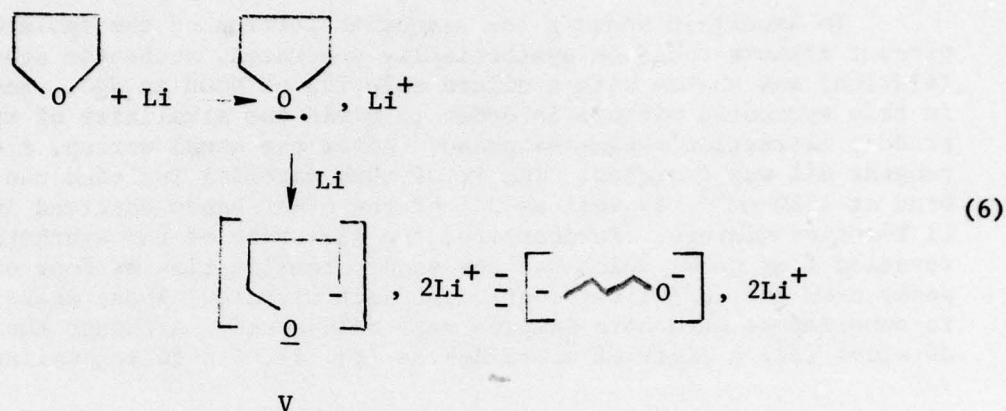


Since *n*-butanol is a known reaction product, and since lithium *n*-butoxide (BuOLi) is present in the reaction mixture prior to hydrolysis (Eq. 2), we set out to determine whether BuOLi could initiate the cleavage reaction. Thus, BuOLi prepared from Li and *n*-butanol was incubated with THF at 71°C for 10 days. No coloration changes were noted, and, after the usual workup, only *n*-butanol was found. Apparently, BuOLi does not participate in the generation of aldehydic degradation products.

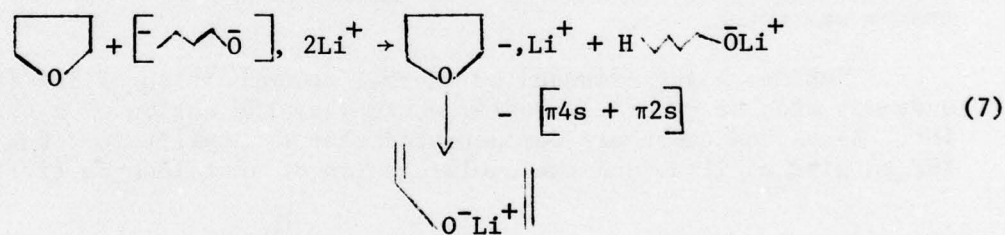
3. Mechanistic Considerations

The spectroscopic results, product analysis, and other observations can be formulated into a reaction mechanism which satisfies all of the data. We

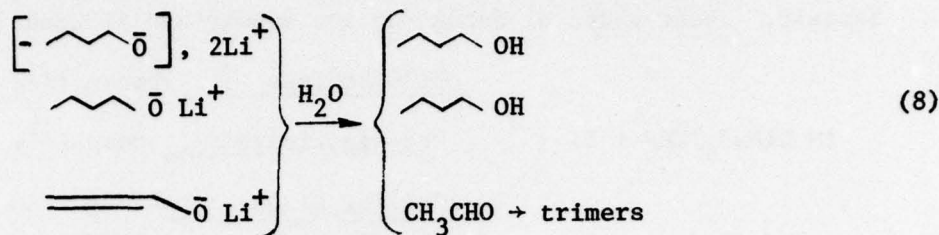
propose an initial one-electron transfer from Li to the lowest unfilled molecular orbital (LUMO) centered on the oxygen atom of THF. Further reduction by Li



yields a ring-opened dianionic species, V. The primary carbanionic center is a strong base, and can abstract an α -proton from another THF molecule in analogy with the action of BuLi on THF (27) Eq. 7.

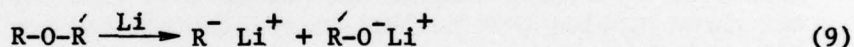


Subsequent cycloreversion according to the Woodward-Hoffmann rules affords ethylene and the enolate anion of acetaldehyde (27). Hydrolysis of these intermediates in the ether/H₂O extraction procedure leads to n-butanol and acetaldehyde. Acetaldehyde can then go on to form the trimeric materials implicit in the ir and pmr spectra (Eq. 8).



