

Thermodynamics and kinetics of homolytic cleavage of carbon–oxygen bonds in radical anions obtained by electrochemical reduction of alkyl aryl ethers

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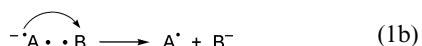
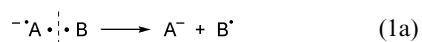
The properties and the reactivity of the radical anions of 4-cyanophenyl alkyl ethers and naphthyl alkyl ethers have been determined by electrochemical methods. Under electrochemical conditions homolytic dissociation is the only observed process. Cyclic voltammetry studies lead to the conclusion that this process is a stepwise one, the initially produced radical anion cleaving by a slow first order reaction followed by a second electron transfer in a DISPI mechanism. A Marcus type relationship between the cleavage rate constants and the standard free energy of the reaction leads to an intrinsic barrier in the range of 0.7 to 0.8 eV. The analysis of the intrinsic barrier values indicates that solvent organisation represents a modest contribution, the bond dissociation energy of the radical anion (structural contribution) being the main factor in the total barrier. Previously unknown bond dissociation energies of naphthyl ethers have been estimated using the correlations established in this work.

Introduction

There are extensive reports on the mechanisms of carbon–halogen bond cleavage by electrochemical means.^{1,2} The initial electron transfer to a molecule leads either to a radical anion that cleaves to produce a radical and an anion in a stepwise process, or directly to a radical and an anion in a concerted process. Both the strength of the carbon–halogen bond and the leaving group ability of the resultant anion play important roles in determining the preferred process.³

Particularly revealing is the possibility of passing, in borderline cases, from one mechanism to the other.^{1,2,4} The dynamics of concerted electron transfer–bond breaking reactions (called dissociative electron transfer) may be modelled on the framework of Marcus's theory,⁵ as proposed by Savéant.⁶

The cleavage reaction of radical ions can be classified as *homolytic* [eqn. (1a)] when the unpaired electron is located on the leaving group and the cleavage leaves the charge mainly in the same region it was in the radical ion;⁷ or *heterolytic* [eqn. (1b)] in which there is “regioconservation” of the spin density.⁸ Savéant has described the heterolytic bond cleavage (where the unpaired electron initially resides in an orbital that does not belong to the leaving group) as an *intramolecular electron transfer*^{1,8} in which the electron in an orbital centred on A is transferred to B with concerted bond breaking.



In the particular case of bifunctional systems,⁹ passage from one mechanism to the other is possible.

The influence of the reaction medium on the kinetics of radical anion cleavage has been the object of several investigations.¹⁰ The results of a recent investigation on the dependence of the cleavage rate constant upon the solvent of two

similar radical anions, those of 3-nitrobenzyl chloride and 3-chloroacetophenone,¹¹ may likewise be interpreted as the outcome of a competition between the Lewis acid solvation of the developing halide ion and of the negatively charged oxygen atom in the initial state. The kinetics of cleavage of radical anions of α -substituted acetophenones^{3d,12} is governed by solvent reorganization and in this case the contribution of molecular structure (related to bond breaking) is negligible.

There are extensive reports on the mechanisms of carbon–halogen bond cleavage by electrochemical means,^{1,2} and significant contributions to the mechanistic knowledge on mesolytic cleavage of a C–C bond in diphenylethane derivatives,^{7a–d} cation radicals of *tert*-butylated NADH analogues,^{7c} the C–S bonds in sulfides,^{7f,13} the S–S bond in diaryl sulfides,¹⁴ the C–O bond in aryloxyacetophenones^{12,15} and the O–O bond in perbenzoates.¹⁶ A rather different situation exists for the corresponding C–O bond fragmentations in ethers. Thus, even though preparatively useful examples of carbon–oxygen bond cleavage in ethers have been reported,¹⁷ very few chemical¹⁸ or electrochemical,¹⁹ mechanistic studies exist and the available kinetic data are very scarce. This is probably due to the inertness of the carbon–oxygen bond in ether *vs.* the carbon–halogen bond in organic halides. It is sometimes necessary to insert an electron-attracting group on the organic moiety to make the reduction potential of ethers more positive; however, this in turns stabilizes the resulting radical anion to preclude rapid unimolecular fragmentation.²⁰

