3136 *J. Am. Chem. Soc.* **1990**, *112*, 3136-3139

Isotopic Selectivity in the One-Electron-Promoted Cleavage of Ring-Deuterated Naphthylmethyl Phenyl Ethers and Naphthyl Benzyl Ethers

Robert D. Guthrie* and Buchang Shi

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506. *Received September 15, 1989*

Abstract: (1-Naphthyl)methyl phenyl ether (**1**) and 1-naphthyl benzyl ether (**2**) have been allowed to compete against isotopically modified **1** or **2** in reactions with fluoranthene radical anion, $F^{\bullet-}$, and biphenyl radical anion, $B^{\bullet-}$. These reactions involve electron transfer followed by CH_2–O bond cleavage. Discrimination is observed in favor of **1** when it competes with naphthalene-ring-deuterated **1** ($C_{10}D_7CH_2OC_6H_5$) in reaction with $F^{\bullet-}$. Discrimination is not observed when the naphthalene ring of **2** is modified. Neither naphthalene-ring-deuterated **1** nor **2** showed isotopic selectivity in reaction with $B^{\bullet-}$. Small but experimentally significant discriminations are detected for the case of **2** with modified benzyl groups ($C_6D_5CH_2$ and $C_6D_5CD_2$) reacting with $F^{\bullet-}$. The results are interpreted as indicating a transition state for cleavage of $\mathbf{1}^{\bullet-}$ in which the extra electron is substantially located in the π^* molecular orbital of the naphthalene ring. Cleavage of $\mathbf{2}^{\bullet-}$ is better viewed as involving a σ^*-like transition state.

Our interest in the cleavage reactions of radical anions began with an attempt to compare the reactions of eqs 1 and 2.[1] We found that while reactions described by eq 1 took place readily under a variety of conditions, comparable versions of eq 2 were not observable and could be shown to be at least 10^4 times slower.

$$^{\bullet-}O_2NC_6H_4CR_2\text{-}OC_6H_5 \xrightarrow{D_N} O_2NC_6H_4CR_2^{\bullet} + {}^{-}\!:\!OC_6H_5 \quad (1)$$

$$C_6H_5CR_2\text{-}OC_6H_4NO_2^{\bullet-} \xrightarrow{D_R} C_6H_5CR_2^{\bullet} + {}^{-}\!:\!OC_6H_4NO_2 \quad (2)$$

It appeared to us that the process of eq 2 should be thermodynamically more favorable than that of eq 1, thus demanding some explanation for the fact that it is much slower. We offered the hypothesis that the transition state for eq 1 can be approximated by a bond-polarized structure ($^{\bullet-}NO_2C_6H_4CR_2^{+}\ {}^{-}\!:\!OC_6H_5$) which is clearly lower in energy than any bond-polarized representation of the transition state for the hypothetical reaction of eq 2. Thus, while the reaction of eq 1 may be viewed as an essentially heterolytic process (D_N),[2] the reaction of eq 2 is formally a homolytic process (D_R).[2] A reasonable picture of the transition state for the reaction of eq 2 is $C_6H_5CR_2^{\bullet}\ {}^{\bullet}OC_6H_4NO_2^{\bullet-}$ but this is apparently inaccessible under conditions which produce cleavage of **1**.

Because the reaction of eq 2 could not be observed, we increased the driving force for the scission reaction by replacing the nitrophenyl moiety with a naphthyl group. We prepared and studied the reactions of (1-naphthyl)methyl phenyl ether (**1**) and 1-naphthyl benzyl ether (**2**) with one-electron donors such as fluoranthene radical anion, $F^{\bullet-}$. In the particular case of $F^{\bullet-}$ the electron-transfer reaction is reversible, and the subsequent cleavage is rate-limiting. Using electrochemical data to estimate the equilibrium constant for electron transfer from $F^{\bullet-}$ to **1** and **2** we found that the D_N process (eq 3) is still much faster than the D_R process (eq 4).[3]

$$\underset{\mathbf{1}^{\bullet-}}{^{\bullet-}C_{10}H_7CH_2OC_6H_5} \xrightarrow{D_N} C_{10}H_7CH_2^{\bullet} + {}^{-}\!:\!OC_6H_5 \quad (3)$$

$$\underset{\mathbf{2}^{\bullet-}}{C_6H_5CH_2OC_{10}H_7^{\bullet-}} \xrightarrow{D_R} C_6H_5CH_2^{\bullet} + {}^{-}\!:\!OC_{10}H_7 \quad (4)$$

