CLEAVAGE RATES FOR RADIOLYSIS-PRODUCED RADICAL ANIONS OF NAPHTHYLMETHYL PHENYL ETHERS AND NAPHTHYL BENZYL ETHERS

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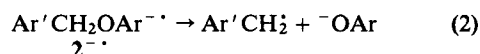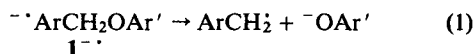*Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, U.S.A.*

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Cleavage reactions of α- and β-naphthylmethyl phenyl ethers and of α- and β-naphthyl benzyl ethers were studied by pulse radiolysis. Transient spectra indicate that reactions occur via electron capture followed by cleavage of the resultant radical anions to give arylmethyl radicals and aryloxide ions. Product studies of extensively irradiated samples are consistent with this scheme and show patterns which are informative for radiation studies in general. The reactions were studied in several solvents. The behavior of transient spectra obtained in acetonitrile for these ethers shows clearly that radical anions of the naphthylmethyl ethers cleave more rapidly than do the radical anions of the naphthyl benzyl ethers.

INTRODUCTION

Several years ago we reported kinetic studies which allowed us to suggest a general advantage in cleavage rate for benzylic ether radical anions with general structure $\mathbf{1}^{-\cdot}$ over those of structure $\mathbf{2}^{-\cdot}$ in cases where the cleavage energetics are comparable.

$$^{-\cdot}ArCH_2OAr' \rightarrow ArCH_2^{\cdot} + {}^{-}OAr' \qquad (1)$$
$$\mathbf{1}^{-\cdot}$$

$$Ar'CH_2OAr^{-\cdot} \rightarrow Ar'CH_2^{\cdot} + {}^{-}OAr \qquad (2)$$
$$\mathbf{2}^{-\cdot}$$

a Ar = 4-NO₂PH, Ar' = Ph

b Ar = naphthyl, Ar' = Ph

The first reactions studied were with Ar = 4-nitrophenyl and Ar' = phenyl (**1a** and **2a**).[1] In this case the rate of the reaction in equation (1) could be followed directly, but that in equation (2) was too slow to compete with side reactions. A second case was studied wherein Ar = α- or β-naphthyl and Ar' = phenyl (**1b** and **2b**).[2] In this instance, both ether radical anions underwent cleavage, but the actual cleavage reactions could not be studied directly. Rather, the reaction of

each ether with a relatively stable radical anion (fluoranthene radical anion) was followed. The rate constant for the cleavage of ether radical anions was calculated from the observed rate of loss of fluoranthene radical anion using electrochemical data to estimate the equilibrium constant for the production of the ether radical anion. In this latter case, a subsequent study involving isotopic selectivity in the cleavage of deuterium-labeled compounds was interpreted in support of the hypothesis that radical anion cleavage reactions of the type exemplified by equation (1) (D_N processes) proceeded via π^*-like transition states whereas those resembling equation (2) (D_R processes) involved σ^*-like transition states.[3]

Residual dissatisfaction with the indirect methods required for study of the cleavage reactions of $\mathbf{1b}^{-\cdot}$ and $\mathbf{2b}^{-\cdot}$ led us to investigate pulse radiolysis as a means for directly measuring the rate constants for these cases. In a number of different solvents, **1b** and **2b** were subjected to pulses of high-energy electrons in order to measure the kinetic behavior of the radical anions. This proved more difficult than expected because the cleavage reactions were so fast as to compete with the initial reaction with solvated electrons. Nevertheless, it was possible to demonstrate that the cleavage rates for $\mathbf{1b}^{-\cdot}$-type radical anions were at least 300 times faster than those of the $\mathbf{2b}^{-\cdot}$-type, as reported below. A side

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benefit from this study was the accumulation of information about products formed after cleavage in a variety of solvents.

