

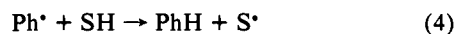
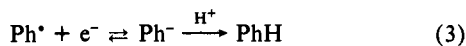
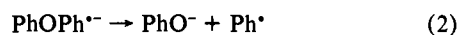
Carbon-Oxygen Bond-Cleavage Reactions by Electron Transfer. 3. Electrochemical Formation and Decomposition of the Diphenyl Ether Radical Anion

Todd A. Thornton, Neil F. Woolsey, and Duane E. Bartak*

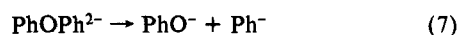
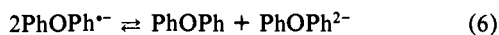
Contribution from the Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202. Received March 24, 1986

Abstract: The electrochemical reduction of diphenyl ether to its unstable radical anion was observed at -2.95 V vs. SCE in dry *N,N*-dimethylformamide. Kinetic studies by cyclic voltammetry and homogeneous redox catalysis techniques resulted in a first-order rate constant of 4×10^5 s $^{-1}$ for the decomposition of the radical anion of diphenyl ether. Controlled-potential electrolysis of diphenyl ether resulted in carbon-oxygen bond cleavage with quantitative formation of phenol and benzene. Electroreduction of diphenyl ether in the presence of D₂O produced 15% monodeuterium incorporation on benzene. The intermediacy of the phenyl radical in the cleavage pathway was tested by deploying an intramolecular radical trap, an *o*-(3-butenyl) substituent, on diphenyl ether. Electrochemical reduction of *o*-(3-butenyl)phenoxybenzene (**1**) in the absence of and in the presence of D₂O confirmed the presence of the *o*-(3-butenyl)phenyl radical in the cleavage mechanism of the radical anion. Electroreduction of **1** in the presence of sodium isopropylate, a hydrogen atom donor, changed the product distribution ratio of 1-methylindan-(3-butenyl)benzene. The rate constant of the intramolecular cyclization reaction of the *o*-(3-butenyl)phenyl radical was estimated to be 1.5×10^8 s $^{-1}$.

There have been several reports on the chemical reductive cleavage of the carbon-oxygen bond in ethers in the literature.¹⁻⁹ These reports deal with the use of chemical reductants including Na/HMPA/THF,¹ K/NH₃,²⁻⁴ Li/naphthalene/THF,⁵ Li/biphenyl/THF,^{5,6} Li/THF,⁷ Na/DME,⁸ and K/naphthalene/THF.⁹ The reductive cleavage of diphenyl ether by chemical means results in the formation of phenol and benzene as products.¹ However, two different schemes have been proposed in these reductive cleavage processes: (1) radical anion cleavage to form the phenoxide ion and a phenyl radical^{1-6,10} and (2) dianion cleavage to form the phenoxide ion and the phenyl anion.⁷⁻⁹ The first scheme is based upon a unimolecular decomposition pathway of the radical anion to products (eq 1-4). The resultant phenyl radical can



either be reduced further to the phenyl anion (eq 3) or abstract a hydrogen atom (eq 4), depending on the concentration of reducing agent and the hydrogen atom donating ability of the solvent. The second scheme involves the further reduction of the radical anion either by direct electron transfer from reductant (eq 5) or by disproportionation (eq 6). The resultant dianion rapidly



cleaves to the phenoxide ion and the phenyl anion (eq 7). Abstraction of a proton by the phenyl anion to form benzene completes the reaction pathway. No information on the reductive electrochemistry of diphenyl ether to indicate its reduction potential or the stability of any intermediates in the reductive process is

presently available. We report herein on the electrochemical reduction of diphenyl ether including its reduction potential and the relative stability of the intermediates in the cleavage process.

Results and Discussions

Cyclic Voltammetry. Cyclic voltammetric data in dry *N,N*-dimethylformamide (DMF) indicate that diphenyl ether is reduced to its radical anion at approximately -2.95 V vs. SCE at 25 °C. Figure 1 shows a poorly resolved wave or shoulder just prior to background reduction of the solvent or tetrabutylammonium ion. Since the reductive background limit in aprotic solvents has been shown to be dependent on the nature of the tetraalkylammonium ion,^{11,12} other electrolytes were also tested. As expected, tetrabutylammonium and tetramethylammonium perchlorate increased the background current (relative to the tetrabutylammonium electrolyte), which resulted in poorer resolution. Although tetraheptylammonium iodide decreased the background current, the electron-transfer rate to diphenyl ether was also decreased so that resolution of the ether reduction wave was not significantly increased.

As the temperature of the electrolyte/solvent system is decreased, the rate for the irreversible reduction of tetrabutylammonium ion is decreased with a resultant increase in the background limit. Since lowering the temperature does not decrease the rate of heterogeneous electron transfer for the reduction of the aromatic ether by the same amount, better resolution can be obtained at lower temperatures. Figure 2 illustrates this process with a clearly resolved reduction wave at -3.02 V vs. SCE at -13 °C. Rapid-scan cyclic voltammetry was attempted to determine directly the kinetics for the disappearance of the radical anion. However, no reoxidation current was observed on the reverse scan at rates of 10 V s $^{-1}$ and temperatures down to -37 °C. Since the reduction wave shifts in the negative direction as the scan rates are increased due to the follow-up chemical reaction and possible slower electron transfer at these temperatures, the wave was not clearly resolved at rates greater than 10 V s $^{-1}$. In addition, if the temperature is decreased below -40 °C, the rate of electron transfer for the aryl ether is significantly decreased, resulting in poor resolution of the wave.

