The Chemistry of C₆H₆O Radical Cations: A Study of Rearrangement Reactions of Halogen Substituted Ethyl Phenyl Ethers

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New experimental data on the rearrangement reaction of various phenoxyethyl halides to give $[C_6H_6O]^{+}$ are presented and compared with previous studies so that a coherent picture of this process can be developed. By examining the metastable kinetic energy release for low energy decomposing molecular ions of the phenoxyethyl halides, it has been concluded that formation of $[C_6H_6O]$ occurs by competitive 1,2 and 1,3 hydrogen shifts from the alkyl carbons to oxygen followed by a rate determining C-O bond cleavage. This is substantiated by the absence of a primary hydrogen isotope effect. For more highly activated molecular ions, a new mechanism comes into play as evidenced by the appearance of a small hydrogen isotope effect. It is postulated that this third mechanism involves transfer of the alkyl hydrogen to the ortho position of the ring by a rate determining 1,5 shift, followed by a 1,3 hydrogen shift from the ortho methylene group to oxygen and rapid C-O bond cleavage. This 1,3 hydrogen shift to oxygen appears to be 'catalysed' by the halogen atoms yielding phenol ions. No indications have been found for the formation of tautomeric 2,4cyclohexadienone ions. Furthermore, more highly activated molecular ions produce $[C_6H_6O]^+$ which can undergo metastable decomposition to lose carbon monoxide. Kinetic energy release measurements for the latter reaction show that the majority of these $[C_6H_6O]^{+}$ ions have been formed as phenol ions as well. These arguments are supported by energetic measurements and by comparisons with previous ion cyclotron resonance and collisional activation studies.

INTRODUCTION

In recent years numerous studies have been reported which deal with the elimination of neutral olefins from ionized alkyl phenyl ethers. The objectives of these studies have been twofold: (1) to understand the mechanism by which the neutral olefin expulsion occurs, and (2) to determine the structure of the resulting $[C_6H_6O]^{+\cdot}$ radical cation. The importance of this unimolecular rearrangement reaction is illustrated by the abundant (often 100% relative intensity) $[C_6H_6O]^{+\cdot}$ radical cations observed in the mass spectra of ethyl phenyl ether (phenetole) and related compounds.

It has been suggested that two structural forms of $[C_6H_6O]^+$ are produced in the unimolecular process, namely phenol (a) and 2,4-cyclohexadienone (b).



On the basis of deuterium labelling experiments, Djerassi¹ originally suggested that the $[C_6H_6O]^+$ ions formed from *n*-butyl phenyl ether involve hydrogen transfer transition states of varying ring sizes giving

rise to the two tautomeric forms *a* and *b*. Further support for this idea of hydrogen transfer has been found by Harrison² in a detailed study involving deuterium labelling of *n*-propyl phenyl ether. Harrison also reports a small but significant primary isotope effect for the hydrogen transfer process to form $[C_6H_6O]^{+-}$.

The results from the recent field ionization study of Borchers and Levsen³ lend additional credence to the hypothesis that the rearrangement occurs via nonspecific hydrogen transfer as opposed to randomization of the alkyl hydrogen atoms prior to a specific hydrogen rearrangement.

Additional ion structure and reaction mechanism techniques have been directed at this rearrangement reaction and the structure of the $[C_6H_6O]^{++}$ ion. The studies have involved isotopic labelling,¹⁻³ isotope effect measurement,^{2,4} substituent effects,^{5,6} kinetic energy release,^{9,10} ion cyclotron resonance (ICR),¹¹⁻¹³ collisional activation (CA),^{10,14} analysis of the neutral species expelled in the rearrangement with an electron bombardment flow reactor¹⁵ and appearance energy studies.¹⁶ With the possible exception of kinetic energy release measurement, these studies suggest that both the stable and decomposing $[C_6H_6O]^{++}$ ions produced via the rearrangement or by direct ionization of phenol are present predominantly as the phenol ion (*a*). Tautomerism to the keto form (*b*) appears to be

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precluded by the significant difference in kinetic energy release for loss of CO from a and b.

In a recent study, Russell, Gross and Nibbering¹⁷ õ,10 have demonstrated, contrary to previous reports,⁵ that the difference in kinetic energy release for a and b is only sustained for rapidly decomposing ions. As longer-lived ions are sampled, the energy releases become nearly equal. This phenomenon has been interpreted to indicate that structures a and b sample a common potential energy surface prior to fragmentation. That is, structure a undergoes a rate determining isomerization to b prior to decarbonylation to form $[C_5H_6]^+$. Because of the high energy requirement for the tautomerism, the rate constant is remarkably insensitive to internal energy, and that gives rise to an unprecedented decrease in kinetic energy release as longer-lived metastable ions are sampled.

