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 DISP1 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.1

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;2 or heterolytic [eqn. (1b)] in which there is “regioconservation” of the spin density.5 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 transfer1,8 in which the electron in an orbital centred on A is transferred to B with concerted bond breaking.

\[
\begin{align*}
\text{A} + \text{B} & \rightarrow \text{A}^- + \text{B}^+ \quad (1a) \\
\text{A}^- + \text{B} & \rightarrow \text{A}^- + \text{B}^- \quad (1b)
\end{align*}
\]

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 acetophenones12,13 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 bond cleavage of a C–C bond in diphenylethane derivatives,5–7 cation radicals of tert-butylated NADH analogues,8 the C–S bonds in sulfoxides,9,10 the S–S bond in diaryl sulfides,11 the C–O bond in aryloxycetophenones12,13 and the O–O bond in perbenzoates.14 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,15 very few chemical16 or electrochemical,17 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 literature17,18 and, on the other hand, the radical anion coupling reactions (that are components of S and reactions21,22) 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.

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, tetra-
alkylammonium salts as supporting electrolyte) always produce
the homolytic dissociation.\textsuperscript{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 Savant’s model,\textsuperscript{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.

<table>
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<th>R</th>
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<td>CH$_3$</td>
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<td>2j</td>
<td>CH$_2$CH$_2$NC$_3$I$_1$(H)$_0$</td>
</tr>
</tbody>
</table>

Results and discussion

Cyclic voltammetry

Fig. 1 shows voltammograms typical of 1a–1j in DMF–0.1 M
However, when increasing the scan rate, the oxidation peak Ox$_2$
disappears and another oxidation wave, Ox$_3$, is obtained. At
high scan rates, only the reversible couple, R$_1$/Ox$_2$, appears (Fig.
1b). For R$_1$, 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, attribut-
able to the oxidation of the piperidine\textsuperscript{25} 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$_3$, appears
approximately at +0.02 V.\textsuperscript{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-tolunitrile 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.\textsuperscript{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.\textsuperscript{28} 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.\textsuperscript{24}

The cyclic voltammetric data are summarised in Table 1. The
values of $E^*$ (standard potential of reversible couple R$_1$/Ox$_2$),
k (first order rate constant) and $k_2$ (heterogeneous electron
transfer rate constant) are determined by simulation of the
experimental curves using DIGISIM$^/$ software.\textsuperscript{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 nBuNBf$_4$ to tributylamine. In a
blank experiment with electrolysis at $-2.6$ V of DMF–0.1 M
nBuNBf$_4$ solution, tributylamine is recovered after passage of
2F. 4-Cyanophenol or naphthol and tributylamine (from the
supporting electrolyte nBuNBf$_4$) 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
formed\textsuperscript{30} (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 (nBuNBf$_4$ and CsClO$_4$) as supporting electrol-
ytes, 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
nBuNBf$_4$, the wave was slightly broad, its peak potential was
more negative and $k_2$ was the same order of magnitude as in
DMF + 0.1 M nBuNBf$_4$. In contrast, in DMF + 0.1 M
CsClO$_4$, and in THF + 0.4 M nBuNBf$_4$, the waves were quite
broad and $k_2$ was smaller than for DMF + 0.1M nBuNBf$_4$.
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 reduc-
tion 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 mecha-
nism such as the one described in Scheme 1. The anion radical

![Fig. 1](image-url)
resulting from single electron transfer to aromatic ether is a fragile species, which decomposes in a stepwise process. In the radical anion, the unpaired electron must be located initially on the Ar portion of the molecule\(^{12}\) 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 \(E^\circ(\text{benzonitrile}^{-})\) of benzonitrile or \(E^\circ(\text{naphthalene}^{-})\) of naphthalene, as expected from the effect of the R group. The cleavage of the bond leads to ArO\(^-\) or ArO\(^{2-}\) as depicted in theScheme 1.

\[ \text{ArO}^- + \text{e}^- \rightarrow \text{ArO}^- + \text{e}^- \]
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**Scheme 1**
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, $D_{ArO-R}$, was approximated to be the same as $D_{PhO-H}$ and it is calculated from comparison with the values for $\alpha$-substituted acetoephones.\(^{11}\)