The reduction peak potential for the aryl ether was measured as a function of scan rate and ether concentration to determine the molecular order for the disappearance of the radical anion. At relatively slow scan rates (i.e., 0.05 - 0.5 V s $^{-1}$) the peak potential

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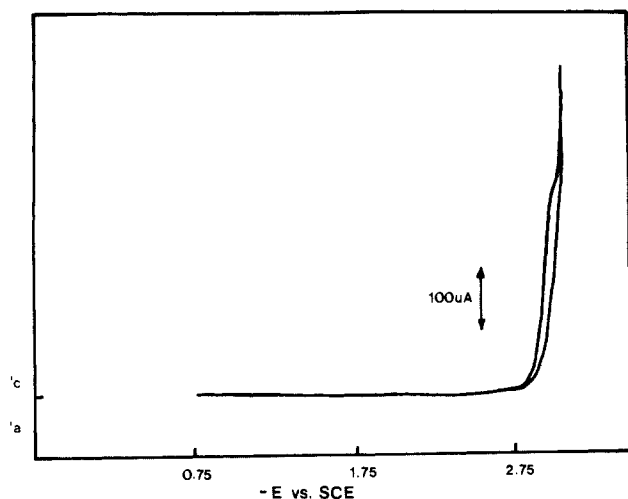


Figure 1. Cyclic voltammogram of 2.9×10^{-3} M diphenyl ether in 0.2 M TBAP-DMF at 25 °C. The scan rate was 0.1 V s^{-1} on a planar platinum electrode with an area of 0.20 cm^2 .

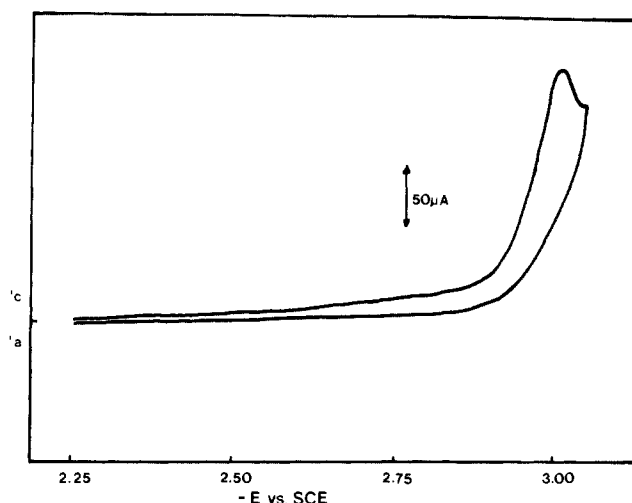


Figure 2. Cyclic voltammogram of 1.8×10^{-3} M diphenyl ether in 0.2 M TBAP-DMF at -13 °C . The voltammogram was obtained with a Cd/CdCl₂/DMF reference electrode, which was -0.75 V vs. SCE . The data is plotted on a potential scale vs. SCE for clarity. The scan rate was 0.1 V s^{-1} on a planar platinum electrode with an area of 0.20 cm^2 .

(E_p) shifted in the positive direction with decreasing scan rate (v) so that $dE_p/d \log v = 30 \text{ mV}$. The peak potential was independent of concentration over a concentration range of $0.49\text{--}4.87 \text{ mM}$ diphenyl ether. These data are consistent with a first-order chemical reaction following electron transfer.¹³ Thus, the cyclic voltammetric data indicated diphenyl ether radical anion cleavage by a first-order rate constant, which must be greater than 10^2 s^{-1} because no reoxidation current is observed for the radical anion at scan rates of 10 V s^{-1} (vide supra).

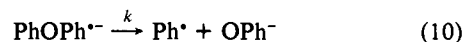
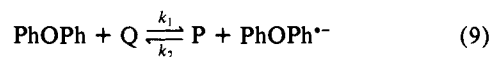
Kinetics by Homogeneous Redox Catalysis. The lifetimes of unstable radical anions ($k > 10^3 \text{ s}^{-1}$) can be determined by the utilization of homogeneous redox catalysis, which has been thoroughly described by Saveant.^{14,15} The catalysis reactions for

Table I. Homogeneous Redox Catalysis of Diphenyl Ether with Acenaphthene Mediator^a