The two kinds of ion fragmentations reported in the literature^{7,9–19,21} and, on the other hand, the radical anion coupling reactions (that are components of S_{RN}I reactions^{21,22}) are formally heterogenic processes [the reverse of eqn. (1b)]. Alkyl aryl ethers can, in principle, show both types of cleavage, and in fact, depending on the conditions, both can be observed.^{17,18} Thus, chemical reduction with alkali metals in apolar solvents leads to dealkoxylation (intramolecular electron transfer), whereas in more polar solvents, dealkylation is observed (homolytic dissociation, the unpaired electron initially resides in an orbital that belongs to the leaving group). Interestingly

enough, typical electrochemical conditions (DMF, tetraalkylammonium salts as supporting electrolyte) always produce the homolytic dissociation.²³ In the present paper, to carry out a complete mechanistic study on the electrochemical homolytic dissociation of alkyl aryl ethers establishing their mechanistic details (concerted vs. stepwise; main factors in the kinetic barrier) and the usefulness of Savéant's model^{6,8} in homolytic dissociations, this study has been carried out with two series of ethers, alkyl 4-cyanophenyl ethers and alkyl naphthyl ethers; as explained before, these substrates are convenient for the electrochemical study.

Compound	Z	R	Compound	R
1a	CN	CH ₃	2a	CH ₃
1b	CN	CH ₂ φ	2b	CH ₂ φ
1c	CN	CH ₂ CH ₂ CH ₃	2d	CH ₂ CHCH ₂
1d	CN	CH ₂ CHCH ₂	2j	CH ₂ CH ₂ NC ₅ H ₁₀
1e	CN	CH ₂ CH ₂ CHCH ₂		
1f	CN	C(CH ₃) ₃		
1j	CN	CH ₂ CH ₂ NC ₅ H ₁₀		



Results and discussion

Cyclic voltammetry

Fig. 1 shows voltammograms typical of **1a–1j** in DMF–0.1 M

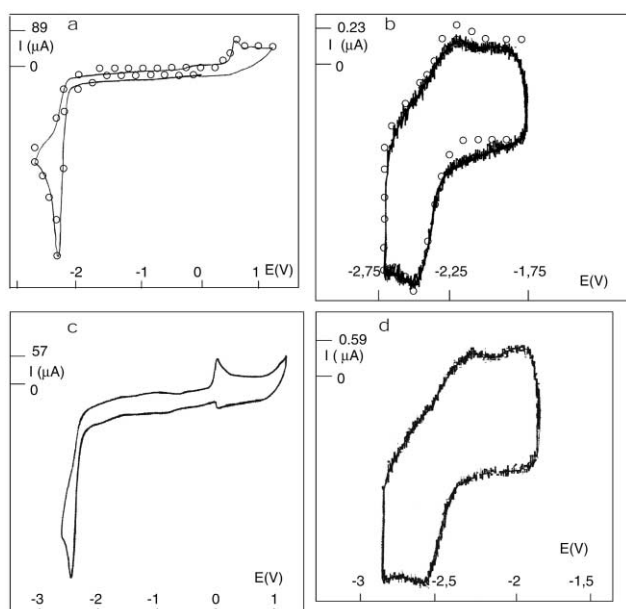


Fig. 1 a. Experimental (—) and simulated (DIGISIM®: ○) cyclic voltammograms of **1d** (10.3 mM) in DMF–0.1 M $n\text{Bu}_4\text{NBF}_4$ at 20 °C. Scan rate 0.1 V s⁻¹. Glassy carbon disk electrode (3 mm diameter). The scan is in the potential range: 0.0/–2.75/+1.0/0.0 V. b. Experimental (—) and simulated (DIGISIM®: ○) cyclic voltammograms of **1d** (6.0 mM) in DMF–0.1 M $n\text{Bu}_4\text{NBF}_4$ at 20 °C. Scan rate 420 V s⁻¹. Gold UME disk electrode (25 μm diameter). The scan is in the potential range: –1.75/–2.75/–1.75 V. c. Cyclic voltammetry of **2b** (4.6 mM) in DMF–0.1 M $n\text{Bu}_4\text{NBF}_4$ at 20 °C. Scan rate 0.5 V s⁻¹. Glassy carbon disk electrode (3 mm diameter). The scan is in the potential range: 0.0/–2.75/+1.0/0.0 V. d. Cyclic voltammetry of **2b** (5.0 mM) in DMF–0.1 M $n\text{Bu}_4\text{NBF}_4$ at 20 °C. Scan rate 3850 V s⁻¹. Gold UME disk electrode (25 μm diameter). The scan is in the potential range: –1.75/–2.75/–1.75 V