Overlapping with this work was a study by Walsh[4] involving cleavage of aryl groups from the 9-position of fluorene radical anions. Here, the same preference for the D_N mode of scission is argued from the effect of substituents on the competitive loss of different aryl groups. Maslak and Narvaez have also provided an example wherein an electron-withdrawing substituent at the end of a C–C bond, remote from the electron-resident functionality, increases the scission rate, despite the fact that a negative charge seems unlikely to reside permanently in the substituent-carrying fragment after cleavage of the bond.[5] Walsh suggests that in one case, the inherent preference for the D_N mode over the D_R mode results in initial formation of contrathermodynamic products. However, an alternative explanation of these substituent effects is that the extra electron is largely transferred to the σ^* orbital of the scissile bond prior to cleavage, a process named D_{RN}.[2] A reaction proceeding by this cleavage mode could possibly respond to substituent effects in much the same way as one with a D_N mechanism.

While searching for better understanding of the distinction between these processes, we became aware of the remarkable effect of ring deuteration on the stability of arene radical anions discovered by Stevenson.[6] Stevenson measured the equilibrium constant for the reaction of naphthalene radical anion with naphthalene-d_8 (see eq 5) and found $K_{eq} = 0.3$, favoring undeuterated radical anion.

$$^{\bullet-}C_{10}H_8 + C_{10}D_8 \rightleftarrows C_{10}H_8 + {}^{\bullet-}C_{10}D_8 \quad (5)$$

Thus, starting with a mixture of equal amounts of naphthalene and naphthalene-d_8 equilibration with a one-electron donor would be expected to produce naphthalene radical anion and deuterated naphthalene radical anion in a ratio of 1.7:1. It follows that if mixtures of naphthalene-ring-deuterated and -undeuterated ethers are allowed to compete in the reaction with one-electron donors, we should see isotopic selectivity in formation of $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$ which is comparable to that documented by Stevenson. If $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$ were formed reversibly, the occurrence of an isotope-dependent selectivity on the complete transformation of **1** or **2** to products would then depend on whether the transition states for eqs 3 and 4 change in energy as a function of isotopic substitution. If the transition state for scission resembles a naphthalene radical anion with the charge substantially present in the π system of the naphthalene ring, isotopic selectivity in the overall reaction would be anticipated. If, however, the transition

---

[1] Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2628–2636.

[2] IUPAC rules for representation of reaction mechanisms: *Pure Appl. Chem.* **1989**, *61*, 23–56. Other material relating to this may be found in the following: Guthrie, R. D.; Jencks, W. P. *Acc. Chem. Res.* **1989**, *22*, 343–349. Guthrie, R. D. *Stud. Org. Chem.* **1986**, *31*, 321–328.

[3] Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2637–2640.

[4] Walsh, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 1511–1518.

[5] Maslak, P.; Narvaez, J. N. *J. Chem. Soc., Chem. Commun.* **1989**, 138–139.

[6] Stevenson, G. R.; Espe, M. T.; Reiter, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 5760–5762.