C_p , mM	v , V s^{-1}	i_p/i_d	$\log k_1$, $\text{L mol}^{-1} \text{ s}^{-1}$ ^b	$\log k$, s^{-1} ^c
0.20	0.1	1.47	2.34	
	0.2	1.37	2.51	
	0.3	1.23	2.72	
0.50	0.1	2.02	2.30	
	0.2	1.55	2.56	
	0.3	1.32	2.58	
1.0	0.1	1.95	1.94	5.26
	0.2	1.64	2.20	5.49
	0.3	1.51	2.33	5.59
2.2	0.1	2.15	1.49	5.47
	0.2	1.64	1.62	5.67
	0.3	1.47	1.67	5.75
4.2	0.1	1.89		5.31
	0.2	1.51		5.56
	0.3	1.29		5.64
7.9	0.1	1.89		5.29
	0.2	1.64		5.42
	0.3	1.47		5.62

^aThe concentration ratio of diphenyl ether-acenaphthene was 49 ± 2 (γ) in all the experiments in DMF-0.2 M TBAP. ^bThe analysis of the rate constant from the current ratios assumed rate control by reaction 9 and utilized the working curve similar to Figure 3 of ref 14d. ^cThe analysis of the rate constant assumed rate control by reaction 10 and utilized the working curve similar to Figure 5 of ref 14d.

reduction of diphenyl ether can be described by the reaction scheme of eq 8–11, where P is an electron-transfer mediator and



Q its radical anion. Mediators tested in this scheme included naphthalene ($E_{pc} = -2.44 \text{ V}$), biphenyl ($E_{pc} = -2.50 \text{ V}$), 2,6-dimethylnaphthalene ($E_{pc} = -2.52 \text{ V}$), and acenaphthene ($E_{pc} = -2.58 \text{ V}$). Cyclic voltammetric data are utilized to characterize quantitatively the above sequence of catalytic reactions. The reduction peak current is measured for the mediator in the absence (i_d) or presence (i_p) of substrate (diphenyl ether). The measurement of i_p/i_d as a function of scan rate, mediator concentration (C_p), and ratio of diphenyl ether concentration to mediator concentration (γ) is utilized to determine the rate constants, k_1 and k . The determination of k_1 is accomplished when the overall rate is controlled by reaction 9. Control by reaction 9 is experimentally observed in the kinetic region where i_p/i_d will increase as C_p is increased (at constant γ). The determination of $k_1 k/k_2$ (i.e., when the overall rate is controlled by reaction 10) with reaction 9 as a pre-equilibrium is obtained in a regime where i_p/i_d is independent of C_p (at constant γ). The strategy is initially to determine k_1 for a particular mediator at relatively low concentrations of mediator (C_p) or large γ so as to permit control by reaction 9. The determination of $k_1 k/k_2$ can subsequently be accomplished at relatively high C_p and low γ . Assignment of a second-order diffusion-controlled rate constant for k_2 in the solvent system subsequently results in the evaluation of k .

Experiments with biphenyl, naphthalene, and 2,6-dimethylnaphthalene as mediators in the electrocatalytic reduction of diphenyl ether resulted in relatively low ratios of i_p/i_d with concomitant large relative errors in the determination of k_1 . Acenaphthene was subsequently used, and the k_1 for the reaction of its radical anion with diphenyl ether was determined to be $3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. As shown in Table I, the value of k_1 remains relatively constant at mediator concentrations (C_p) of $0.2\text{--}0.5 \text{ mM}$ and at varying scan rates. Subsequent analysis of i_p/i_d at higher C_p values ($4.2\text{--}7.9 \text{ mM}$, Table I) resulted in the determination of kk_1/k_2 . Assignment of a value of $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for k_2 resulted in a value

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Table II. Reductive Cleavage of Diphenyl Ether by Controlled-Potential Electrolysis^a

entry	concn, mM	E_{applied}^b	additives	F mol ⁻¹ added	product yields, ^c %		
					diphenyl ether remaining	phenol	benzene (benzene- <i>d</i> ₁) ^d
1	45.3	-2.98	none	2	50	46	42
2	49.9	-2.98	none	4.5	2	94	94
3	29.8	-2.71 ^f	14 mM C ₁₂ H ₁₀ ^e	2	38	54	51
4	31.0	-2.98 ^f	200 mM D ₂ O	4	11	81	76 (15)
5	30.3	-2.71 ^f	13 mM C ₁₂ H ₁₀ ^e 210 mM D ₂ O	2	63	31	34 (31)
6	29.7	-2.71 ^f	3 mM C ₁₂ H ₁₀ ^e 230 mM D ₂ O	2	42	56	55 (16)

^aThe solvent was DMF with 0.2 M TBAP. ^bPotentials are in volts vs. aqueous saturated calomel electrode. ^cThe yields of products were determined by gas chromatography and are calculated on the basis of the original amount of diphenyl ether. ^dThe values in parentheses represent the extent of monodeuterium incorporation as measured from mass spectral data. ^eHomogeneous reduction utilizing acenaphthene as the mediator. ^fThe working electrode was a large, reticulated vitreous carbon basket.