$n\text{Bu}_4\text{NBF}_4$. At low scan rates the reduction wave for each compound, R_1 , is chemically irreversible (Fig. 1a). In the anodic scan, and only after firstly carrying out one reduction scan, an oxidation wave appears, Ox_2 , at approximately 0.60 V.²⁴

However, when increasing the scan rate, the oxidation peak Ox_2 disappears and another oxidation wave, Ox_1 , is obtained. At high scan rates, only the reversible couple, R_1/Ox_1 , appears (Fig. 1b). For **1j**, in addition to the waves corresponding to reduction R_1 and oxidation Ox_2 , it is possible to observe—at any scan rate—another irreversible oxidation wave at +1.1 V, attributable to the oxidation of the piperidine²⁵ present in the aliphatic part of the initial compound. Similar cyclic voltammetric behaviour is obtained for the alkyl naphthyl ethers **2a–2j** (Figs. 1c and 1d). At low scan rates, the oxidation peak Ox_2' appears approximately at +0.02 V.²⁶

Analysis of the peak intensity, at low and high sweep rates, shows a two-electron process for low sweep rates and a one-electron process at high sweep rates (by comparison with the reduction of *p*-toluonitrile in the same medium). The shape of voltammograms (peak width) suggests a mixed kinetic control by electron transfer and chemical reaction for the R_1 reduction curve.²⁷ The peak potential is not concentration dependent (in the range 1–10 mM) and the variation of the peak potential with the scan rate is in the range 30–60 mV by unit log scan rate, for low scan rates.²⁷ For example, for **1a** in the range 0.1 to 1 V s⁻¹ the slope is 30 mV. Therefore, we can conclude that the initially produced radical anion reacts following a slow first order reaction pathway leading to a second electron transfer following a DISP1 mechanism.²⁸

The cyclic voltammetric data are summarised in Table 1. The values of E° (standard potential of reversible couple R_1/Ox_1), k (first order rate constant) and k_s (heterogeneous electron transfer rate constant) are determined by simulation of the experimental curves using DIGISIM® software.²⁹

Controlled potential electrolysis

Electrolysis was carried out until 2F at a potential slightly more negative than the peak potential for each compound solution. The electrolysis was carried out at potentials close to electrolyte background reduction, therefore the initial compound is not totally electrolysed. The current efficiency was less than 100% due to partial reduction of $n\text{Bu}_4\text{NBF}_4$ to tributylamine. In a blank experiment with electrolysis at –2.6 V of DMF–0.1 M $n\text{Bu}_4\text{NBF}_4$ solution, tributylamine is recovered after passage of 2F. 4-Cyanophenol or naphthol and tributylamine (from the supporting electrolyte $n\text{Bu}_4\text{NBF}_4$) were the only products obtained in each case. Analysis of the electrolysed solutions by electrochemical and GC + MS techniques indicated that no benzonitrile, 4,4'-dicyanobiphenyl or naphthalene were formed³⁰ (Table 2 summarises the results obtained), so the cleavage appears to be selective at the level of the aliphatic carbon–oxygen bond, leaving the oxygen atom attached to the aromatic part of the initial molecule.

In our cases, the effect of solvation and ion-pairing seems negligible. Using different solvents (DMF, ACN or THF) and different salts ($n\text{Bu}_4\text{NBF}_4$ and CsClO_4) as supporting electrolytes, no significant changes in the cleavage rates, standard potentials, and nature and yields of products were observed. The results for **1a** are summarized in Table 3. In ACN + 0.1 M $n\text{Bu}_4\text{NBF}_4$, the wave was slightly broad, its peak potential was more negative and k_s was the same order of magnitude as in DMF + 0.1 M $n\text{Bu}_4\text{NBF}_4$. In contrast, in DMF + 0.1 M CsClO_4 and in THF + 0.4 M $n\text{Bu}_4\text{NBF}_4$ the waves were quite broad and k_s was smaller than for DMF + 0.1 M $n\text{Bu}_4\text{NBF}_4$. The reversible wave was expected in the same range of scan rate values, in all the cases. The 4-cyanophenol was the only electrolysis product but with minor current efficiency (5 to 10%). This was possible due to great negative values of reduction applied potential and a large reduction of the supporting electrolyte (ACN and THF cases).