0002-7863/90/1512-3136$02.50/0 © 1990 American Chemical Society

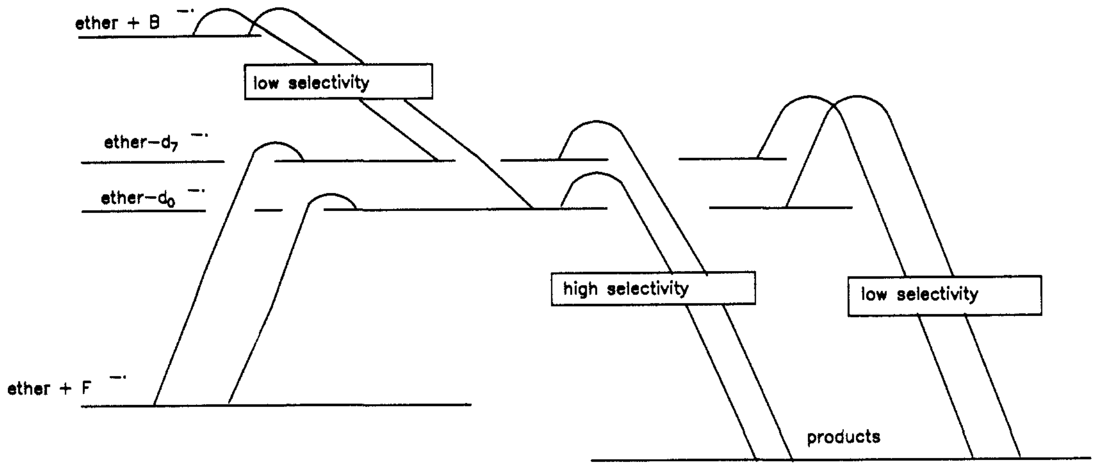

Figure 1. Schematic free energy diagram for reaction of mixtures of deuterated and undeuterated ethers with one-electron donors.

state resembles a benzene radical anion (electron transfer to the phenyl ring prior to scission) or a σ^* radical anion (localization of the extra electron in the scissile bond) a smaller isotopic selectivity should be found because even though formation of undeuterated radical anion is still favored, the free energy of activation leading to products would be higher in comparison to the deuterated compound and would cancel its stability advantage. A schematic energy diagram representing these alternative situations is given in Figure 1, starting at the lower left and proceeding to products by routes labeled "high selectivity" and "low selectivity". Other paths in Figure 1 are described in the Discussion section. We decided to study competitions involving the reactions of eqs 3 and 4 in the hope of making a distinction between the transition states for these reactions. This paper reports the results of our study.

Results

The experiments of eqs 6 and 7 were carried out by treating ether samples with substoichiometric amounts of fluoranthene radical anion, $F^{\bullet-}$, or the radical anion of biphenyl, $B^{\bullet-}$. Reaction

$$\begin{array}{lcll} C_{10}H_7CH_2OC_6H_5 & & C_{10}H_7CH_3 & \text{Starting ether enriched in D.} \\ & + F^{\bullet-} \rightarrow & & \qquad (6) \\ C_{10}D_7CH_2OC_6H_5 & & C_{10}D_7CH_3 & \text{Product enriched in H.} \end{array}$$

$$\begin{array}{lcll} C_6H_5CH_2OC_{10}H_7 & & HOC_{10}H_7 & \text{No isotopic enrichment observed.} \\ & + F^{\bullet-} \rightarrow & & \qquad (7) \\ C_6H_5CH_2OC_{10}D_7 & & HOC_{10}D_7 & \end{array}$$

$F^{\bullet-}$ = fluoranthene radical anion

mixtures were separated by gas chromatography, and the unreacted starting ether as well as the isotopically labeled product fraction were compared to standard mixtures by mass spectrometry. The results are listed in Table I.[7]

Runs 1, 2, 4, 5, and 6 involve the reaction of **1**, deuterated in the naphthalene ring, with $F^{\bullet-}$. The isotopic selectivity is not as large as for the equilibrium of eq 5, but is, nevertheless, of significant magnitude. With $F^{\bullet-}$ as the donor, the product is methylnaphthalene, requiring 2 mol of $F^{\bullet-}$/mol of ether;[3] thus runs 1–2 produce an approximately 25% yield of product, run 5, 50%, and run 6, 75%. The data show that the residual ether is enriched in deuterium content with the extent of the enrichment increasing with conversion. The methylnaphthalene produced is enriched in undeuterated material with the extent of enrichment decreasing with conversion. There is some scatter in the data, particularly in residual ether at high conversion, probably due to the difficulty of knowing radical anion concentrations exactly, but the data nevertheless clearly show that $F^{\bullet-}$ selectively converts undeuterated **1** to methylnaphthalene with a selectivity factor **1**-d_0/**1**-d_{3-7} = 1.3. Run 2 was carried out with excess fluoranthene added to the reaction mixture in order to see whether changing the fraction of $\mathbf{1}^{\bullet-}$ being converted to product affects the selectivity, but the selectivity was unchanged. Run 4 was carried out in dimethylformamide rather than in THF, but again this did not change the selectivity.