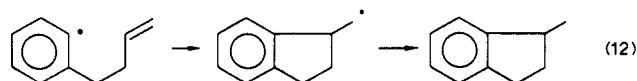
of $4 \times 10^5 \text{ s}^{-1}$ for k .¹⁶ This value of k is consistent with the lower limit as determined by cyclic voltammetry (vide ante). Furthermore, the rate constant of $4 \times 10^5 \text{ s}^{-1}$ will be shown to be consistent with the products obtained after electrolysis (vide infra). These results can also be compared with the rate of cleavage of the weaker carbon-sulfur bond in the diphenyl sulfide radical anion, which has been reported to be $6 \times 10^6 \text{ s}^{-1}$.¹⁷

Controlled-Potential Electrolysis. A series of controlled-potential electrolyses were conducted (Table II). The products from electrochemical reduction were consistent with those obtained by chemical reductants. Direct reduction at -2.98 V resulted in the formation of two major products, phenol and benzene, which were obtained in at least 90% yield based upon the initial ether concentration. Biphenyl or oligomeric products were not observed by either gas chromatography or HPLC. However, the current yields (efficiencies) for the ether reduction process were considerably less than 100%. Significant quantities of charge were apparently consumed by the reduction of the electrolyte/solvent at these negative potentials. Therefore, direct coulometric measurements to determine the electron stoichiometry were not possible for diphenyl ether. Homogeneous reduction of diphenyl ether with an electron-transfer mediator, the acenaphthene radical anion (Table II, entry 3), resulted in similar product distribution with a slightly better current efficiency.

Electrolysis experiments were conducted in the presence of D₂O, to test for the intermediacy of the phenyl anion. Direct reduction of diphenyl ether (Table II, entry 4) in the presence of D₂O resulted in decreased current efficiency due to concomitant reduction of D₂O as well as electrolyte/solvent. Analysis of the electrolyzed solutions showed phenol and benzene again as the major products in the presence of D₂O. Mass spectroscopic analysis of the gas chromatographic benzene peak indicated that 15% of the benzene was in the monodeuterated form. In comparison, previous work on the direct reduction of bromobenzene under the same conditions, utilizing a 15:1 ratio of D₂O-substrate, resulted in greater than 90% deuterium incorporation in the resultant benzene.¹⁸ These data indicate that the phenyl anion, which is an important intermediate in the direct reduction of bromobenzene, represents an intermediate in a minor reaction pathway for the direct electrochemical cleavage of diphenyl ether.

Homogeneous mediated reductions of diphenyl ether were carried out in the presence of D₂O to test for the importance of anion intermediacy in a system which utilizes chemical reductants (e.g., sodium in liquid NH₃). The extent of the increase in deuterium incorporation was significant (e.g., 15-31%) and increased with increasing ratios of mediator to substrate (Table II, entries 5 and 6). These data imply that the phenyl anion can be produced in a homogeneous reduction if the mediator concentration (reductant) is relatively high compared to the substrate concentration.

Intermediacy of the Phenyl Radical. Beckwith has reported on the intramolecular cyclization of the *o*-(3-butenyl)phenyl radical, which undergoes regiospecific formation of 1-methylindan (eq 12).^{19,20} Recent data from our laboratory indicate that the



o-(3-butenyl)phenyl anion is also capable of cyclizing to form methylindan.¹⁸ However, by control of the conditions, including the addition of proton donors and temperature, differentiation of radical vs. anion intermediacy can be accomplished.²¹ Electrochemical methods can be utilized to selectively generate the phenyl anion vs. the phenyl radical by direct vs. mediated reduction of halobenzenes which undergo rapid ($k \geq 10^8 \text{ s}^{-1}$) cleavage of the radical anion.¹⁸ Since the kinetic data indicated a rate constant of $4 \times 10^5 \text{ s}^{-1}$ (vide supra) for the cleavage of the diphenyl ether radical anion, a series of experiments were run to demonstrate clearly the intermediacy of the phenyl radical.

The *o*-(3-butenyl) substituent was employed as a probe for the intermediacy of the phenyl radical vs. the phenyl anion in the reductive cleavage of diphenyl ether. Cyclic voltammetric experiments on *o*-(3-butenyl)phenoxybenzene (**1**) produced a reduction wave at -2.96 V which was chemically irreversible at scan rates up to 10 V s^{-1} in the same manner as diphenyl ether (vide ante). Direct electrochemical reductions of **1** at a platinum basket cathode under potential-controlled conditions were conducted (Table III, entry 1). Reduction of background electrolyte/solvent occurred simultaneously; however, greater than 80% of the ether was consumed after 4 F mol⁻¹. Due to the asymmetry of **1**, the product analysis data are capable of indicating the specific carbon-oxygen bond undergoing cleavage (eq 13-15). Inspection of the data indicates that α -cleavage (cleavage of the carbon-oxygen bond adjacent to the substituted phenyl ring) is preferred over β -cleavage by a ratio of 5:4. Comparison of the reduction potentials of alkyl-substituted vs. unsubstituted aromatic compounds indicates reduction of the unsubstituted aromatics occurs more easily, which is expected due to the electron-donating ability of alkyl groups. However, reduction of the unsubstituted phenyl ring in the diphenyl ether case should result in β -cleavage since previous data on 1-phenoxy-naphthalene indicate cleavage of the carbon-oxygen bond adjacent to the naphthalene ring produces phenoxide ion and naphthalene.²² Thus, the cleavage in the case of the radical anion **1** appears to be kinetically, rather than thermodynamically, controlled, since the radical anion stability