These results show that the electrochemical reduction for studied alkyl aryl ethers, in aprotic solvents, follows a mechanism such as the one described in Scheme 1. The anion radical

Table 1 Cyclic voltammetric data of **1a–1j** and **2a–2j** in DMF + 0.1 M nBu₄NBF₄ at 20.0 °C

Compound	$E_{pc}(R_1)^a$ (0.1 V s ⁻¹)	$\Delta E_p/mV$ (0.1 V s ⁻¹)	$E_{pa}(Ox_2)^a$ (0.1 V s ⁻¹)	k_s^b/cm s ⁻¹	$E^\circ(R_1/Ox_1)^{a,b}$	$[\log(k^b/s^{-1})] \pm 0.2$
1a	-2.49	60	0.59	0.07	-2.47	1.0
1b	-2.35 ₅	60	0.62	0.20	-2.39	2.9
1c	-2.51	66	0.59	0.02	-2.47	0.5
1d	-2.42 ₅	73	0.62	0.02	-2.42	3.1
1e	-2.50 ₅	59	0.56	0.03	-2.47	0.7
1f	-2.36	60	0.61	0.03	-2.36	2.3
1j	-2.53	60	0.61	0.02	-2.51	1.6
2a	-2.62	76	0.01	0.01	-2.57	0.7
2b	-2.45	82	0.02	0.02	-2.45	3.7
2d	-2.45 ₅	66	0.03	0.03	-2.46	2.7
2j	-2.59 ₅	60	0.02	0.02	-2.55	0.1 ₅

^a Potentials are in V vs. SCE. ^b The values of k_s , E° , and k are determined by simulation of the experimental cases using DIGISIM[®] software.

Table 2 Electrolysis of **1a–1j** in DMF–0.1 M nBu₄NBF₄ at 20.0 °C

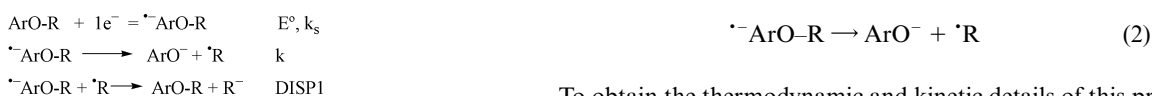
Compound ^a	E_{app}^b	% product ^c	% alkyl phenyl ether recovered ^d
1a	-2.55	34, (4-cyanophenol)	37
1b	-2.50	74, (4-cyanophenol)	23
1c	-2.53	23, (4-cyanophenol)	32
1d	-2.50	37, (4-cyanophenol)	15
1j	-2.55	6, (4-cyanophenol)	75
2a	-2.64	9, (1-naphthol)	69
2b	-2.55	26, (1-naphthol)	60
2d	-2.48	90, (1-naphthol)	4
2j	-2.60	20, (1-naphthol)	80

^a All concentrations were 10 mM. ^b Potentials are in V vs. SCE. Working electrode, fibre carbon. ^c The yield of products was determined by GC + MS spectroscopy. ^d The initial compound was not totally electrolysed. The current efficiency was less than 100% due to the slow reduction of the nBu₄NBF₄ electrolyte to tributylamine.