Because the nature of decomposing $[C_6H_6O]^{+}$ radical cations is now better understood, the rearrangement reaction to produce $[C_6H_6O]^{+}$ can be examined in greater detail. As a starting point, we note the report of Nibbering *et al.*,¹⁸ who have shown on the basis of combined ICR and deuterium labelling experiments, that $[C_6H_6O]^{+}$ ions are generated from 2phenoxyethyl halides via 1,2 and 1,3 hydrogen shifts to oxygen, and via a 1,5 hydrogen shift to one of the *ortho* positions of the aromatic ring (cf. Scheme 1, reactions A to C).

The percentage of the 1,5 hydrogen shift is about 15% for 2-phenoxyethyl fluoride and rises to about 70% and 90% for the corresponding chloride and bromide, respectively. These observations have been taken as evidence that a substantial part of the $[C_6H_6O]^+$ ions generated from 2-phenoxyethyl halides initially possesses the structural form b. It was not known, however, whether or not tautomerism to the enol form (a) of these $[C_6H_6O]^+$ ions has taken place within the ICR time scale (milliseconds). More recently, Maquestiau *et al.*¹⁰ and Levsen in co-operation with Nibbering *et al.*¹⁴ have shown independently by CA that ions a and b are distinct, stable species in the gas phase up to times $\ge 10^{-5}$ s. From the latter study, there is evidence that after the 1,5 hydrogen shift in the molecular ions of 2-phenoxyethyl halides (especially chloride and bromide), a direct C—O cleavage to generate ions b competes with proton transfer from the original ortho position, probably via the halogen atom to the oxygen atom, followed by expulsion of C_2H_3X to generate ions a (cf. Scheme 1, reaction D). On the basis of the CA results¹⁴ it has been suggested that $[C_6H_6O]^{+}$ ions gen-



erated from 2-phenoxyethyl halides are present as a mixture of both *a* and *b*, a conclusion which was also reached in the previous ICR study.¹⁸ The proportion of *b* would range from about 10% to 30% according to the CA results.¹⁴ This set of substituted phenetoles presents an ideal opportunity to study by metastable kinetic energy release measurements¹⁹ the mechanisms of unimolecular decompositions involved in both the formation and decomposition of $[C_6H_6O]^+$ ions, particularly those formed from phenoxyethyl halides. Moreover, the sensitivity of metastable kinetic energy release for the detection of isomeric species may be evaluated further. This paper is a report of these studies.

RESULTS AND DISCUSSION

Elimination of C₂H₃X from 2-phenoxyethyl halides

It may be anticipated that formation of two structural forms of $[C_6H_6O]^+$ ions will be accompanied by composite metastable peaks whose intensities can be related to the relative importance of each reaction channel in the metastable time window. For phenoxyethyl halides this is not the case, as revealed by the kinetic energy release for the formation of $[C_6H_6O]^+$ (Table

Table 1. Kinetic energy release (meV) accompanying formation of $[C_7H_7O]^+$ and $[C_6H_6O]^{++}$ from $[C_6H_5OCH_2CH_2X]^{++}$ (X = H, F, Cl, Br)

		·			
Compound	$[M-CH_2X]^+$	$[M-CD_2X]^+$	[M-C ₂ H ₃ X] ^{+.}	[M−C ₂ H ₂ DX] ⁺	
C ₆ H ₅ OCH ₂ CH ₃			16		_
C ₆ H ₅ OCH ₂ CH ₂ F	26		39		—
C ₆ H ₅ OCH ₂ CD ₂ F		18	_	33	28
C ₆ H ₅ OCD ₂ CH ₂ F	27			28	34
C ₆ H ₅ OCH ₂ CH ₂ CI	17		27	_	_
C ₆ H ₅ OCH ₂ CD ₂ CI	16	16	_	22	26
C,H,OCD,CH,CI	19	20	_	25	28
C ₆ H ₅ OCH ₂ CH ₂ Br			19	—	_

1). All of the various phenoxyethyl halides, as well as phenetole, giving narrow Gaussian metastable peaks for the loss of C_2H_3X , and this indicates that the final step in the mechanism is common to all the metastable decomposing precursors of $[C_6H_6O]^{+\cdot}$. From the previous experimental studies, four competitive mechanisms for olefin elimination have been suggested as summarized in Scheme 1: reactions A, B and D form exclusively *a*, whereas reaction C would generate exclusively *b*.