Ethylene was detected by refluxing THF with Li foil over a 48 hour period. Reaction gases were passed through a solution of Br₂ in CCl₄ as per Carnahan and Clossan (28). Workup of the trap contents yielded a mixture of organic products, one of which had the same glc retention time as authentic 1,2-dibromoethane

There is ample precedent for the overall stoichiometry of cleavage reactions of ethers with alkali metals (29), namely



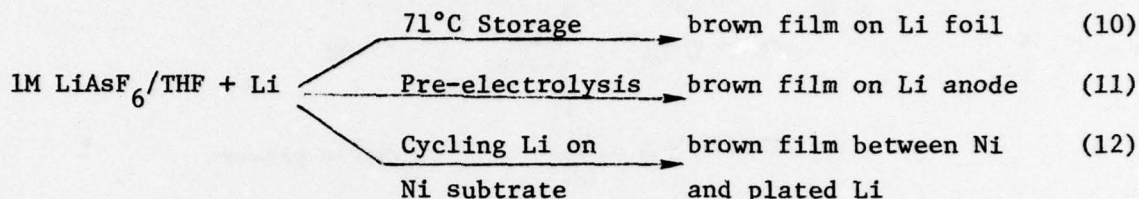
The details of electron transfer are, however, less certain. Molecular orbital calculations and electrochemical reductive cleavage reactions conducted on chlorinated benzenes indicate that the first electron enters a LUMO - σ* antibonding orbital (30). This molecular orbital is approximated by a linear combination of localized sp² C and 3p Cl atomic orbitals. CNDO/2 calculations indicated that virtually all of the excess electron density lies in the C-Cl bond, the electronegative Cl atom bearing from 2/3 to 3/4 of the total density (30). We envisage the reduction of ethers to be similarly initiated in that the LUMO of the ether may be approximated by sp³ C and 2p O atomic orbitals. Transfer of an electron from Li to this LUMO places excess electron density in the C-O bond, thus predisposing it to subsequent cleavage or ring opening as in the case of THF.

4. The Role Played by AsF₆⁻ in Electrolyte Degradation Reactions

Anions of a supporting electrolyte are generally perceived to be chemically inert. Yet, BF₄⁻ is known to interact with electron-deficient organic intermediates during electrochemical oxidation reactions (31). It was therefore not surprising to find AsF₆⁻ active with respect to Li.

In an earlier report (32) and paper (13) we observed that Li in the presence of THF/LiAsF₆ electrolyte developed a chocolate brown coating. This material formed after several days when electrolyte was stored with Li at 71°C, and after several minutes on the anode when the electrolyte was

pre-electrolyzed. Furthermore, on cycling Li to and from a Ni substrate a thin, transparent brown film formed on the Ni surface beneath the electrodeposit. These modes of formation are summarized in Equations 10-12.



THF or THF/LiClO₄ stored with Li at 71°C resulted in a grey coloration on the Li surface. Neither pre-electrolysis nor cycling studies utilizing THF/LiClO₄ electrolyte resulted in the brown coloration.

5. Characterization of the Brown Film

The brown material, when scraped off either the Li foil, the Li anode, or the Ni substrate yielded a fine brown powder. After washing with THF and distilled H₂O, these samples were dried in a 71°C oven. The ir spectra of all three samples (KBr pellet) were identical and manifested a single band at 795 cm⁻¹ indicative of As-O-As stretch (33).

Small samples of the brown powder were burned off a Nichrome wire in a gas flame imparting a blue then red coloration to the flame. This implicates the presence of Li and As. In an attempt to determine a melting point, the brown powder was heated to 400°C. Although no melting was observed, the brown material turned grey ~300°C with concurrent condensation of colorless crystals on the upper walls of the capillary tube. These crystals were octahedral in form and, when burned, manifested only a blue flame, while the grey residue at the bottom of the capillary tube burned red.

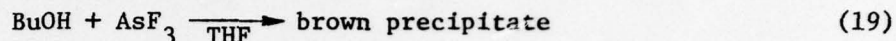
An ir spectrum of the sublimed crystals revealed bands at 795 and 505 cm⁻¹. This spectrum was identical to that of authentic As₂O₃ (Ventron). An ir of the grey residue manifested no significant bands, but subsequent elemental analysis indicated the presence of Li and F.

Elemental analysis of the brown film from pre-electrolysis found the major components to be Li, F, and As with trace amounts of C and H. Calculating for oxygen by difference, an empirical formula of Li_{1.17} F_{1.20} As_{0.66} O_{1.08} was obtained. By grouping As and O, and Li and F the compounded stoichiometry of the sample gives As₂O₃ and LiF. Thus the brown film appears to be composed of an As₂O₃ precursor and LiF.