Table I. Isotopic Selectivity for Reaction of 1:1 Mixtures of Deuterated and Undeuterated Ethers with Radical Anions

run no.	deuterated[a] ether	radical anion[b]	$X^{\bullet-}$/ ether	residual ether $d_0/\sum d_{3-7}$[c]	product $d_0/\sum d_{3-7}$[c]
1	$C_{10}D_7CH_2OC_6H_5$	$F^{\bullet-}$	0.5	0.83 ± 0.04	1.31 ± 0.05[e]
2	$C_{10}D_7CH_2OC_{H5}$	$F^{\bullet-}$[d]	0.5	0.85 ± 0.02	1.34 ± 0.04[e]
3	$C_{10}D_7CH_2OC_6H_5$	$B^{\bullet-}$	0.5	0.92 ± 0.06[f]	0.99 ± 0.05[g]
4	$C_{10}D_7CH_2OC_6H_5$	$F^{\bullet-}$[h]	0.8	0.85 ± 0.04	1.33 ± 0.04[e]
5	$C_{10}D_7CH_2OC_6H_5$	$F^{\bullet-}$	1.0	0.67 ± 0.02	1.32 ± 0.13[e]
6	$C_{10}D_7CH_2OC_6H_5$	$F^{\bullet-}$	1.5	0.74 ± 0.06[j]	1.16 ± 0.02[e]
7	$C_{10}D_7OCH_2C_6H_5$	$F^{\bullet-}$	0.5	1.04 ± 0.11	0.89 ± 0.10[i]
8	$C_{10}D_7OCH_2C_6H_5$	$B^{\bullet-}$	0.5	0.96 ± 0.07	0.94 ± 0.06[i]
9	$C_{10}D_7OCH_2C_6H_5$	$F^{\bullet-}$[h]	0.8	1.05 ± 0.14	0.93 ± 0.09[i]
10	$C_{10}D_7OCH_2C_6H_5$	$F^{\bullet-}$	1.0	0.97 ± 0.13	1.01 ± 0.07[i]
11	$C_{10}D_7OCH_2C_6H_5$	$F^{\bullet-}$	1.0[k]	1.04 ± 0.10	
12	$C_{10}D_7OCH_2C_6H_5$	$F^{\bullet-}$	1.5	1.01 ± 0.09	1.12 ± 0.03[i]
13	$C_{10}H_7OCH_2C_6D_5$	$F^{\bullet-}$	1.0[l]	1.00 ± 0.06	
14	$C_{10}H_7OCH_2C_6D_5$	$F^{\bullet-}$	1.0[m]	1.00 ± 0.08	
15	$C_{10}H_7OCH_2C_6D_5$	$F^{\bullet-}$	1.5[n]	0.87 ± 0.09[o]	
16	$C_{10}H_7OCD_2C_6D_5$	$F^{\bullet-}$	1.0[l]	0.96 ± 0.04	
17	$C_{10}H_7OCD_2C_6D_5$	$F^{\bullet-}$	1.0[p]	0.85 ± 0.06	
18	$C_{10}H_7OCD_2C_6D_5$	$F^{\bullet-}$	1.5[n]	0.71 ± 0.07[q]	