Nibbering¹¹ and Djerassi,¹² working independently, have shown that $[C_6H_6O]^{+\cdot}$ ions generated from phenetole and phenyl acetate are present exclusively as phenol on the ICR time scale. Any significant initial formation of these ions as the dienone tautomer was excluded.

In the *n*-propyl phenyl ether study of Harrison et al.² the results were interpreted as a composite of three separate hydrogen transfer reactions involving hydrogens on each of the carbon atoms in the propyl chain. Preferential transfer from the terminal carbon atom in low energy ions is favoured. At high energies, all of the hydrogen transfer rates are approximately equal. The overall mechanism proposed by Harrison² is initial transfer of hydrogen to oxygen followed by a rate determining C-O bond cleavage to give $[C_6H_6O]^+$ ions as the phenol structure. However, the rearrangement reaction for *n*-propyl phenyl ether is accompanied by a small but definite primary isotope effect² ($k_{\rm H}/k_{\rm D} \simeq 1.5$), which may indicate that C--H bond breaking, and not C-O bond cleavage, is the rate determining step in some stage of the rearrangement. The same is true for the generation of $[C_6H_6O]^+$ ions from phenetole and the 2phenoxyethyl halides within 10^{-6} s and at an electron energy of 70 eV, where the following isotope effects $(k_{\rm H}/k_{\rm D})$ are observed: 1.27 (H), 1.15 (F), 1.23 (Cl) and 1.38 (Br). Thus, in these cases C--H bond breaking is also the rate determining step. But it should be stressed that this is not necessarily valid for all the reaction channels A, B, C and D in Scheme 1.

Of course, isotope effects are sensitive to the internal energy of decomposing ions and to the activation energies required for decomposition. Therefore it is essential to consider the energetics for the elimination of C_2H_3X via the reaction channels A, B, C and D in Scheme 1 before any definite conclusion can be drawn about the nature of the rate determining step in each of these channels. The most suitable compound for this purpose is 2-phenoxyethyl fluoride, where



deuterium labelling has shown that the two methylene carbon atoms retain their identity in the loss of CH₂X from the molecular ion, a process which is in competition with $[C_6H_6O]^+$ formation.²⁰ Thus, the molecular ion of $C_6H_5OCH_2CD_2F$ loses CD₂F, but not CH₂F or CHDF, so that hydrogen transfer from the α and β carbon atoms during the elimination of C_2H_3F can be distinguished. Such a distinction cannot be made for hydrogen transfer from the α and β carbon atoms in the cases of the chloride and bromide because the two alkyl carbon atoms become equivalent²⁰ via intermediate c. The interchange is a time-dependent process as shown by the field ionization kinetic method.²¹

Energetics for the elimination of C₂H₃X

Based on the relative metastable peak intensities for transfer of a hydrogen atom from the α and β carbon atoms in phenoxyethyl fluoride to form [C₆H₆O]⁺ ions, as revealed by the two deuterium labelled compounds, hydrogen transfer from the α carbon atom appears to have the lower activation energy because this process is favoured for lower energy decompositions (see Table 2). To provide a quantitative measure of the relative activation energies for H-transfer from the α carbon atom and H-transfer from the β carbon atom, the appearance energy differences were measured for $[C_6H_6O]^{+}$ and $[C_6H_5DO]^{+}$ formed from both the α - d_2 - and the β - d_2 -phenoxyethyl fluorides. In this way, it has been established that the H-transfer from the β carbon atom has a 0.3 eV higher energy requirement. The trends noted in Table 2 are readily understood in terms of this energetic difference in favour of the larger ring transition state for H-transfer.