Table 3 Cyclic voltammetric data of **1a** at 20 °C in different solvents and electrolytes

Compound	$E_{pc}(R_1)^a$ (0.1 V s ⁻¹)	$\Delta E_p/mV$ (0.1 V s ⁻¹)	$E_{pa}(Ox_2)^a$ (0.1 V s ⁻¹)	k_s^b/cm s ⁻¹	$E^\circ(R_1/Ox_1)^{a,b}$	$[\log(k^b/s^{-1})] \pm 0.2$
1a DMF–0.1 M nBu ₄ BF ₄	-2.49	60	0.59	0.07	-2.46	1.0
1a DMF–0.1 M CsClO ₄	-2.60 ₅	80	0.64	0.004	-2.52	0.9
1a ACN–0.1 M nBu ₄ BF ₄	-2.57 ₅	50	0.58	0.07	-2.55	0.9
1a THF–0.4 M nBu ₄ BF ₄	-2.56 ₅	80	0.63	0.004	-2.48	0.6

^a Potentials are in V vs. SCE. ^b The values of k_s , E° , and k are determined by simulation of the experimental cases using DIGISIM[®] software.

**Scheme 1**

resulting from single electron transfer to aromatic ether is a frangible species, which decomposes in a stepwise process. In the radical anion, the unpaired electron must be located initially on the Ar portion of the molecule³¹ since its standard potential is very close to that of benzonitrile or naphthalene for the **1a–1j** and **2a–2j** series respectively. However it is always slightly more negative than $E^\circ(\text{benzonitrile}/\cdot\text{benzonitrile})$ or $E^\circ(\text{naphthalene}/\cdot\text{naphthalene})$, as expected from the effect of the R group. The cleavage of the bond leads to ArO⁻ and R[·] and thus involves an homolytic dissociation of the C_{aliphatic}–O bond in the radical anion ArO–R[·]^{1,8} since only the products arising from this reaction were recovered. The final reduction of R[·] takes place in solution by another radical anion³² due to the low value of the cleavage rate constant (DISP 1 mechanism^{27,28}).

Thermodynamics and kinetics of homolytic C–O bond cleavage in compounds **1a** to **1j**

We have just demonstrated that the bond cleavage between the oxygen and the aliphatic carbon, in the reduction of compounds **1a–1j**, leads to the initial homolytic dissociation:

To obtain the thermodynamic and kinetic details of this process we will follow the theoretical model for cleavage of radical anions described by Savéant.^{6a,b,8}

The standard free energy, ΔG° , of the overall reaction [eqn. (2)] is:

$$\Delta G^\circ = D_{\text{ArO-R}} + E^\circ_{\text{ArO-R}/\cdot\text{ArO-R}} - E^\circ_{\text{ArO}^-/\text{ArO}^\cdot} - T(S_{\text{ArO}^\cdot} + S_{\text{R}^\cdot} - S_{\cdot\text{ArO-R}}) \quad (3)$$

the D , E° and S values are the bond dissociation energies, the standard potentials and the molar entropies of the subscript species, respectively.

The activation free energy, ΔG^\ddagger , is related quadratically to standard free energy of the reaction, ΔG° :

$$\Delta G^\ddagger = \Delta G^{\circ\ddagger} (1 + \Delta G^\circ/4\Delta G^{\circ\ddagger})^2 \quad (4)$$

The standard activation free energy (intrinsic barrier), $\Delta G^{\circ\ddagger}$, is the sum of two contributions, one related to bond breaking (D) and the other to solvent reorganization (λ_o):

$$\Delta G^{\circ\ddagger} = (D_{\cdot\text{ArO-R}} + \lambda_o)/4 \quad (5)$$

Table 4 Reactivity data for the homolytic cleavage of aryl alkyl ethers^a

Compound	$D_{\text{ArO-R}}$	$-E^{\circ}_{\text{ArOR}'^-\text{ArOR}}$	$E^{\circ}_{\text{ArO}'^-\text{ArO}^-}$ ^b	$-\Delta G^{\circ}$	$\text{Log}(k/\text{s}^{-1})$	$\Delta G^{\circ\ddagger}$	Contribution, intra
1a	3.19 (73.6)	2.47	0.56	0.13	1.0	0.74 ₅	0.74
1b	2.52 (58.2)	2.39	0.56	0.72	2.9	0.89 ₅	0.60
1c	3.31 (76.4)	2.47	0.56	0.01	0.4 ₈	0.77 ₅	0.77 ₅
1d	2.71 (62.5)	2.42	0.56	0.59	3.0 ₈	0.83	0.64
1e	3.22 (74.3)	2.47	0.56	0.10	0.7	0.75	0.75
1f	3.06 (70.6)	2.36	0.56	0.15	2.3	0.68	0.74
1j	3.31 (76.4)	2.51	0.56	0.05	1.6	0.67	0.76 ₅