RESULTS AND DISCUSSION

Kinetic measurements

Compound α-**1b** was studied in tetrahydrofuran (THF), dimethylformamide (DMF), DMF–water, propan-2-ol–water and acetonitrile. In all cases, transient absorption after the electron pulse appeared in a broad envelope extending from *ca* 310 to 370 nm. Literature spectra of α-naphthylmethyl radical show a sharp peak at 365 nm and a broad peak at 340 nm.[4] The sharp peak was not well resolved under our detection conditions, but the broad envelope observed was identical in shape with that produced under similar radiolysis conditions from either 1-naphthylmethyl benzoate or 1-naphthylmethyl acetate[5a] (the esters were subjected to radiolysis under conditions shown[5b] to give benzyl radicals from the corresponding benzyl esters). The transient spectrum for this radical in acetonitrile is shown in Figure 1. The absorption decayed in second-order fashion at a relatively slow rate (first half-life ranging from 40 to 200 μs, concentrations estimated at 10^{-5}–10^{-6} M). Curve fitting at 340 nm gave a rate constant range of 4×10^5–$23 \times 10^5 \varepsilon$. The value of the molar absorptivity (ε) for the transient radical is not known, but assuming a reasonable value near 10^4 would suggest that the transient disappears by a diffusion-limited, second-order process wherein both reactants are present at similar, low concentrations, presumably generated by the pulse. A similar result was obtained for β-**1b**, with the transient absorbance at about 380 nm in acetonitrile (see Figure 1) corresponding approximately to literature characteristics reported for β-naphthylmethyl radical in cyclohexane.[6]
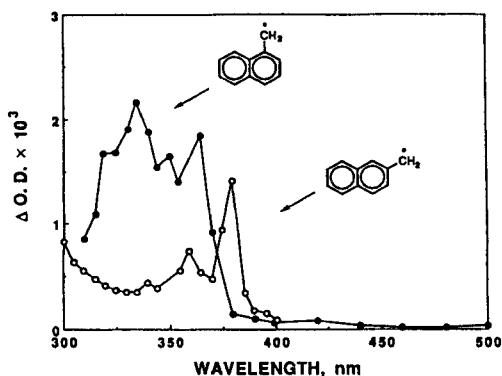

Figure 1. (•) Transient spectrum in acetonitrile from α-**1b**; (○) transient spectrum in acetonitrile from β-**1b**

Table 1. Approximate first-order rates (s^{-1}) for appearance of naphthylmethyl radical absorbance following the electron pulse in acetonitrile

Ether	Concentration (mM)		
	0·4	1	9
β-**1b**	$2·5 \times 10^7$	$3·8 \times 10^7$	$(4·0 \pm 1·0) \times 10^7$
α-**1b**	$1·8 \times 10^7$	$6·5 \times 10^7$	$>6 \times 10^7$

The appearance of the transient absorbances for the naphthylmethyl radicals from α- and β-**1b** was almost simultaneous with the pulse. However, it was possible to measure rise times approximately for the absorbance of each in acetonitrile. The results are given in Table 1. It is clear that with α-**1b**, the rate of appearance of α-naphthylmethyl radical is too fast to be distinguished from the one-electron reduction of the ether. The rate increases with increasing concentration of the ether, also suggesting that the process being measured is electron transfer, probably from a solvent-derived species.[7] With β-**1b**, the rate appears to level off slightly below the upper limit for detection. Direct comparison of the rise curves for α- and β-**1b** suggests that the process observed with the β-isomer is measurably slower. We therefore tentatively assign the value of 4×10^7 s^{-1} as the rate constant for dissociation of β-**1b**$^{-\cdot}$. In any event, the measured value constitutes a lower limit for this process.

Compounds α and β-**2b** were also studied in several solvents. In isopropyl alcohol–water (70 : 30, v/v) with 0·05 M NaOH present, a broad maximum appears extending from 500 past 800 nm. This absorption is due to the solvated electron because it appears in the absence of the ethers. Its disappearance is promoted by the ethers with the rate constant of $8·5 \times 10^5$ s^{-1}, increasing to about 4×10^6 s^{-1} in the presence of 2 mM α- or β-**2b**. In the case of α-**2b**, the solvated electron spectrum is replaced by absorbance at 335 nm corresponding to that for α-naphthoxide, measured in this solvent mixture. As expected, this absorption does not decay when the measurement is carried out in the presence of 0·05 M NaOH. For β-**2b**, the product from decay of the long-wavelength transient grows in at the approximate wavelength for β-naphthoxide, but it decays by a second-order process and thus seems unlikely to be naphthoxide. It could possibly be due to the radical anion but, if so, the process observed for its disappearance is not unimolecular.