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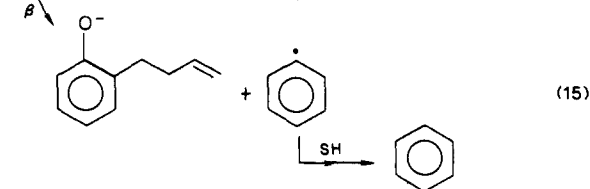
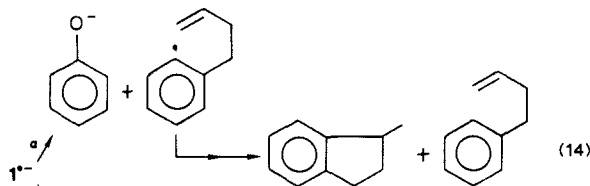
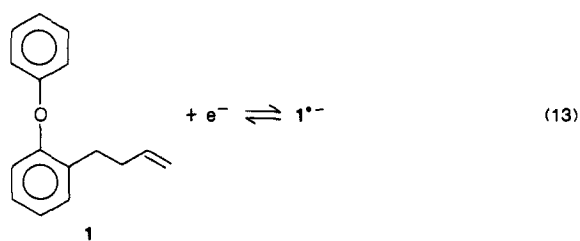
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of an alkyl-substituted aromatic compound should be less than that of the unsubstituted one.

The initial products from α -cleavage of the radical anion of **1** are the phenoxide ion and the *o*-(3-butenyl)phenyl radical (eq 14). Inspection of Table III shows that apparent cyclization of the *o*-(3-butenyl)phenyl radical to 1-methylindan is the predominant product of the substituted phenyl moiety obtained from α -cleavage. Ratios greater than 10:1 for the yields of 1-methylindan-(3-butenyl)benzene are obtained on both platinum and mercury electrodes. However, it should be noted that formation of 1-methylindan cannot be regarded as *prima facie* evidence for phenyl radical intermediacy. Therefore, reduction of **1** was carried out in the presence of D_2O , which has been previously shown to substantially decrease the yield of 1-methylindan by deuteration of the *o*-(3-butenyl)phenyl anion to form (3-butenyl)benzene- d_1 .¹⁸ The results (Table III, entry 3) clearly show that the presence of D_2O has little effect on the absolute yield of (3-butenyl)benzene. Thus, these data indicate that the products from direct reduction of diphenyl ether are the phenyl radical and the phenoxide ion. Furthermore, the data from both kinetic and product analysis clearly indicate that the resultant phenyl radical is not appreciably reduced to the phenyl anion.

Dicyclohexylphosphine (DCPH) has been utilized to trap alkyl radical intermediates including those capable of intramolecular cyclization reactions (e.g., 5-hexenyl radicals).²³⁻²⁵ Based on a first-order rate constant of $2 \times 10^5 \text{ s}^{-1}$ for the cyclization of the 5-hexenyl radical, reported data on the trapping efficiency of DCPH indicate that the second-order rate constant for hydrogen abstraction from DCPH by an alkyl radical is on the order of $10^6 \text{ M}^{-1} \text{ s}^{-1}$.²⁴ Since an aryl radical should be more reactive toward hydrogen atom abstraction than the alkyl radical, an attempt was made in this study to trap the phenyl radical before cyclization. However, due to low solubility of DCPH in DMF ($\sim 0.1 \text{ M}$), the effectiveness of DCPH in this system was limited. That is, no appreciable change in the yield of 1-methylindan or the ratio of cyclized-uncyclized products from the *o*-(3-butenyl)phenyl radical was noted.

Alcoholates have been shown to be more effective hydrogen atom donors than the corresponding alcohols. For example, the hydrogen-donor reactivity of methoxide ion was shown to be 45 times more than that of methanol with regard to a *p*-nitrophenyl radical.²⁶ Recently, Saveant utilized electrochemical techniques

to determine the rate constant ($k = 2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) for the reaction of the 2-quinoyl radical with isopropylate ion in liquid ammonia at -40°C .²⁷ Due to temperature differences and the reactivity of the phenyl vs. the quinoyl radical, the rate constant for hydrogen atom abstraction from isopropylate ion by a phenyl radical at 25°C should be greater than $2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Electrolysis experiments on **1** using sodium isopropylate as the hydrogen atom donor in DMF/TBAP were carried out. Electrochemical reduction of **1** in the presence of 0.14 M sodium isopropylate (Table III, entry 4) resulted in a significant decrease in the product ratio of 1-methylindan-(3-butenyl)benzene as compared to reduction of **1** in the absence of alcoholate. In particular, direct electrochemical reduction of **1** in the absence of isopropylate resulted in a cyclized:uncyclized product ratio of 9 (Table III, entry 2), while reduction in the presence of isopropylate produced a ratio of 5 (Table III, entry 4).

