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GAS PHASE ANIONIC IPSO SUBSTITUTION REACTIONS OF SOME ALKYL PHENYL ETHERS

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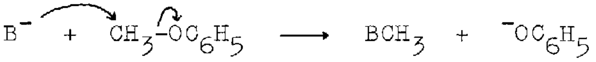
Abstract It is shown by ^{18}O labelling that phenoxide anions are formed both by an S_N2 and a nucleophilic aromatic substitution mechanism in the reaction of OH^- with methyl phenyl ether. These mechanisms are of minor importance in the ethyl phenyl ether system where phenoxide anions are generated almost exclusively by an E_2 mechanism.

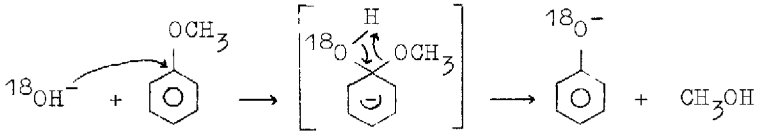
Brauman et al. have recently proposed a double potential well model for some thermal ion-molecule reactions which occur in the gas phase[1-5]. The central barrier in this model is assumed to be lower than the potential energies of either the separated reactants or products. They have shown that variation of the height of the central barrier (dependent of course upon the nature of reactants and products) results in a variation of the overall rate constant. In this way they have been able to account for the trends observed in the rate constants of some proton transfer reactions[1,2], S_N2 displacement reactions[3] and nucleophilic displacement reactions at carbonyl carbon centers[4]. One of the systems studied was the reaction between methyl phenyl ether ($C_6H_5OCH_3$) and various anions. These reactions were all assumed to proceed purely through the S_N2 mechanism[3] (reaction 1).



$$B^- + CH_3\text{-}OC_6H_5 \longrightarrow BCH_3 + {}^-OC_6H_5 \tag{1}$$

$$B^- = OH^-,\ F^-,\ CH_3O^-,\ CH_3S^-,\ CN^-$$

The authors did not consider the possibility that some reactant anions might attack the phenyl ring at the substituted carbon atom - the ipso position[6]. Phenoxide anions could then be generated by what would formally be a 1,2-elimination of BCH_3. It should be noted that ion-molecule reactions are known which have been proved to proceed via nucleophilic attack upon aromatic rings[7].
We now present results which show that part of the phenoxide anions formed in the reaction of OH^- with methyl phenyl ether are formed by a mechanism which involves an initial ipso attack. We have generated $^{18}OH^-$ via H^- from $H_2{}^{18}O$ by dissociative electron attachment (6.5 eV) in an ion cyclotron resonance (ICR) drift cell[8]. These labelled hydroxide anions react with methyl phenyl ether to yield 85 ± 1% $C_6H_5{}^{16}O^-$ and 15 ± 1% $C_6H_5{}^{18}O^-$ [9]. The formation of the $C_6H_5{}^{16}O^-$ ions can be explained by reaction 1, but for the formation of the $C_6H_5{}^{18}O^-$ ions an ipso attack of $^{18}OH^-$ upon methyl phenyl ether is required. This is represented in reaction 2.



(2)

Similar results have been obtained for the reaction of $^{18}OH^-$ with methyl pentafluorophenyl ether, the product ions being $C_6F_5{}^{16}O^-$ 84 ± 1% and $C_6F_5{}^{18}O^-$ 16 ± 1%. In this system there is an additional reaction (reaction 3) which resembles the loss of alkyl fluorides from the collision complexes of alkoxide anions and hexafluorobenzene[7a].

$$CH_3OC_6F_5 \quad + \quad {}^{18}OH^- \longrightarrow CH_3OC_6F_4{}^{18}O^- \quad + \quad HF \tag{3}$$

This is another example of a nucleophilic aromatic substitution reaction, but the site(s) of the attack upon the ring is not known. Methyl phenyl ether has also been allowed to react with $CH_3{}^{18}O^-$ and $NH_2{}^-$ ions[9], because in principle differentation between S_N2 (reaction 1, formation of $C_6H_5{}^{16}O^-$) and ipso attack (reaction 2, formation of $C_6H_5{}^{18}O^-$ and of $C_6H_5NH^-$, respectively) might be observed. However, both ions are found to react exclusively by the S_N2 mechanism and not by ipso attack. It should be noted that in the case of $NH_2{}^-$ the formation of the $C_6H_5{}^{16}O^-$ ions is a minor process compared to proton abstraction, presumably from the aromatic ring[10].

Ipso attack by $^{18}OH^-$ upon ethyl phenyl ether ($C_6H_5OCH_2CH_3$) is negligible, the ratio of $[C_6H_5{}^{18}O^-]$ $[C_6H_5{}^{16}O^-]$ being less than 0.01. Moreover, the anions $NH_2{}^-$, $C_2H_5O^-$ and $n\text{-}C_4H_9O^-$ which hardly react or do not react at all with methyl phenyl ether to give phenoxide ions, generate $C_6H_5O^-$ ions in abundance from ethyl phenyl ether. It may be concluded that the chemistry of ethyl phenyl ether is being dominated by the occurrence of facile E_2 elimination reactions[11,12]

$$B^- \quad + \quad H\text{-}CH_2\text{-}CH_2\text{-}OC_6H_5 \longrightarrow BH \quad + \quad C_2H_4 \quad + \quad {}^-OC_6H_5 \tag{4}$$

$$B^- = OH^-,\ NH_2{}^-,\ C_2H_5O^-,\ n\text{-}C_4H_9O^-$$

Although reaction 4 is kinetically favoured, it is calculated to be less exothermic than the S_N2 displacement reaction 5 (see Table 1).

$$B^- \quad + \quad CH_3CH_2\text{-}OC_6H_5 \longrightarrow BCH_2CH_3 \quad + \quad {}^-OC_6H_5 \tag{5}$$

Table 1. Exothermicities[13] (in kJ mol^{-1}) of reactions 1, 4 and 5.

Reaction type	Reactant neutral	Reactant Anion			
		NH_2^-	OH^-	$C_2H_5O^-$	$n\text{-}C_4H_9O^-$
S_N2 (1)	$C_6H_5OCH_3$	-202.5	-147.7[a]	-108.8	- 97.9[b]
E_2 (4)	$C_6H_5OCH_2CH_3$	-149.4	-112.6	- 51.0	- 38.9
S_N2 (5)	$C_6H_5OCH_2CH_3$	-201.7	-157.7	-120.5	-108.4

[a] Has been proved to proceed partially via an ipso substitution reaction, see this paper.

[b] Reaction has not been observed under the present experimental conditions, see ref. 9.

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