^a Energies in eV (kcal mol⁻¹), potentials in V vs. SCE. ^b From ref. 24b.

where the first term may be derived from accessible molecular parameters when, as explained before, the electron is initially accommodated in an orbital belonging to the Ar group

$$D_{-\text{ArO-R}} = D_{\text{ArO-R}} + E^{\circ}_{\text{ArO-R}'^-\text{ArO-R}} - E^{\circ}_{\text{ArO}'^-\text{ArO}^-} - T(S_{\text{ArO}'} - S_{-(\text{ArO}')} - S_{\text{ArO-R}} + S_{-\text{ArO-R}}) \quad (6)$$

(the D , E° and S values are the bond dissociation energies, the standard potentials and the molar entropies of the subscript species, respectively). The notation $'^-(\text{ArO}')$ represents from the radical ArO' , the injection of one electron into the π^* orbital. $'^-(\text{ArO}')$ is thus an excited state of the carbanion ArO' where one electron of the pair located in a σ orbital has been transferred to the π^* orbital.⁸

The cleavage rate constant of the radical anion and the standard potential for the formation of the radical anions of **1a** to **1j** were derived from the cyclic voltammetric data. The bond dissociation energy, $D_{\text{ArO-R}}$, was approximated to be the same as $D_{\text{PhO-R}}$ and it is calculated from comparison with the values for α -substituted acetophenones:¹²

$$D_{\text{R-OC}_6\text{H}_5} - D_{\text{R-Br}} = D_{\text{C}_6\text{H}_5\text{COCH}_2\text{-OC}_6\text{H}_5} - D_{\text{C}_6\text{H}_5\text{COCH}_2\text{-Br}} \quad (7)$$

the $D_{\text{R-Br}}$ values are obtained from the literature (tBuBr,³³ C₆H₅CH₂Br,¹² and 4-CNC₆H₄CH₂Br¹²) or from the reduction peak potential of the alkyl halide and the approximate linear correlation: $D_{\text{R-Br}} = -\frac{2}{3}(E_p - E^{\circ}_{\text{X}/\text{X}^-}) + \text{constant}$.^{3b} The standard free energy of radical anion cleavage ΔG° (the driving force for bond cleavage) may be obtained from eqn. (3), with ΔS (the entropy cleavage ArO-R) approximately equal to 1 meV K⁻¹; ΔS corresponding to the formation of two molecules from one is small and does not vary significantly in the series. The activation free energy ΔG^{\ddagger} may be obtained from $k = A \exp(-\Delta G^{\ddagger}/RT)$ in the application of eqn. (4); the pre-exponential factors are taken to be equal to $5 \times 10^{12} \text{ s}^{-1}$.¹² The intrinsic barrier free energy $\Delta G^{\circ\ddagger}$ was calculated according to the Marcus equation [eqn. (4)]. These values are of the same order of magnitude 0.7–0.8 eV for all compounds. We may calculate the contribution of the intramolecular factor to the bond cleavage: $D_{-\text{ArO-R}}/4$ by application of eqn. (6). In eqn. (6), $E^{\circ}_{\text{ArO}'^-\text{ArO}^-}$ was approximated to $E^{\circ}_{\text{benzonitrile}'^-\text{benzonitrile}}$ considering that the radical part located on the oxygen atom is not involved in the injection of one electron into the π^* orbital of the ArO'. Therefore $D_{-\text{ArO-R}}$ must be considered as a superior limit. The results are summarized in Table 4. In any case, as can be seen in Table 4, $D_{-\text{ArO-R}}$ represents the main factor of the total barrier, the solvent reorganisation providing a modest contribution for the intrinsic barrier in homolytic dissociations of radical anions. This is in strong contrast with the reported behaviour of α -substituted acetophenones, typical examples of intramolecular dissociative electron transfer.³⁴ Our observation confirms the previously proposed fact that solvent reorganisation is very much linked to charge reorganisation during the reaction.³⁴ In intramolecular dissociative electron transfer the solvent is organised around a negative charge, which develops on the leaving group during the reaction [eqn. (1b)]. In homolytic dissociations (the examples studied here), the cleavage

leaves the charge mainly in the same region, as in the radical anion.