[a] Naphthalene-ring-deuterated ethers contained substantial amounts of d_6 material as well as small amounts of d_5, d_4, and d_3 material. No significant difference in d_6:d_7 ratio was observed after reaction. Concentrations of ether were 0.05–0.10 M in THF and reaction temperature was 25 °C unless otherwise noted. [b] F = fluoranthene, B = biphenyl. [c] Ratios represent sum of molecules containing deuterium vs those containing no deuterium as determined by mass spectrometric analysis as described in the Experimental Section. [d] Excess fluoranthene added: $[F^{\bullet-}] = 0.022$ M, $[F] = 0.021$ M. [e] Product analyzed was methylnaphthalene. [f] Duplicate runs gave ratios of 0.93 ± 0.07 and 0.91 ± 0.04, suggesting a small selectivity in substrate destruction. [g] Product analyzed was 1,2-dinaphthylethane. [h] Solvent changed to dimethylformamide (DMF). [i] Product analyzed was naphthol. [j] Duplicate runs gave $d_0/\sum d_{3-7} = 0.79 \pm 0.09$ and 0.71 ± 0.04 for recovered starting material and 1.13 ± 0.05 and 1.18 ± 0.02 for product. [k] Reaction was carried out at 52 °C; estimated conversion was 50%. [l] Reaction at 25 °C for 43 h gave 10–12% reaction. [m] Reaction at 58 °C for 115 h gave 58% reaction. [n] Reaction at 58 °C for 144 h gave 90% reaction. [o] An attempt to duplicate this run gave a ratio of 0.72 ± 0.05. [p] Reaction at 58 °C for 144 h gave 39% reaction. [q] An attempt to duplicate this run gave a ratio of 0.54 ± 0.06.

In run 3, the donor radical anion was changed to biphenyl radical anion. For this reactant, the major product is 1,2-bis(1-naphthyl)ethane, and the stoichiometry changes such that only 1 mol of radical anion is required to convert 1 mol of ether to product. Thus the yield in run 3 is about 50%. Mass spectral analysis of ether and dinaphthylethane indicated little or no discrimination with this donor, a situation represented schematically in Figure 1 by the curves starting at the upper left.

The results for compound **2**, deuterated in the naphthalene ring, are listed as runs 7–12 in Table I. Mass spectral analysis of both

---

[7] This work was presented in preliminary form at the 195th National Meeting of the American Chemical Society, Toronto, Canada, June 1988.

residual ether and product naphthol indicates no discrimination between deuterated and undeuterated ethers within the error limits of the measurements. There appears to be a marginally significant trend in the naphthol samples of decreasing deuterated component as extent of conversion increases. This could be explained by some side reaction which destroyed part of the product selectively or possibly by a nondiscriminant side reaction of the radical anion intermediate itself; however, no extra products were observed either by GC or NMR, and the magnitude of the effect, if real, is barely outside of the experimental uncertainty.

Because Stevenson had also measured a large equilibrium isotope effect on the benzene–benzene-d_6 radical anion interconversion ($K_{eq} = 0.26$ at −100 °C),[8] we decided also to examine the effect of deuterium substitution on the benzyl side of the ether linkage in **2**. Runs 13–15 are reactions of **2** with the hydrogens of its phenyl ring replaced by deuterium in competition with undeuterated **2**. In runs 13 and 14 for which the conversions were 10% and 58%, respectively, there was no evidence of isotopic selectivity. To try to determine whether there was any selectivity at all, the conversion was pushed to 90% in run 15 and a small selectivity favoring reaction of undeuterated compound was observed. The selectivity was reproducible but it was difficult to reproduce the 90% conversion level because of the difficulty in accurately measuring donor radical anion concentration. It seems safe to say that the ratio of reactivity of D-substrate to H-substrate was no greater than 0.9:1. Such relative reactivity would have led to a d_0/d_n ratio of 0.91 at 58% reaction (run 14) and a ratio of 0.78 at 90% reaction (run 15). This value increases rapidly past 90% reaction, and the difficulty in measuring the percent reaction accurately at high conversion makes us reluctant to draw any conclusion other than that the selectivity is real but small.

Runs 16–18 are reactions of **2** with the benzyl group completely deuterated. Run 17 shows that there is significant selectivity at 39% conversion, and this increases substantially in run 18 where only 10% starting material remains. It is apparent that there is a real, albeit small, increase in isotopic selectivity that results from replacement of $C_6D_5CH_2$ with $C_6D_5CD_2$. Even here, however, an easily measurable selectivity is only obtained by running the reaction to high conversion.