More directly interpretable results were obtained with acetonitrile. With α-**2b**, a broad transient absorbance was observed in the region between 375 and 500 nm, in addition to a sharper absorbance at 330 nm (see Figure 2; the plot of the 'short-time' spectrum was obtained by subtraction of the 'long-time' plateau). The
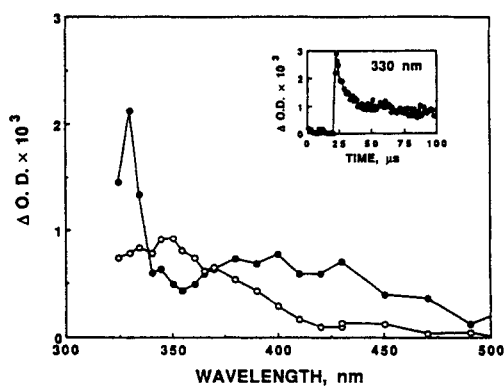
Figure 2. (●) Transient spectrum in acetonitrile from α-2b after 2 μs with 90 μs spectrum subtracted; (○) transient spectrum in acetonitrile from α-2b after 90 μs

spectral properties observed are very similar to those reported for chloronaphthalene radical anions in HMPA.[8] The absorbances at both longer shorter wavelengths decayed by first-order processes with the same rate constant, $1·2 \times 10^6$ s^{-1} (Figure 2, inset). Transient behavior in the intermediate region from 340 to 375 nm was more complicated, showing an initial growth and a slow decay. This could possibly be due to the formation of naphthoxide and its protonation to give naphthol. In the case of β-2b, the absorbance from 375 to 500 nm was also observed (Figure 3) and decayed at a ca ten times slower rate, $1·5 \times 10^5$ s^{-1} (Figure 3, inset). At the edge of the accessible spectral region, about 340 nm (at shorter wavelengths the ether absorbs), a slowly decaying transient absorption appears which may be naphthoxide.

Using the appearance kinetics for naphthylmethyl radicals from α- and β-1b and the disappearance

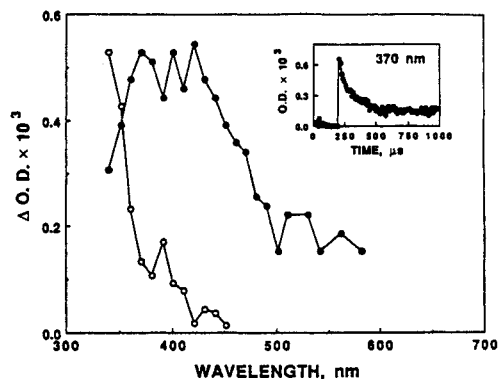Figure 3. (●) Transient spectrum in acetonitrile from β-2b after 10 μs with 900 μs spectrum subtracted; (○) transient spectrum in acetonitrile from β-2b after 900 μs

Table 2. Summary of rate constants for dissociation of ether radical anions

Ether	Rate constant for radical anion dissociation (s^{-1})
β-NpOCH$_2$Ph, β-2b	$(1·5 \pm 0·5) \times 10^5$
α-NpOCH$_2$Ph, α-2b	$(1·2 \pm 0·2) \times 10^6$
β-NpCH$_2$OPh, β-1b	$(4·0 \pm 1·0) \times 10^7$
α-NpCH$_2$OPh, α-1b	$>6 \times 10^7$

kinetics for α- and β-2b$^-$ allows us to present the summary of results for the pulse radiolysis of these ethers given in Table 2.

Product studies

Product studies were carried out as part of the investigation to find an appropriate solvent. Available data, in some cases partial, are reported for a number of solvents in the experimental section. Cleavage was observed for ethers of both types 1 and 2 in THF and in DMF−water. In isopropyl alcohol−water, and also in acetonitrile, only the type 1 ethers gave detectable amounts of cleavage products.

In acetonitrile, the solvent which best facilitated kinetic studies, the products identified were those shown in Table 3. In each case, analysis of solutions in which a measured amount of a reference material was added to both the pre- and post-irradiated samples showed that a substantial amount of ether was converted into products which were not easily quantified by gas chromatography. We are finding this to be a general problem with aromatic substrates containing two or more fused rings. In the case of naphthalene itself, for example, we have been able to detect a large number of products, no one of which makes up more than 1% of the loss but which together account for most of the missing material. Most of these appear by gas chromatography−mass spectrometry (GC−MS) to be derived from addition of one or more solvent radicals to the aromatic ring followed by disproportionation and other reactions of the resultant radicals. The large number of possible isomeric structures for each product type leads to an extremely complex mixture. With naphthyl halides, the mixture of products derived from addition of solvent radicals is even more complex but, in general, the compounds produced retain halogen or are in other ways distinct from radical anion-derived products.[9] Because radiolysis necessarily produces solvent radical cations in equal number to solvated electrons and the radical cations usually deprotonate to give radicals, it is likely that the problem documented here exists for all studies involving radiolysis-produced radical anions.