Finally, we will consider the factors that govern the driving force [Table 4 and eqn. (3)] and the rate constants for the cleavage reaction (Table 4). The E° values of ArOR'⁻ArOR are practically constant (differences of 0.150 eV). E° values of ArO'⁻/ArO⁻ and ArO'⁻/(ArO⁻) are the same for each series of compounds, therefore the bond dissociation energy $D_{\text{ArO-R}}$ must be the main factor dictating the observed differences. The log (k/s^{-1}) values were in the range 0.48 to 3.08, the greater values of log k and the smaller $D_{\text{ArO-R}}$ values correspond to **1b** and **1d** compounds, with R being benzyl and allyl, respectively. For these compounds the values of ΔG° are the more negative in good concordance with Marcus's law. In this series of alkyl aryl ethers, the bond dissociation energy is quite large. Due to the bond cleavage leaving the oxygen atom in the aromatic part, the standard potential value of the leaving group [$E^{\circ}_{\text{ArO}'^-\text{ArO}^-}$] is very negative and close to the value of the standard potential of the reduction of the initial compound. It must be noticed that the ΔG° value for the cleavage reaction in the **1a** to **1j** compounds is in the same order of magnitude as the C–C bond cleavage⁷ or the C–O bond cleavage in α -substituted acetophenones¹² but the lower rate constant obtained here is due to the very negative E° value of the leaving group.

Thermodynamics and kinetics of homolytic C–O bond cleavage in compounds **2a** to **2j**

For these compounds no bond dissociation energy data, $D_{\text{ArO-R}}$, are available. We will demonstrate that it is possible to estimate reasonable values for $D_{\text{ArO-R}}$ in naphthyl ethers in a very simple way. As discussed before, neglecting the quadratic character of eqn. (4)^{3b} and introducing the values of $\Delta G^{\circ\ddagger}$ [eqn. (5) and (6)] with $\lambda_0 = 0$ and ΔG° [eqn. (3)],

$$\Delta G^{\ddagger} = \Delta G^{\circ\ddagger} + \Delta G^{\circ}/2 \quad (8)$$

$$\Delta G^{\ddagger} = 3D_{\text{NaphO-R}}/4 + 3E^{\circ}_{\text{NaphO-R}'^-\text{NaphO-R}}/4 - E^{\circ}_{\text{NaphO}'^-\text{NaphO}^-}/4 - E^{\circ}_{\text{NaphO}'/\text{NaphO}^-}/2 \quad (9)$$

leading to:³⁵

$$D_{\text{NaphO-R}} = 4[0.123 - 0.058 \log k - 3E^{\circ}_{\text{NaphO-R}'^-\text{NaphO-R}}/4]/3 \quad (10)$$

The results are presented in Table 5. The bond dissociation energy for naphthyl ethers is lower than for the corresponding 4-cyanophenyl ethers in good accordance with available thermodynamic data. For example, $D_{\text{ArO-R}}$ for compound **2a** is 2.67 and for compound **1a** is 3.19 eV. This variation is in good accord with available thermodynamic data on C–H bond values for analogous compounds,³⁶ $D_{\text{H-1-naphthylmethyl}} \cong 3.69$ eV and $D_{\text{H-CH}_2\text{C}_6\text{H}_5} \cong 3.84$ eV. Therefore, one last outcome of the present study could be the estimation of reliable values for the bond dissociation energy of naphthyl ethers, since data for simple ethers are currently available but no such values exist in the literature for naphthyl ethers.

Table 5 Bond dissociation energy for alkyl naphthyl ethers^a **2a–2j**

Compound	$-E^{\circ}_{\text{ArOR}^{\cdot-}/\text{ArOR}}$	$-E^{\circ}_{\text{ArO}^{\cdot}/\text{ArO}^{\cdot-}}$ ^b	Log (k/s^{-1})	$D_{\text{ArO-R}}$ ^c
2a	2.57	0.03	0.7	2.67 (61.6)
2b	2.45	0.03	3.7	2.33 (53.8)
2d	2.46	0.03	2.7	2.41 (55.6)
2j	2.55	0.03	0.1 ₅	2.70 (62.3)

^a Energies in eV (kcal mol⁻¹), potentials in V vs. SCE. ^b From ref. 20b. ^c See text.