If one assumes that the major precursor to (3-butenyl)benzene is a phenyl radical (and not the phenyl anion), the rate constant for the intramolecular cyclization of the *o*-(3-butenyl)phenyl radical can be calculated. By use of a simple competitive reaction approach with the ratio of cyclized-uncyclized products and the above rate constant for isopropylate, a rate constant of $2 \times 10^8 \text{ s}^{-1}$ is obtained from the isopropylate experiments. This value should be regarded as a lower limit because of the above limitations. In addition, a cyclization rate constant can be estimated from the data obtained in the absence of isopropylate (Table III, entry 2). In the solvent/electrolyte system of DMF/TBAP the major hydrogen atom donor will be DMF. Russell has reported the relative hydrogen atom donor reactivity of DMF vs. a primary aliphatic hydrocarbon toward the phenyl radical to be a value of 55 at 60°C .²⁸ Ingold has estimated the rate constant for the reaction between a phenyl radical and primary aliphatic hydrocarbons to be $1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 60°C .²⁹ Thus, a rate constant for the hydrogen atom abstraction reaction of a phenyl radical with DMF can be estimated to be $6.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. From these data and the assumption that the phenyl anion is not a major precursor to products, the cyclization of the *o*-(3-butenyl)phenyl radical in DMF can be calculated to be $8 \times 10^8 \text{ s}^{-1}$ at 60°C . A value for the rate constant for cyclization at 25°C can be estimated to be $1 \times 10^8 \text{ s}^{-1}$, assuming doubling of the rate constant with each 10-deg increase. Therefore, a rate constant for the intramolecular cyclization of the *o*-(3-butenyl)phenyl radical can be estimated to be in the range 1×10^8 to $2 \times 10^8 \text{ s}^{-1}$ in DMF at 25°C . Beckwith reported an upper limit of $6 \times 10^7 \text{ s}^{-1}$ for the cyclization of the *o*-(3-butenyl)phenyl radical, which was based upon reaction of the halide precursor with tin hydride.^{20a} More recently, Ingold and co-workers calculated a rate constant of $4.0 \times 10^8 \text{ s}^{-1}$ at 30°C for the cyclization of the *o*-(3-butenyl)phenyl radical based upon Beckwith's method.³⁰ Thus, the range of values obtained in this study is in good agreement with literature reports considering the differences in the type of experiments which were conducted.

Conclusions. The reduction of diphenyl ether to its unstable radical anion can be observed by cyclic voltammetry at -2.95 V vs. SCE in DMF. Kinetic studies by cyclic voltammetric and homogeneous redox catalysis techniques indicate a first-order rate constant of $4 \times 10^5 \text{ s}^{-1}$ for the decomposition of the radical anion of diphenyl ether. Controlled-potential electrolysis of diphenyl ether results in quantitative formation of phenol and benzene. Reduction of diphenyl ether in the presence of D_2O results in minor ($\sim 15\%$) deuteration of benzene, which suggests the absence of

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Table III. Electrochemical Reduction of *o*-(3-Butenyl)phenoxybenzene^a

entry	type of reduction	products, % yield ^b						
		1	<i>o</i> -(3-butenyl)-phenol	benzene	phenol	(3-butenyl)-benzene	1-methylindan	cyclized: uncyclized
1	direct on Pt	23	31	27	45	3	40	13
2	direct on Hg	7	47	35	49	5	47	9
3	direct on Hg in the presence of 0.40 M D ₂ O	23	30	29	39	3	39	13
4	direct on Hg in the presence of 0.14 M sodium isopropylate	8	37	31	47	11	50	5

^a The concentration of *o*-(3-butenyl)phenoxybenzene was 10 mM in DMF-0.2 M TBAP in all runs. The electrolyses were carried out at -2.95 V vs. SCE and were terminated prior to completion at 3-4 F mol⁻¹. ^b The % yields of products including the starting ether, 1, are based on the initial concentration of the starting ether, 1.

significant further reduction of the radical to the anion. The intermediacy of the phenyl radical is conclusively demonstrated by employing an intramolecular radical trap in the form of an *o*-(3-butenyl) substituent, i.e., *o*-(3-butenyl)phenoxybenzene (1). Electrochemical reduction of 1, in the absence of or the presence of D₂O, confirmed the presence of the *o*-(3-butenyl)phenyl radical intermediate. The presence of a good hydrogen atom donor, isopropylate ion, in electrolysis experiments of *o*-(3-butenyl)phenoxybenzene results in an appreciable change in product distribution. A rate constant for the intramolecular cyclization reaction of the *o*-(3-butenyl)phenyl radical is estimated to be in the range 1×10^8 to 2×10^8 s⁻¹.

Therefore, carbon-oxygen bond cleavage of diphenyl ether by reductive means is accomplished by initial radical anion formation. Subsequent rapid cleavage ($k = 4 \times 10^5$ s⁻¹) results in the formation of a phenyl radical and the phenoxide ion. These results indicate that dianion formation in the reaction pathway is improbable, based upon the following: (1) further reduction of the radical anion to the dianion would require a reductant with a reduction potential more negative than -3.5 V, and (2) the lifetime of the radical anion via the unimolecular cleavage pathway clearly precludes the possibility of a relatively slow disproportionation pathway. However, work in progress from this laboratory indicates the importance of dianion intermediacy in the reductive cleavage of carbon-oxygen bonds in phenoxy-substituted polycyclic aromatic ethers.