However, a very important observation is that a difference of 0.3 eV was found for *both* the α - d_2 - and the β - d_2 -phenoxyethyl fluoride. In other words, there seems to be no primary isotope effect for H versus D transfer during the elimination of $C_2H_{3-n}D_nX$ from molecular ions of deuterated 2-phenoxyethyl fluorides

Table 2. Comparison of hydrogen/deuterium transfer from the α and β carbon atoms in labelled 2-phenoxyethyl fluoride and chloride to form $[C_6H_6O]^+$ and $[C_6H_5DO]^+$ ions^a

Energy region	βα C ₆ H ₅ OCD ₂ CH ₂ F	βα C ₆ H ₅ OCH ₂ CD ₂ F	β α C ₆ H₅OCD₂CH₂CI	β α C ₆ H ₅ OCH ₂ CD ₂ Cl
	[C ₆ H ₆ O] ⁺⁺	[C ₆ H ₆ O] ^{+,}	[C ₆ H ₆ O]⁺`	[C ₆ H ₆ O] ⁺⁻
	[C ₆ H ₅ DO] ⁺	[C ₆ H ₅ DO] ⁺	[C ₆ H ₅ DO] ⁺	[C ₆ H ₅ DO]**
Ion source (70 eV)	50/50	57/43		_
1st field free region (70 eV)	59/41	40/60	46/54	56/44
1st field free region (12 eV)	66/34	35/65	45/55	—
2nd field free region (70 eV)	67/33	34/66	_	—

^a All values are expressed as percent of total integrated area for all metastable decompositions.

Table 3.	The isotope effect in
	the generation of
	[C ₆ H ₆ O] ⁺⁻ ions from
	[2-phenoxyethyl
	fluoride] ⁺⁻ as a func-
	tion of the molecu-
	lar ion lifetime"

t(in s)	i
<3.10 ⁻¹¹	1.89
3.10 ⁻¹¹	1.80
6.10 ⁻¹¹	1.32
1.10 ⁻¹⁰	1.16
2.10 ⁻¹⁰	1.14
~ 1.10 ⁻⁶	1.00
~ 1.10 ⁻⁵	1.00

^a The isotope effects at times $<1\,\mu$ s were obtained from field ionization kinetic measurements and those at times $>1\,\mu$ s from the electron impact method (70 eV).

decomposing at threshold energies. The absence of an isotope effect is also true for the metastable molecular ions, as indicated by the metastable peak intensities ratio for formation of $[C_6H_6O]^{+-}$ and $[C_6H_5DO]^{+-}$ ions from α -d₂-phenoxyethyl fluoride. It can be seen that the intensities are just the inverse of that for formation of $[C_6H_6O]^+$ and $[C_6H_5DO]^+$ ions from β - d_2 -phenoxyethyl fluoride (Table 2). The same is true for the chloride (Table 2) and probably for the bromide (not measured), although the interchange of the halogen and the phenoxy groups in their molecular ions is an interfering factor (vide supra). Thus we see an unusual phenomenon; that is, the isotope effect operating in the generation of $[C_6H_6O]^+$ ions from 2-phenoxyethyl halides decomposing within 10^{-6} s (high energy ions) becomes vanishingly small when the 2-phenoxyethyl halides decompose in the metastable time window of 10^{-6} to 10^{-5} s (low energy ions). The decreasing isotope effect at ever increasing molecular ion lifetimes is also shown by field ionization kinetic measurements (see Table 3).

A decreasing isotope effect with a decreasing internal energy of decomposing ions is an unexpected and unprecedented observation. A possible explanation is that one of the reaction channels A to D in Scheme 1 is available only for high energy molecular ions which decompose by a rate determining C-H bond breaking step. Decompositions by this channel cannot compete with other fragmentations of low energy molecular ions. The rate determining step in the latter channels is certainly not C-H bond breaking because of the absence of any significant isotope effect. Furthermore, based on the metastable kinetic energy release, the amount of reverse activation energy observed as kinetic energy release must not change significantly for the channels open to low energy molecular ions. In other words, the mechanisms for the low energy processes share a common step. We suggest that the common step is an ultimate transfer of a hydrogen atom to oxygen followed by a rate determining cleavage of the carbon-oxygen bond (Scheme 2). This interpretation implies a relatively rapid hydrogen transfer to oxygen. It may be argued then that alkyl hydrogen atom



Scheme 2

randomization should be expected by reciprocal hydrogen transfers between the oxygen atom and the two alkyl carbon atoms, which has not been observed.²⁰ However, as soon as a hydrogen atom has been transferred to oxygen, its character has been changed from an atom to a proton which may then serve as a bridge between the oxygen and halogen atoms. Thus, the possible reciprocal hydrogen transfers between the oxygen and alkyl carbon atoms (Scheme 2) have been inhibited.