Conclusions

The initially produced radical anion of alkyl aryl ethers reacts by a slow first order reaction. The cleavage of the bond leads to ArO⁻ and R[•] and thus involves an homolytic dissociation of the C_{aliphatic}-O bond in the molecule ⁻ArO-R.^{1,8} The final reduction of R[•] takes place in solution by the radical anion due to the low value of the cleavage rate constant (DISP1 mechanism^{23,24}). A Marcus type relationship between the cleavage rate constants and the standard free energy of the reaction leads to an intrinsic barrier in the range of 0.7 to 0.8 eV. In our approximation, $D_{\text{ArO-R}}$ represents the main factor of the total barrier, the solvent reorganisation being a modest contribution to the intrinsic barrier for homolytic dissociations of radical anions. This observation confirms the early proposal that solvent reorganisation is very much linked to charge reorganisation during the reaction. In intramolecular dissociative electron transfer the solvent, which is organised around a negative charge in the initial state of the radical anion, has to reorganise around a negative charge on the leaving group during the reaction [eqn. (1)]. In homolytic dissociations (the examples studied here), the charge is placed in the leaving group from the initial electron transfer beginning and therefore, little solvent reorganisation is needed during the reaction.

From our approach, it is also possible to determine reliable values for the bond dissociation energy of naphthyl ethers (no such values exist in the literature).

Experimental

Chemicals

4-Cyanophenyl benzyl ether³⁷ **1b**, *tert*-butyl 4-cyanophenyl ether³⁸ **1f**, 1-piperidino-2-(4-cyanophenoxy)ethane³⁹ **1j**, benzyl naphthyl ether⁴⁰ **2b**, and 1-piperidino-2-(1-naphthoxy)ethane⁴¹ **2j** were prepared and identified following previously described procedures.

All products were identified by comparison of their spectroscopy behaviour with those reported in the literature.

All chemicals were obtained from Aldrich and were of the highest purity available. They were used as received.

4-Cyanophenyl propyl ether,⁴² **1c**. Compound **1c** was prepared by the reaction of 4-cyanophenol with alkyl bromide in a basic medium, butanone-K₂CO₃. The solution was refluxed for 15 h. After cooling, the solution was poured into water and extracted with ether. After drying and recrystallizing the residue some colorless crystals were obtained. ¹H NMR(CDCl₃) δ (ppm) 7.56 (d, 2H), 6.92 (d, 2H), 3.93 (t, 2H), 1.80 (m, 2H), 1.02 (t, 3H).

Allyl 4-cyanophenyl ether,⁴³ **1d**. Compound **1d** was prepared by the reaction of 4-cyanophenol with alkenyl bromide in a basic medium, butanone-K₂CO₃, as previously described, **1c**. The solution was refluxed for 8 h. After cooling, the solution was poured into water and extracted with ether. After drying and recrystallizing the residue some white crystals were obtained. ¹H NMR(CDCl₃) δ (ppm) 7.56 (d, 2H), 6.94 (d, 2H), 6 (m, 1H), 5.32 (dd, 2H), 4.57 (d, 2H).

But-3-enyl 4-cyanophenyl ether,⁴⁴ **1e**. Compound **1e** was prepared by the reaction of 4-cyanophenol with alkenyl bromide in

a basic medium, butanone-K₂CO₃ as previously described, **1c**. ¹H NMR(CDCl₃) δ (ppm) 7.55 (d, 2H), 6.92 (d, 2H), 5.86 (m, 1H), 5.17 (dd, 2H), 4.05 (t, 2H), 2.54 (dd, 2H).

Allyl naphthyl ether,⁴⁵ **2d**. Compound **2d** was prepared by the reaction of 1-naphthol with allyl bromide in a basic medium, butanone-K₂CO₃ as previously described, **1c**. ¹H NMR(CDCl₃) δ (ppm) 8.22–6.53 (m, 7H), 5.97 (m, 1H), 6.0 (m, 1H), 5.3–5.15 (dd, 2H), 4.45 (d, 2H).

Instruments and procedures

Instruments and procedures were the same as previously described for cyclic voltammetry and electrolysis.⁴⁶

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