Experimental Section

Solvents and Solutions. Purification of solvents was described in an earlier paper.[3]

D_2SO_4. Sulfuryl chloride (67.2 g, 0.5 mol) was added to D_2O (24.9 g, 1.25 mol) over 2 min. The mixture was heated at 60–65 °C for 20 h.

Preparation of 2,3,4,5,6,7,8-Heptadeuterio-1-methylnaphthalene. 1-Methylnaphthalene (10.2 g, 0.072 mol) was treated with D_2SO_4, and the mixture was stirred at 120 °C for 72 h. The organic layer was separated and combined with a CH_2Cl_2 extract of the diluted H_2SO_4 layer. Drying and evaporation of the CH_2Cl_2 layer gave the crude exchanged material as a clear liquid. This was subjected to the above procedure two additional times. Distillation under reduced pressure gave 5.0 g (46%) of pure product bp 70 °C (1 Torr). ^{1}H NMR (90 mHz, $CDCl_3$): δ 2.7 (s, 3 H), 7.5 (m, 0.7 H). MS: *m/e* 149, *148*, 120.

Preparation of 2,3,4,5,6,7,8-Heptadeuterionaphth-1-ylmethyl Phenyl Ether. The deuterium-containing methylnaphthalene (4.25 g, 0.029 mol) and *N*-bromosuccinimide (6.0 g, 0.034 mol) were dissolved in 30 mL of CCl_4, and the mixture was refluxed for 20 h. The solids were separated by filtration, and the filtrate was washed with cold, 5% aqueous NaOH solution and water. After drying and evaporation of the solvent, the product was distilled under reduced pressure (130 °C, 1 Torr). The product (5.0 g, 76) was obtained as a low-melting solid and used without further purification. ^{1}H NMR (90 MHz, $CDCl_3$): 5.0 (s, 2 H), 7.5 (m, 0.5 H). This material was converted to the ether by a previously described procedure.[3] The ether had mp 76–77 °C (lit.[3] mp 76–7 °C). ^{1}H NMR (90 MHz, $CDCl_3$): δ 5.5 (s, 2 H), 7.5 (m, 5.6 H). MS: *m/e* 241, 149, *148*, 120.

Preparation of 2,3,4,5,6,7,8-Heptadeuterio-1-naphthol. 1-Naphthol, purified by base extraction and reprecipitation, was treated three successive times with D_2SO_4 in the manner described above for 1-methylnaphthalene. Distillation (140 °C, 1 Torr) gave 22% of deuterated 1-naphthol, mp 95–96 °C. ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.3 (m, 0.76 H vs internal 18-crown-6).

Preparation of 2,3,4,5,6,7,8-Heptadeuterionaphth-1-yl Benzyl Ether. The ether was prepared from deuterated 1-naphthol in the manner described earlier.[3] The ether was obtained in 63% yield, mp 77–78 °C (lit.[3] mp 75–77 °C). ^{1}H NMR (90 MHz, $CDCl_3$): δ 5.3 (s, 2 H), 7.5 (m, 5.6 H). MS: *m/e* 241, 240, 151, *91*.

Preparation of Naphth-1-yl 2,3,4,5,6-Pentadeuteriophenylmethyl Ether and Naphth-1-yl Perdeuteriobenzyl Ether. 2,3,4,5,6-Pentadeuteriotoluene was prepared by treating toluene with D_2SO_4 as described above for methylnaphthalene except that the reaction temperature was 98 °C and the time was 48 h for each exchange. Toluene-d_7 was purchased from Aldrich Chemical Co. (99+% D). The corresponding benzyl bromides were prepared with *N*-bromosuccinimide as described above, and the ethers were produced as described earlier.[3]

Cleavage Reactions. Cleavage reactions were carried out on mixtures of d_0- and d_7-ethers by treatment of a THF solution (or in two cases a DMF solution) with the appropriate volume of a solution of the potassium salt of fluoranthene radical anion or biphenyl radical anion prepared by treatment of the corresponding hydrocarbon with metallic potassium in THF. All transfers were carried out by gas-tight syringe under argon. Concentrations of ether substrates were generally in the range of 0.02–0.03 M. Reactions were usually allowed to proceed for 72 h at 25 °C except where noted otherwise and were subjected to the work-up procedure described earlier.[3] Unreacted ether and naphthalene-group-containing product were separated from fluoranthene or biphenyl by gas chromatography on a 17 × $^1/_4$ in. column of 25% Apiezon L on 60–80-mesh Chromosorb W at 280 °C or on a 15-ft column of 10% SE 30 on Chromosorb W at 180 °C.