Decomposing $[C_6H_6O]^{+}$ radical cations

As was discussed in the introduction, $[C_6H_6O]^{+\cdot}$ formed as the phenol ion undergoes a rate determining isomerization to the keto tautomer (b) prior to decomposing to $[C_5H_6]^{+\cdot}$. The evidence for this interconversion is the rapid decrease in kinetic energy released for this reaction as longer-lived ions are sampled by a straightforward decrease in the source accelerating field.¹⁷

As a result of this property of $[C_6H_6O]^{+\cdot}$ ions which have been formed initially as the phenol ion, we have available three criteria by which we can judge the structure of metastable decomposing $[C_6H_6O]^{+\cdot}$ formed from the various phenoxyethyl halides. They are metastable abundance ratios, metastable kinetic energy release and variation of kinetic energy release as a function of ion lifetime in the metastable time frame.

The metastable abundance ratios and the kinetic energy release data $[C_6H_6O]^{++}$ generated from the phenoxyethyl halides, from phenol and as the 2,4cyclohexadienone are tabulated in Tables 4 and 5. For each of the precursors, the metastable characteristics of the $[C_6H_6O]^{++}$ radical cations are nearly identical both in terms of relative metastable abundance and kinetic energy release. These results can be understood by invoking a common potential energy surface for all metastable decomposing $[C_6H_6O]^{++}$ radical cations. We now know that the lower kinetic energy released for the keto form (355 meV) does not violate this conclusion (vide supra).

The third criterion is sensitive to the initial structure of the decomposing $[C_6H_6O]^{+\cdot}$. That is, if the rearrangement reactions yield a phenol ion, the kinetic energy released is expected to vary with ion lifetime in the metastable time frame. However, if the keto tautomer (b) is formed, the kinetic energy release will be constant as different metastable ion lifetimes are sampled. Thus, the time dependence for kinetic energy release is unique to $[C_6H_6O]^{+\cdot}$ ions initially formed

	[C ^e H ^e O]+.	[C ₆ H ₅ DO] ^{+.}	[CeHeO]+.	[C ₆ H ₅ DO] ⁺⁻	(C ₆ H ₆ O) ^{+∙}	[C ₆ H ₅ DO] ^{+.}
Compound	[C5H6]+.	[C ₅ H ₅ D] ⁺	(C₅H ₅]⁺	[C₅H ₆]⁺	$\{C_3H_3O\}^+$	$[C_3H_3O]^+$
C ₆ H₅OH	96		2.5		1.5	—
0	95		3.0	_	2.0	_
	94		3.3	_	2.7	
C ₆ H ₅ OCH ₂ CH ₂ F	94		3.5	_	2.5	
C ₆ H ₅ OCH ₂ CD ₂ F	50	46	3.0	0.6	0.6	
C ₆ H ₅ OCD ₂ CH ₂ F	55	40	3.0	1.2	0.8	—
C6H5OCH2CH2CI	92		4.6	—	3.4	_
C ₆ H ₅ OCH ₂ CD ₂ CI	60	35	3.0	1.0	1.0	1
C ₆ H ₅ OCD ₂ CH ₂ CI	58	36	3.0		2.0	1
C ₆ H ₅ OCH ₂ CH ₂ Br	92		5.0		3.0	—

Table 4. Metastable abundance ratios for decomposing [C₆H₆O]⁺⁺ ions formed from phenol, bicyclo[2,2,2]-oct-2-en-5,7-dione, phenetole and 2-phenoxyethyl halides^a

^a All values are expressed as percent of total integrated *area* for all metastable decompositions.

Table 5. Metastable kinetic energy release for decomposing $[C_6H_6O]^+$ ions formed from phenol, bicyclo[2,2,2]-oct-2-en-5,7-dione, phenetole and 2-phenoxyethyl halides (in meV)

	[C ₆ H ₆ O] ⁺⁺	[C ₆ H ₅ DO] ⁺⁻	[C ₆ H ₆ O] ⁺⁺	[C ₆ H ₅ DO] ⁺	[C ₆ H ₆ O] ⁺⁻	[C ₆ H ₅ DO] ^{+,}
Compound	[C ₅ H ₆] ⁺⁻	[C₅H₅D]+·	[C ₅ H ₅] ⁺	[C₅H₅]⁺	[C ₃ H ₃ O] ⁺	[C ₃ H ₃ O] ^{+.}
C ₆ H₅OH	455	465	150	154	27	28
0	355	_	161	-	28	_
	492		160	_	32	
C _e H ₅ OCH ₂ CH ₂ F	480		170		30	_
C ₆ H ₅ OCH ₂ CD ₂ F	492 ª	446ª	150		30	—
C ₆ H ₅ OCD ₂ CH ₂ F	452ª	478 ^a	142		29	_
C ₆ H ₅ OCH ₂ CH ₂ CI	483		150	_	31	_
C ₆ H ₅ OCH ₂ CD ₂ Cl	470	458	152	—	35	_
C ₆ H ₅ OCD ₂ CH ₂ CI	480	477	140		22	—
C ₆ H ₅ OCH ₂ CH ₂ Br	480		165	-	30	—

 a These differences in kinetic energy release are also observed as 0.3 eV differences in appearance energies of the $[C_6H_6O]^{+\cdot}$ ions.