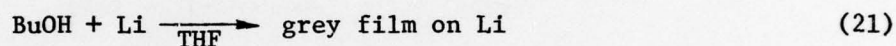
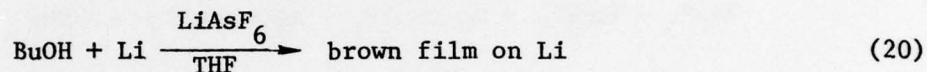
ESCA scans on the transparent brown film adhering to a Ni substrate revealed the presence of Li, F, As, O, and C. The As/O ratio was found to be 1.1, and Li/F, 1.6.

where S = $-\text{OAsF}_2$, $-\text{O}_2\text{AsF}$, $-\text{O}_3\text{As}$

The "brown film" could be prepared synthetically by reacting n-butanol (BuOH) with authentic AsF_3 (Ventron) in THF (Eq. 19). A brown precipitate resulted which gave an ir spectrum identical to that of brown



films generated from AsF_6^- and Li. When treated in a melting point capillary tube, this material formed As_2O_3 and LiF. Elemental analysis of the precipitate yielded stoichiometries essentially identical to that of the brown film from electrolyte pre-electrolysis. Other control experiments are summarized in Eqs. 20-23.



While direct evidence for the reduction of AsF_6^- to AsF_3 is lacking, we confidently infer its intermediacy on the basis of the aforementioned experiments.

That brown film formation can be used as a simple qualitative technique to assess the stability of other ethers towards Li has not escaped us. Samples of new ether/ LiAsF_6 electrolytes would be electrolyzed, and the rates of brown film formation noted.

6. The Effect of Pre-electrolysis on Electrolyte Acidity

Since Li-THF degradation reactions produce basic material, and since we observe the formation of brown film during pre-electrolysis, we set out to measure the pH of pre-electrolysis aliquots as a function of time. This was accomplished by withdrawing 1 ml portions of electrolyte and diluting them up to 10 ml with H_2O .

The pH of aliquots from 1M $\text{LiAsF}_6/\text{THF}$ and 1M $\text{LiClO}_4/\text{THF}$ pre-electrolyses were determined, and the results are plotted in Fig. 2. Prior to initiating pre-electrolysis, the pH values of both electrolytes are seen to be slightly acidic. In this regard, the pH of 1M $\text{LiAsF}_6/\text{H}_2\text{O}$ was reported to be