The $D_{ArO-R}$ values are obtained from the literature (tBuBr,\(^{13}\) C\(\text{H}_\text{Me}_\text{C}_\text{H}_\text{Br}\), and 4-CN\(\text{C}_\text{H}_\text{Me}_\text{C}_\text{H}_\text{Br}\)) or from the reduction peak potential of the alkyl halide and the approximate linear correlation: $D_{R-BR} = \gamma(E_x - E_{NAP}) + \text{constant}$.\(^{7,10}\) The standard free energy of radical anion cleavage $\Delta G^\circ$ (the driving force for bond cleavage) may be obtained from eqn. (3), with $\Delta S$ (the entropy cleavage ArO-R) approximately equal to 1 meV K\(^{-1}\). $\Delta S$ corresponding to the formation of two molecules from one is small and does not vary significantly in the series. The activation free energy $\Delta G^\circ$ may be obtained from $E_a = \lambda \Delta G^\circ/RT$ in the application of eqn. (4); the pre-exponential factors are taken to be equal to 5 $\times$ 10\(^{-19}\) s\(^{-1}\).\(^{12}\) The intrinsic barrier free energy $\Delta G^\circ$ 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: $D_{ArO-R}/4$ by application of eqn. (6). In eqn. (6), $E_{ArO^-}/(ArO^-)$ was approximated to $E_{\text{benzenoid}}/E_{\text{benzenoid}}$ considering that the radical part located on the oxygen atom is not involved in the injection of one electron into the $\pi$ orbital of the ArO. Therefore $D_{ArO-R}$ must be considered as a superior limit. The results are summarized in Table 4. In any case, as can be seen in Table 4, $D_{ArO-R}$ 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 $\alpha$-substituted acetoephones, typical examples of intramolecular dissociative electron transfer.\(^{24}\) Our observation confirms the previously proposed fact that solvent reorganisation is very much linked to charge reorganisation during the reaction.\(^{24}\) In intramolecular dissociative electron transfer the solvent is organised around a negative charge, which develops on the leaving group during the reaction [eqn. (1)]. 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 $E^o$ values of ArOR$^\circ$/ArOR are practically constant (differences of 0.150 eV). $E^o$ values of ArO$^\circ$/ArO and ArO$^\circ$/ArO$^-$/ArO$^\circ$ are the same for each series of compounds, therefore the bond dissociation energy $D_{ArO-R}$ must be the main factor dictating the observed differences. The log ($\text{ks}^{-1}$) values were in the range 0.48 to 3.08, the greater values of log $k$ and the smaller $D_{ArO-R}$ values correspond to 1b and 1d compounds, with R being benzyl and allyl, respectively. For these compounds the values of $\Delta G^\circ$ are the more negative in good concordance with Marcus’s law. In this series of alkyl 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 $E_{\Delta G^\circ}$ 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 $\Delta G^\circ$ value for the cleavage reaction in the 1a to 1j compounds is in the same order of magnitude as the C-C bond cleavage\(^7\) or the C-O bond cleavage in $\alpha$-substituted acetoephones\(^{21}\) but the lower rate constant obtained here is due to the very negative $E^o$ 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, $D_{ArO-R}$, are available. We will demonstrate that it is possible to estimate reasonable values for $D_{ArO-R}$ in naphthyl ethers in a very simple way. As discussed before, neglecting the quadratic character of eqn. (4)\(^{10}\) and introducing the values of $\Delta G^\circ$ in eqn. (3) and (6) with $\lambda_o = 0$ and $\Delta G^\circ$ in eqn. (3),

$$\Delta G^\circ = \Delta G^\circ + \Delta G^\circ/2$$

leading to:

$$\Delta G^\circ = 3D_{NapH-O-R}/4 + 3E_{\text{NapH-O-R}/NapH-O-R}}/4 - E_{\text{NapH-O-R}/NapH-O-R}}/2$$

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, $D_{ArO-R}$ 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.\(^{26}\) $D_{H-O-naphthylethyl} = 3.69$ eV and $D_{H-C\text{-CH}_{2}R}$ $= 3.84$ 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 4 Reactivity data for the homolytic cleavage of aryl alkyl ethers

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<th>Compound</th>
<th>$D_{ArO-R}$</th>
<th>$-E^o_{ArO^-}/ArO^-R$</th>
<th>$E^o_{ArO^-}/ArO^-R$</th>
<th>$-\Delta G^\circ$</th>
<th>Log ($\text{ks}^{-1}$)</th>
<th>$\Delta G^\circ$</th>
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<td>3.19 (73.6)</td>
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<tr>
<td>1b</td>
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<td>2.39</td>
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<td>0.72</td>
<td>2.9</td>
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<td>0.60</td>
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<td>1c</td>
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<td>1d</td>
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<td>2.42</td>
<td>0.56</td>
<td>0.59</td>
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<td>2.47</td>
<td>0.56</td>
<td>0.10</td>
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<td>0.75</td>
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<tr>
<td>1j</td>
<td>3.06 (70.6)</td>
<td>2.36</td>
<td>0.56</td>
<td>0.15</td>
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<td>0.68</td>
<td>0.74</td>
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<tr>
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<td>0.05</td>
<td>1.6</td>
<td>0.67</td>
<td>0.76</td>
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*Energies in eV (kcal mol\(^{-1}\)), potentials in V vs. SCE. From ref. 24b.*
pared by the reaction of 4-cyanophenol with alkenyl bromide in the examples studied here), the charge is placed in the leaving group ing the reaction \[eqn. (1)\]. In homolytic dissociations (the reorganise around a negative charge on the leaving group during the reaction). In intramolecular dissociations this observation con rms the early proposal.