Mass Spectral Analysis. Samples recovered from gc separation were subjected to mass spectrometric analysis using a ZAB-2F instrument. The sample was introduced by using a solid probe, and the spectrum was scanned repetitively while sample pressure persisted. At least 30 and often 50–100 scans were analyzed in all spectral regions representing the labeled part of the molecule in question. Where it was possible to carry out an analysis in more than one region of the spectrum, the results agreed within the precision of the measurements. The uncertainties quoted in Table I represent one standard deviation for the multiple measurements. It was possible to do separate analyses for d_0 vs d_7 and for d_0 vs d_6 molecules, but the differences were not significant relative to the uncertainty in the measurements. Also in some cases significant P − 1 peaks appeared in the spectra of d_0 materials making it impossible to assign a particular mass ion as d_6. Consequently, the values reported in Table I represent the ratio of the d_0 ions to the d_{3-7} ions taken as a group. For runs 1–12 standard mixtures of deuterated and undeuterated substrate as well as product were prepared and analyzed. For these standards, the measured and calculated ratios of deuterated and undeuterated materials agreed within the uncertainty of the measurement which was less than 10% of the measured ratios. For runs 13–18 a sample of the mixture of deuterated and undeuterated ethers used in each run was analyzed, and its mass spectrum was compared to the ether recovered from the reaction.

Discussion

What can be concluded from these data? We would suggest that for the reaction of **1** with $Fl^{\bullet-}$ the observed selectivity reflects the greater stability of $^{-\bullet}C_{10}H_7CH_2OC_6H_5$ compared to $^{-\bullet}C_{10}D_7CH_2OC_6H_5$ resulting in more of the former being present at equilibrium. When $\mathbf{1}^{\bullet-}$ undergoes bond breaking, the transition state retains at least some of the sensitivity to isotopic substitution present in the radical anion, suggesting that the transition state resembles, to some extent, the π^* radical anion which precedes it in the reaction sequence. At the very least, it may be said that the extent of the resemblance is greater for $\mathbf{1}^{\bullet-}$ than for $\mathbf{2}^{\bullet-}$, which completely loses its sensitivity to naphthalene-ring deuteration at the transition state for cleavage and must, therefore, no longer resemble a π^* radical anion, at least not one involving the naphthalene-ring π system. Restated with reference to the pictorial representation of Figure 1, the competition of **1** and naphthalene-ring-deuterated **1** using $F^{\bullet-}$ as donor, starts at the lower left-hand level of the figure, and the radical anions formed proceed to products via the first set of routes, marked "high selectivity". The same competition for **2** proceeds to products via the second set of routes, marked "low selectivity". If $B^{\bullet-}$ is used as donor (starting at the upper left-hand level in the figure), the deuterated and undeuterated radical anion intermediates are apparently formed unselectively. When this happens, the overall reaction will be unselective, even if the second route to products is involved

---

[8] Reference 6 and Stevenson, G. R.; Reidy, K. A.; Peters, S. J.; Reiter, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 6578–6581.

(which is the case for **2**), because the radical anions have no alternative to product formation under the conditions of this experiment.[9]

The fact that runs 13–18 show a small selectivity which is greater for deuterium substitution in the CH_2 group than in the phenyl ring suggests that the transition state for cleavage of **2**$^{\bullet-}$ is best viewed as a σ^* radical anion wherein the extra electron is largely localized in the CH_2O bond with some minor delocalization into the benzene ring. Of course, a secondary isotope effect[10] of this magnitude would be anticipated if an appreciable hybridization change was realized at the transition state;[11] however, this seems unlikely for the type of rapid exergonic bond breaking involved in the present case.