Compounds α- and β-1b gave phenol along with naphthalenecarboxaldehyde in the former case and the

Table 3. Products from ^{60}Co radiation of ethers (1·05 Mrad over 17 h) as assayed by GC and GC–MS

Ether	Et₃N	Ar(')OH	Ar(')CH=O	Ar(')Me	Other	Recovered ether
						Product mixture (%)[1]
α-1b	No	8·5	4·8	<0·5	<0·5	57
α-1b	Yes	6·9	1·2	0·7	[b]	58
β-1b	No	[c]	<0·5	0·7	3·5[d]	67
β-1b	Yes	8·0	2·1	0·9	1[e]	60
α-2b	No	<0·5	<0·5	n·d·[f]	<0·5	84
α-2b	Yes	1–3[g]	<0·5	n·d·[f]	[g]	68
β-2b	No	<0·5	<0·5	n·d·[f]	<0·5	83
β-2b	Yes	Trace[h]	<0·5	n·d·[f]	<0·5	81

[a] Yield given as % of possible maximum assuming flame ionization detector peak area proportional to weight of material.
[b] Two additional GC peaks observed (<1%). GC–MS shows ion at m/z 141, suggesting ArCH₂ group.
[c] Phenol present but amount not measured.
[d] GC–MS shows ion at m/z at 181, 141 and 115, suggesting coupling product of ArCH₂ and acetonitrile-derived radical.
[e] GC–MS shows ion at m/z 100, suggesting Et₃N-derived fragment.
[f] Not detected. Toluene would appear within solvent envelope.
[g] Naphthol and 1,2-diphenylethane were not separable, but both present.
[h] Detected in very small amount by GC–MS.

coupling product of naphthylmethyl radical and a solvent radical in the latter. For α- and β-2b, no significant amounts of products were obtained in pure acetonitrile. When triethylamine, 0·14 M was added to the reaction mixture for radiolysis of α-2b, however, α-naphthol and 1,2-diphenylethane were observed in small amounts. In the case of β-2b, a trace of β-naphthol was detected.

Despite the fact that in all cases considerable fraction of the starting ether is not accounted for by the products formed, it seems fair to say that radiation-produced reaction is more extensive with the 1b ethers than with their 2b counterparts. We suggest that the radical anions α- and β-2b⁻·, which undergo cleavage more slowly than α- and β-1b⁻·, are subject to oxidation by species which result from persistent forms of oxidatively modified solvent molecules. Such species are possibly generated as by-products of electron production. In this regard, it is interesting that the naphthylmethyl radical from α-1b is apparently oxidized to naphthalenecarboxaldehyde under continuous radiation. We therefore suggest that even though the radical anions are observed to undergo cleavage after a single pulse of radiation, continuous irradiation of acetonitrile solutions allow the oxidizing species to build to sufficiently high concentrations that they oxidize the slower reacting radical anions and prevent cleavage from occurring. In the presence of triethylamine, we suggest that such oxidized by-products or possibly radical cations which are precur-

sors to these by-products are reduced by triethylamine and, therefore, do not reach high enough concentrations to allow oxidation of the two radical anions to compete with cleavage. Under such circumstances, solvated electrons are used more efficiently and measurable amounts of cleavage products are obtained.

DISCUSSION

As can be seen in Table 2, the pulse radiolysis experiments carried out in acetonitrile are consistent with our earlier conclusions. In our earlier study,[1] we concluded that the rate for the dissociation of α-1b⁻· was faster than that for β-1b⁻· by a factor of ca 40. Similarly, the rate for α-2b⁻· was faster than that for β-2b⁻· by a factor of 13. These ratios are within experimental error of those measured in the present study, considering that the value for the fastest reacting isomer is clearly beyond the range of measurement. In the previous study, the relative rates for the 1 isomers were estimated to be 10^4 times faster than those for the 2 isomers. This is a substantially greater spread than the roughly 300 reported in Table 2. However, even the slower of the two fast processes is barely measurable and the value of 300 is reasonably viewed as a minimum value. The kinetic studies agree with product studies in that, in the absence of triethylamine, the extent of formation of cleavage products from ^{60}Co irradiation is substantially less for the isomers labelled 2b.

We believe that we have come as close as will be poss-

ible to measuring rates for the four cleavage reactions using pulse radiolysis methods. The rates for the faster reactions are slightly too fast for this technique. We hope, in the future, to prepare a comparable series of ethers in which the radical anions are slightly more stable, thus allowing direct measurement of cleavage for isomeric ether radical anions of type $1^{-\cdot}$ and $2^{-\cdot}$ under the same experimental conditions. The data in this paper, nevertheless, clearly show that the cleavage reactions of $1b^{-\cdot}$ are faster than those of $2b^{-\cdot}$.