Experimental Section

Instrumentation. Cyclic voltammetric and controlled-potential electrolysis experiments were carried out with a PAR Model 173 potentiostat equipped with a Model 179 digital coulometer. Cyclic voltammetric wave forms were generated by using a digital-controlled, multifunction generator³¹ coupled with the PAR 173. Cyclic voltammetric data were recorded on a Houston 2000 X-Y recorder. All electrochemical measurements were made with positive feedback electronic compensation of ohmic potential loss.

Chemicals. Diphenyl ether (Matheson, Coleman & Bell) and acenaphthene (Eastman) were checked for purity by gas and high-pressure liquid chromatographic techniques. *o*-(3-Butenyl)phenoxybenzene (1) was prepared by the coupling of allyl bromide and (*o*-phenoxybenzyl)magnesium bromide.³² 1-Methylindan and (3-butenyl)benzene were prepared by previously described procedures.¹⁸ Deuterium oxide (Aldrich, Gold Label) was used as received. Electrochemical grade tetra-*n*-butylammonium perchlorate (TBAP, Southwestern Analytical Chemicals) was dried under vacuum at 100 °C for 24 h and used as the supporting electrolyte. Spectroscopic grade *N,N*-dimethylformamide (DMF, Burdick and Jackson) was employed as the electrochemical solvent. DMF solutions of 0.2 M TBAP were dried by passage through a column of freshly activated, anhydrous alumina. The alumina, Woelm W200 neutral grade Super I, was activated by heating under vacuum at 550 °C for 24 h. All solvent preparation, including the alumina treatment, took place in a Vacuum Atmospheres HE-43-2 Dri-Lab glovebox equipped with a HE-493 Dri-Train as previously described.³³ The DMF-TBAP solutions were transferred to an all-glass vacuum line and subsequently

degassed by several freeze-pump-thaw cycles. The dry, deoxygenated DMF-TBAP solutions were stored in the glovebox under an argon atmosphere.

Electrodes and Cells. Solvent and electroactive chemicals were introduced into airtight, all-glass, electrochemical cells in the glovebox. The electrochemical cells for cyclic voltammetry and controlled-potential electrolysis have been previously described.³⁴

The working electrode for cyclic voltammetric experiments was a Beckman platinum button (No. 39273), with an area of approximately 0.20 cm². The reference electrode used in most experiments was a cadmium amalgam, which is in contact with dry DMF, saturated with CdCl₂ and NaCl.³⁵ The potential of this electrode was -0.75 V vs. the aqueous saturated calomel electrode.

Bulk controlled-potential electrolyses were performed in an all-glass, vacuum-tight cell. Several working electrode materials were employed. A vitreous carbon basket was used in some experiments in combination with a planar glassy carbon electrode (Bioanalytical Systems, Inc.), which was used to record cyclic voltammograms before and after electrolysis. Electrolyses in which a mercury pool was used as the bulk working electrode employed a planar mercury electrode as the probe electrode for CV. The planar mercury electrode was prepared via amalgamation of a planar gold electrode (Bioanalytical Systems, Inc.).³⁶ All microelectrodes were hand polished with alumina prior to use and thoroughly rinsed. A platinum basket was used as the working electrode in other electrolysis experiments with a spherical platinum-bead electrode as a probe CV electrode. The auxiliary electrode for all electrolysis experiments was a large coil of platinum wire, which was isolated from the bulk solution by means of a glass frit and bridge containing saturated TBAP-DMF solution.

Reduced temperatures for low-temperature electrochemical experiments were obtained by using reagent grade solvents and dry ice slurries. Carbon tetrachloride/CO₂ (-26 °C) or ethylene glycol/CO₂ (-13 °C) slurries were used and their temperatures monitored with an iron/constantan thermocouple. Each cell was allowed to equilibrate to temperature for 30 min before cyclic voltammetric experiments were run.

Product Analysis. After bulk controlled-potential electrolysis, the products were analyzed by gas chromatography (GC) and/or high-pressure liquid chromatography (HPLC). Deuterium incorporation was determined by coupled GC/mass spectrometry (GC/MS). GC analysis was carried out with a Shimadzu GP-6AM equipped with dual-flame ionization detectors (FID) and dual 3% Dexsil 300, 6-m columns. GC data acquisition was by a Hewlett-Packard 3390A integrator. GC/MS was accomplished on a Hewlett-Packard 5790 capillary GC with a 5970A MS detector equipped with a 9825B microcomputer. The capillary column was poly(dimethylsiloxane) (Alltech) (0.25 mm × 30 m). Electrolyzed solutions were extracted as previously described prior to gas chromatographic or GC/MS analysis.³³ Identification of the hydrocarbon products including 1-methylindan and (3-butenyl)benzene in electrolysis mixtures was carried out by both gas chromatography (GC/FID) and GC/MS using the above two systems with standard solutions for comparison.