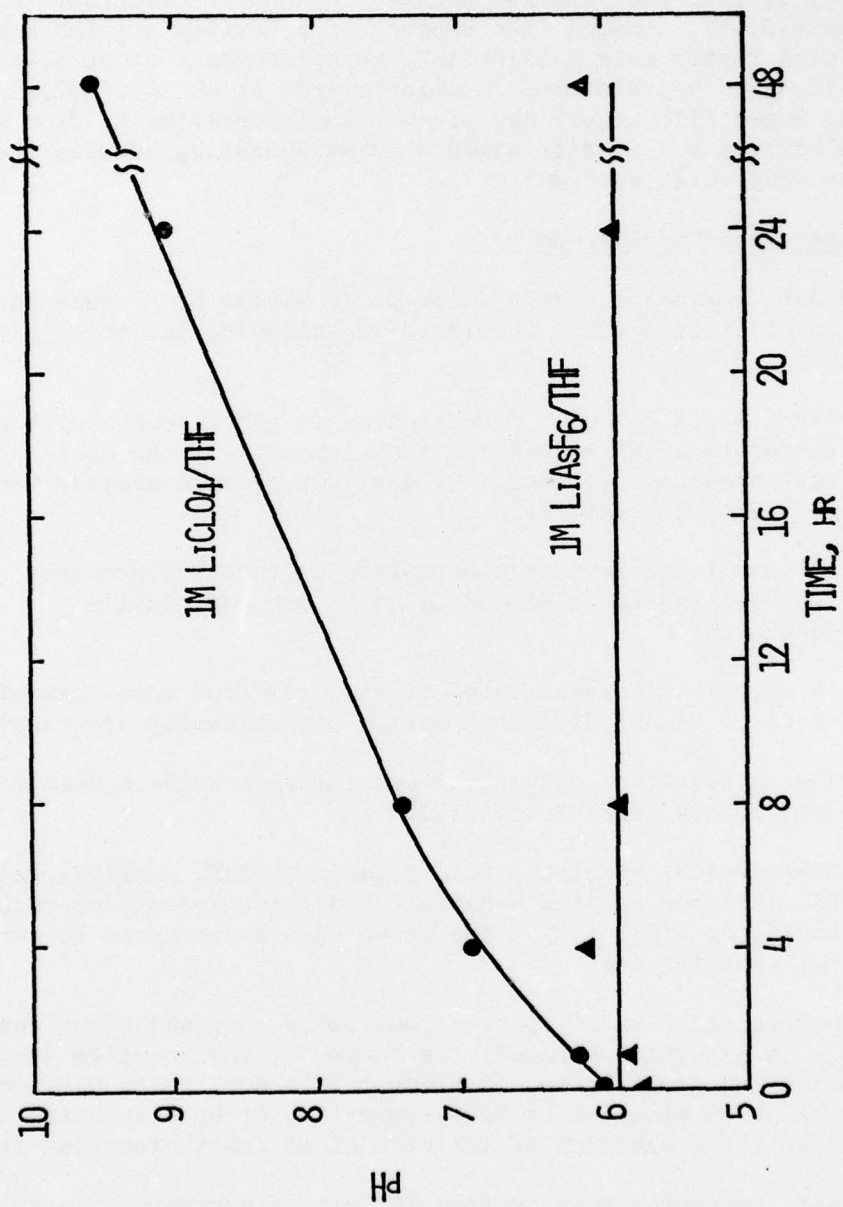


Fig. 2. Variation of pH with time for H₂O-quenched pre-electrolysis aliquots.

~6 (37). After pre-electrolysis commenced, $[\text{OH}^-]$ in H_2O quenched samples of ClO_4^- electrolyte increased as expected. However, there was essentially no change in the pH of the AsF_6^- -based electrolyte. It therefore appears as though the AsF_3 generated at the Li electrode scavenges all basic material from concurrent Li/THF degradation reactions. The absence of basic by-products may explain the superior behavior of the Li electrode in LiAsF_6 -based media (13,14). Indeed, the concept of a "buffer system" has been suggested with regard to a $\text{LiBF}_4/\text{LiAsF}_6/\text{methyl formate}$ electrolyte, a medium which was found to be relatively stable towards Li at 74°C (37). Alternatively, the brown film itself may protect the underlying Li from attack by the bulk electrolyte. Studies aimed at distinguishing between these possibilities are currently underway.

D. Summary and Conclusions

The data presented herein allow us to arrive at a consensus regarding the reaction of Li with THF. Consider the following set of experimental observations:

- THF free of O_2 and H_2O and sealed in glass reacts with Li faster than THF containing small amounts of the aforementioned contaminants. UV analysis reveals similar kinds of reaction products.
- UV data indicate that electrolyte degradation products from cycling Li on Ni and Li on Li are essentially equivalent.
- IR spectra of organic product mixtures from a variety of electrolytes of different purity are virtually identical.
- The introduction of gaseous contaminants helps maintain good cycling efficiency (13).
- THF-based electrolytes incorporating LiAsF_6 manifest better Li electrode cycling behavior than those containing either LiClO_4 or LiBF_4 (13). The brown film is presumed to account for this finding.

Taken together, these observations imply that while the rate of Li-THF reaction is impurity mediated, the course of the reaction (and therefore the kinds and distribution of products) is not. Although contaminants can hinder reaction kinetics by film formation, or by scavenging degradation products, the reactivity of THF with Li is nonetheless inevitable.

Organic products isolated from THF ring cleavage implicate the intermediacy of lithium n-butoxide, the enolate anion of acetaldehyde, and

ethylene. Furthermore, the AsF_6^- anion also reacts with Li to give AsF_3 . Then, in a rapid series of redistribution reactions, AsF_3 and lithium n-butoxide combine at the Li surface to form an adherent brown film. This material appears to be composed of an $(-\text{As}-\text{O}-\text{As}-)_n$ polymer and LiF .

III. FURTHER WORK

Knowledge of the reaction of AsF_6^- and THF with Li to give the brown film immediately raises two questions: Does the brown film act as an in situ separator which protects underlying Li from bulk THF? Or, does the brown film serve as a sink for THF degradation products? We plan to distinguish between these possibilities by assessing the effects of added AsF_3 and BuOLi on the behavior of the secondary Li electrode.

On the basis of the proposed mechanism for THF/Li reactivity, other cyclic ethers will be investigated with respect to their stability towards Li. We predict that Li-ether stability will improve as the energy of the ether's $\text{sp}^3\text{C}-2\text{p O LUMO}$ is raised.

A concurrent vein of research will focus on the purification of other supporting electrolytes. Promising candidates include LiAlCl_4 , LiO_3SCF_3 , and LiO_2CCF_3 .

Finally, the synergistic effects of blended electrolytes on the Li electrode will be explored. We have preliminary evidence which suggests that combinations of cyclic ethers with other solvents exert beneficial influences on the cycling efficiencies and cycle life of the Li electrode.

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