**Conclusions**

The initially produced radical anion of alkyl aryl ethers reacts with ether. After drying and recrystallizing the residue some processes.

**Experimental**

**Chemicals**

4-Cyanophenyl benzyl ether\(^{37}\) \(1b\), tert-butyl 4-cyanophenyl ether\(^{38}\) \(1f\), 1-piperidino-2-(4-cyanophenoxy)ethane\(^{39}\) \(1j\), benzyl naphthyl ether\(^{40}\) \(2b\), and 1-piperidino-2-(1-naphthoxy)ethane\(^{41}\) \(2i\) 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-\(\text{K}_2\text{CO}_3\). 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. \(^1\)H NMR(CDC\(_3\)) \(\delta\) (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\(^{33}\) \(1d\). Compound \(1d\) was prepared by the reaction of 4-cyanophenol with alkyl bromide in a basic medium, butanone-\(\text{K}_2\text{CO}_3\) 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. \(^1\)H NMR(CDC\(_3\)) \(\delta\) (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\(^{34}\) \(1e\). Compound \(1e\) was prepared by the reaction of 4-cyanophenol with alkyl bromide in a basic medium, butanone-\(\text{K}_2\text{CO}_3\) as previously described, \(1c\).

\(^{1}\)H NMR(CDC\(_3\)) \(\delta\) (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**\(^{35}\) \(2d\). Compound \(2d\) was prepared by the reaction of 1-naphthol with alkyl bromide in a basic medium, butanone-\(\text{K}_2\text{CO}_3\) as previously described, \(1c\).

\(^{1}\)H NMR(CDC\(_3\)) \(\delta\) (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.\(^{43}\)

**References**


20 (a) The first reduction wave, at = −1.0 V, in 4-nitrophenyl allyl ethers, 4-nitrophenyl phenyl ether, 4-nitrobenzyl phenyl ether, remains reversible at any scan rate. That is to say, within the time of cyclic voltammetric measurement the reductive cleavage of the C–O bond in the anion radical does not occur. 208 (b) M. Farriol, PhD Thesis, Universitat Autonoma, Barcelona, March 2000.


24 (a) This potential is identical to the one found for the oxidation of the anion 4-cyanophenoxide. 248 (b) P. Hapiot, J. Pinson and N. Youn, New J. Chem., 1992, 16, 877.

25 Addition of authentic piperidine (Aldrich, 99.5%) to a solution of 1j causes an increase in intensity of the +1.1 V oxidation peak. This potential is identical to the one found for the oxidation of the anion naphtinoxide. 249


28 Notice that the peak potential measured at 0.1 V s⁻¹ is slightly more negative than the reported E°’s in concordance with the kₐ value (<0.1 cm s⁻¹), except for 1b when the larger value of kₐ (0.2 cm s⁻¹) leads to a peak potential value more positive than the E° value.

29 The RH products (volatile products) were not quantified.

30 (a) Theoretical calculations 149 point to a significantly larger spin distribution (the unpinned electron) on the cyanophenyl region and a not Cα-C≡N–O bond stretching in the formation of radical anions in contrast with what was inferred by scission of the S–S bond in diaryl disulfides. 12 (b) L. Pisan, M. Farriol, X. Asensio, I. Gallardo, A. Gonzalez-Lafont, J. M. Lluch and J. Marquet, J. Am. Chem. Soc., in the press.

31 Another reaction was possible leading to a two electron process: H-atom abstraction from DMF by the alkyl R⁺, however no reduction products of the DMF part were recovered.


33 In the acetonaphthene series, the solvent is organised around a negative charge which is mostly concentrated on the carbonyl oxygen and has to realign around the negative charge which develops on the leaving group during the reaction. The contribution of solvent realignment to the intrinsic barrier appears to be less in 4-NO₂ and 4-CN substituted acetophenones, where the charge of the radical anion is more delocalised. 12

34 In the application of eqn. (9): E⁻ₐ₉ₐ₈o(Nₐ₈o) = –2.40 V and E⁻ₐ₈o(Nₐ₈o) = –0.03 V. 249


40 V. Daukasia and V. Paplausis, Zh. Khim., 1972, 14, 121.