Quantitation of the phenol products was accomplished by isocratic HPLC with an Altex 110A pump and LDC 1203 UV monitor detector (254 nm). The electrolysis solutions were acidified with HClO₄ and injected directly into a 0.25 × 25-cm C18 column (Alltech) with a 5-μm mean particle packing. Mobile-phase composition (acetonitrile/4% acetic acid in H₂O) was varied to obtain separation. Products were identified by spiking techniques. Calibration curves were prepared daily and em-

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ployed for HPLC product quantitation.

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Registry No. PhOPh (radical anion), 34534-14-0; 2-H₂C=CH-(CH₂)₂C₆H₄O, 57056-96-9; PhOPh, 101-84-8; C₁₂H₁₀, 83-32-9; D₂O, 7789-20-0; 2-PhOC₆H₄(CH₂)₂CH=CH₂, 103751-30-0; (H₃C)₂CHONa, 683-60-3; 2-HOC₆H₄(CH₂)₂CH=CH₂, 14003-84-0; Ph(CH₂)₂CH=CH₂, 768-56-9; 1-methylindan, 767-58-8.

Strong Hydrogen Bonding in Gas-Phase Ions: A High Pressure Mass Spectrometric Study of Formation and Energetics of Methyl Fluoride Proton Bound Dimer

T. B. McMahon*[†] and P. Kebarle[‡]

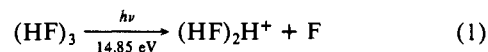
Contribution from the Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada, and the Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada.

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Abstract: The hydrogen bond energy in the proton bound dimer of methyl fluoride, (CH₃F)₂H⁺, has been determined by pulsed electron beam high pressure mass spectrometric experiments. Due to the rapid nucleophilic displacement reaction, CH₃FH⁺ + CH₃F ⇌ (CH₃)₂F⁺ + HF, the direct termolecular clustering of CH₃FH⁺ with CH₃F could not be examined. Instead the hydrogen bond energy in (SO₂)₂H⁺ was determined and then successive displacement equilibria of SO₂ by CH₃F molecules from the proton were examined. These data, coupled with the relative proton affinities of CH₃F and SO₂, yield a hydrogen bond energy in (CH₃F)₂H⁺ of 32 ± 2 kcal mol⁻¹ in good agreement with ab initio calculations for (HF)₂H⁺. Periodic trends in hydrogen bond energies in symmetric proton bound dimers of binary hydrides are discussed.

The growing body of gas-phase data from both experimental¹ and ab initio² methods recently available for hydrogen bonded cluster ions provides valuable insight into the nature of solvation of ions by both protic and aprotic solvents. To date most of the data available have been obtained for proton bound dimers of oxygen and nitrogen n-donor bases and anionic dimers of HO⁻, RO⁻, and halide ions, X⁻, with Brønsted acids. Examination of the limited amount of data available reveals a number of interesting trends. In symmetric proton bound dimers of the binary hydrides the order of hydrogen bond strengths observed is H₃O⁺-H₂O³ > NH₄⁺-NH₃⁴ > H₃S⁺-H₂S⁵ > PH₄⁺-PH₃.⁶ In symmetric anionic dimers the order of hydrogen bond strengths is F⁻-HF⁷ > HO⁻-H₂O⁸ > Cl⁻-HCl⁹ > Br⁻-HBr¹⁰ > I⁻-HI¹¹ > HS⁻-H₂S⁴ > NH₂⁻-NH₃¹² > PH₂⁻-PH₃.¹³ From these data the apparent trend is that all hydrogen bond strengths in symmetric dimers of the binary hydrides increase in proceeding from left to right across a row of the periodic table and decrease from top to bottom proceeding down a group of the periodic table. This order is known to be paralleled in neutral dimers as well with dimer bond strengths decreasing in the order (HF)₂ > (H₂O)₂ > (NH₃)₂.¹⁴ Further, a comparison of cationic and anionic dimer hydrogen bond energies reveals H₃O⁺-H₂O > HO⁻-H₂O; H₃S⁺-H₂S > SH⁻-H₂S; and NH₄⁺-NH₃ > NH₂⁻-NH₃, suggesting that cationic dimers will be more strongly bound than their anionic counterparts. This correlation has a notable omission of considerable interest in the (HF)₂H⁺ dimer. The strongest hydrogen bond known to date is that in the bifluoride ion, FHF⁻. If the above trends hold it may then be the case that the hydrogen bond strength for H₂F⁺-HF will be greater than both those of H₃O⁺-H₂O and of F⁻-HF. This possibility, that a hydrogen bond stronger than that in FHF⁻ may exist, caused us to undertake the present study.

The only experimental study to date of (HF)₂H⁺ has been that of Lee et al.^{15,16} involving photoionization appearance energy measurements of (HF)₂H⁺ from HF trimer formed in a supersonic expansion, eq 1.



These data give a hydrogen bond energy in (HF)₂H⁺ of 25 kcal mol⁻¹. However, similar experiments involving appearance energy measurements of H₂F⁺ from HF dimer, eq 2, yield a proton affinity for HF of 96 kcal mol⁻¹, significantly lower than the currently accepted value of 121 kcal mol⁻¹.^{17,18} This discrepancy

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[†]University of Waterloo.

[‡]University of Alberta.