Regardless of the picture drawn to explain the marginal effects observed in runs 13–18, it is clear that the transition state for cleavage of **2**$^{\bullet-}$ does not resemble a π^* radical anion involving either the benzene or the naphthalene π system. The former conclusion may also be inferred from the inaccessibility of a benzene-type radical anion (reduction potential estimated at −3.4 V vs SCE)[12] with $F^{\bullet-}$ as a donor and is confirmed by the present findings. The latter conclusion is clear from a comparison of the effect of naphthalene-ring deuteration on radical-anion-provoked cleavage of **1** and **2** summarized in eqs 6 and 7. Because the extra electron must reside somewhere in the molecule at the transition state for scission, a σ^*-type model seems the only reasonable choice for cleavage of **2**$^{\bullet-}$. This would also explain why the reaction of **2** with $F^{\bullet-}$ is much slower than the same reaction with **1**. The electron in **2**$^{\bullet-}$ must be largely detached from the naphthalene π system and moved into the σ^* orbital of the C–O bond prior to scission.

Why is this not required for scission of **1**$^{\bullet-}$? We have argued before,[3] that the transition state for scission of **1**$^{\bullet-}$ is reasonably represented as $^{\bullet-}C_{10}H_7CH_2^+\ ^-{:}OC_6H_5$. The present data are consistent with this view in that bond-polarized contributions to the transition state allow the extra electron to remain substantially localized in the π system of the naphthalene ring. It will be noted, however, that the observed isotopic selectivity is not as large as anticipated from Stevenson's equilibrium measurements on naphthalene-d_8,[6] possibly reflecting the extent of delocalization into the σ bond at the transition state. Bond-polarized contributions are not as important in the transition state for the scission of **2**$^{\bullet-}$, because $C_6H_5CH_2{:}^-\ ^+OC_{10}H_7^{\bullet-}$ requires polarization against the electronegativity gradient for the atoms involved, and $C_6H_5CH_2^+\ ^-{:}OC_{10}H_7^{\bullet-}$ places two negative charges in the same fragment. These factors apparently raise the energy of such contributions to the point that, at transition state geometries, they are not significant.

It must also be asked, why $C_6H_5CH_2^\bullet\ ^\bullet OC_{10}H_7^{\bullet-}$, which would retain the extra electron in the naphthalene ring, does not make a sufficiently important contribution to produce isotopic selectivity. Such a contribution might have been expected in light of a recently proposed theory which argues that single-electron processes are better models for many reactions which are traditionally viewed in terms of two-electron changes.[13] We do not know the answer to this question and can only reemphasize the constraints imposed by our experimental observations. If $C_6H_5CH_2^\bullet\ ^\bullet OC_{10}H_7^{\bullet-}$ were a realistic representation of the transition state for cleavage of **2**$^{\bullet-}$, we should have observed isotopic selectivity for naphthalene-ring-deuterated **2**. The transition state for scission of **2**$^{\bullet-}$ seems best represented with the extra electron localized in the σ bond.

Summary

The difference in stability of ring-deuterated and -undeuterated arene radical anions discovered by Stevenson[6] has been employed to examine the transition states for radical anion cleavage reactions. Selectivity in competition reactions between deuterated and undeuterated ethers of the structural type $ArCH_2OAr'$ has been taken as evidence for a transition state with the added electron in the deuterated ring. The method adds a valuable tool for use in probing the chemistry of radical anions.

Acknowledgment. The authors thank the Research Corp. for a Research Opportunity Award which helped to support the research described in this paper.

---

[9] This of course assumes that cleavage is fast relative to diffusive equilibration by electron transfer between substrate molecules. Rates estimated previously suggest that this is certainly true for **1** and is very likely the case of **2** as well.[3] Further evidence on this point will be given in subsequent papers.

(10) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980; Chapter 6.

(11) Streitwieser, A. D., Jr.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326.

(12) Streitwieser, A. D., Jr. *Molecular Orbital Theory*; Wiley: New York, 1962; p 176.

(13) (a) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212–219. (b) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363–370.