EXPERIMENTAL

Solvents and reagents. Solvents were of HPLC grade from Aldrich Chemical and were used without purification, except for THF, which was distilled from sodium benzophenone ketyl. HPLC-grade acetonitrile proved superior to 'anhydrous 99%' which contained an impurity which interfered with transient production. The four ethers were prepared as described earlier.[1]

Pulse radiolysis experiments. The pulse radiolysis experiments were performed using a 10 ns pulse of 8 MeV electrons from the Notre Dame Radiation Laboratory linear accelerator. The LINAC pulse radiolysis apparatus has been described in detail previously.[10] The doses used were ca 500 rad per pulse as determined by thiocyanate dosimetry. Solutions were flowed through a 1 cm optical path length cylindrical Suprasil cell at a rate of 3–5 ml min^{-1} from a solution reservoir connected by glass tubing. Unless stated otherwise, solutions were deoxygenated by bubbling continuously with high-purity nitrogen throughout the experiment.

Product studies. For several solvents, experiments were carried out in which solutions of the ethers were subjected to multiple electron pulses or extended continuous irradiation by a ^{60}Co source. The products obtained were consistent with ether cleavage although, in many cases, involved participation by solvent. In THF, multiple pulse irradiation of α-**1b** gave as a major product a compound with major intensity mass spectral ions at m/z 212, 141 and 71, suggesting the structure 1-(1-naphthylmethyl)tetrahydrofuran. A small amount of 1,2-dinaphthylethane was also observed. Phenol was necessarily lost in concentration of the solution for analysis. With α-**2b**, a similar solvent adduct with mass spectral ions at m/z 162, 91 and 71 suggested 1-benzyltetrahydrofuran. In this case naphthol was also observed. In dimethylformamide (DMF) solution, α-**1b** gave a product with a parent ion at m/Z 213 and prominent peaks at m/z 141 and 72, suggesting combination of a naphthylmethyl radical with a solvent-derived radical. Interestingly, when the radiolysis of α-**1b** was carried out in DMF in the presence of sodium tetraphenylborate, the main product became

dinaphthylethane along with some methylnaphthalene, producing biphenyl as a side product. As it is known that the BPh_4^- ion is readily oxidized to biphenyl,[11] it is our suggestion that the BPh_4^- ion traps the radical cation of DMF and prevents its subsequent involvement in forming a solvent adduct. The solvated electrons produced in the radiolytic separation then react with ether molecules to give radical anions which give the expected arylmethyl radicals. Similar behavior was observed in DMF–water mixtures. Both α-**1b** and α-**2b** were run in DMF–water with methylnaphthalene, dinaphthylethane and solvent adduct appearing as products in the former case and naphthol in the latter.

The full set of ethers were run in isopropyl alcohol–water (70 : 30, v/v). For α- and β-**1b**, the major products were methylnaphthalenes, dinaphthylethanes, a compound assigned to be 2-methyl-3-naphthylpropan-1-ol [solvent adduct: mass spectrum, $m/z = 200$, 142, 115 and 59; ^{1}H NMR (CDCl$_3$) δ 3·3 (s, 2 H), 1·3 ppm (s, 6 H)] along with a few minor products. Neither α- nor β-**2b** gave measurable amounts of products in this solvent.

We subjected all four ethers at concentrations of 5 mM in acetonitrile to radiolysis by 1·4 mR of γ-radiation from a ^{60}Co source over a period of 17 h. Reaction solutions were analysed before and after irradiation after adding a measured amount of biphenyl to an aliquot prior to analysis. The results are summarized in Table 3. Compound α-**1b** gave mainly naphthalene-1-carboxaldehyde as identified by its retention time and mass spectrum, along with phenol. Compound β-**1b** gave, in addition to phenol, mainly a solvent (acetonitrile) adduct of the naphthylmethyl radical showing prominent ions at m/z 181 and 141. A trace of methylnaphthalene was also observed. Compounds α- and β-**2b**, remarkably, gave no gas chromatographically observable products after the same treatment. Detection limits suggested that the amount of cleavage products (specifically naphthol could be expected) were less than 5% of the amount of products from α- and β-**1b**. When the radiolysis of these ethers in acetonitrile was carried out in the presence of triethylamine, an additive selected to consume strongly oxidizing transients, the same products were observed for α- and β-**1b**. However, α- and β-**2b** now gave naphthols along with several other products.

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