Table 6. Variation of metastable kinetic energy release^a (in meV) as a function of average internal energy for the reaction $[C_6H_6O]^+ \rightarrow [C_5H_6]^+ + CO$

Accelerating			Cor	npound		
voltage	C ₆ H₅OH	Ц	C ₆ H ₅ OCH₂CH₃	C ₆ H₅OCH₂CH₂F	C ₆ H ₅ OCH ₂ CH ₂ CI	C ₆ H ₅ OCH ₂ CH ₂ Br
4200	501	b	530	525	528	
3600	452	355	480	480	482	475
3000	436	_		446		
2500	414	350	430	422	419	464
2000	393	351	405	_		
1500	388			386	381	369
1000	366	342	364	_		352

^a Measured on a Hitachi RMU-6D instrument.

^b Values not determined for this accelerating voltage.

Table 7.	Calculated	metast	lable	kinetic
	energy rele	ase for	the	reaction
	[C ₆ H ₆ O] ⁺⁻ -	→[C₅H	6] ^{+.} +	CO in
	mixtures	of 2	,4-cy	clohexa-
	dienone and	d pheno	l ions	5

% Dienone	Calc. T1 (meV)	
100	375	
80	380	
67	404	
50	432	
45	455°	
33	452	
20	466	
11	476	
0	486 (100% pl	nenol)

^a Experimental data point (see text), measured on an AEI MS 5076 instrument.¹⁷

with the phenol structure. The results of the study of metastable kinetic energy release as a function of ion acceleration (ion lifetime) are given in Table 6. It is readily seen that, in each case, an unusual variation in kinetic energy release is detected. We interpret these results to mean that the majority of $[C_6H_6O]^{+}$ (or $[C_6H_5DO]^{++}$ ions which decompose with rate constants of 10^5 to 10^6 s⁻¹ (i.e. as metastable ions) do so from a structure which was initially the phenol radical cation. This is further corroborated by analysis of metastable peak shapes for loss of carbon monoxide from ionized phenol (a) and 2,4-cyclohexadienone (b). The resultant peak shape can then be calculated by adding various ratios of the two peaks together, giving rise to the values in Table 7. As can be seen, the kinetic energy release is quite sensitive to the composition of the metastably decomposing mixture of $[C_6H_6O]^{+}$ structures. Note the experimental data point in Table 7 which was obtained by mixing phenol and 2,4-cyclohexadienone in the ion source and assuming that the metastable peak/molecular ion intensity ratio is the same for both phenol and 2,4cyclohexadienone (this is approximately true; the ratio for phenol is 1.3 times greater than that for 2,4-cyclohexadienone). The interpretation given in this section is consistent with the conclusion drawn in the previous section; that is, the rearrangement reaction of metastably decomposing phenoxyethyl halides (and other alkyl phenyl ethers) produces a significant fraction of $[C_6H_6O]^+$ as the phenol ion.

Summary of experimental details—formulation of mechanistic models

Based on a large amount of experimental work, we are now able to construct the following detailed summary of our knowledge of decomposing phenoxyethyl halides. A convenient way of discussing the data is in the form of a hypothetical energy distribution function for $[C_6H_5OCH_2CH_2X]^+$ as shown in Fig. 1. The distribution is divided in five sharply defined regions for purposes of discussion

Region 1. These are stable (non-decomposing) $C_6H_5OCH_2CH_2X$ ⁺⁻ radical cations.



Figure 1. Hypothetical energy distribution function for $[C_6H_5OCH_2CH_2X]^{+*}$ ions.

Region 2. A narrow energy region of higher energy includes $[C_6H_5OCH_2CH_2X]^{+\cdot}$ ions which decompose to $[C_6H_6O]^{+\cdot}$ as metastable ions. The decomposition occurs without any detectable isotope effect for transfer of a hydrogen atom from both the α and β carbons of the sidechain. We postulate that the mechanism is a rapid, unidirectional transfer of a hydrogen atom to oxygen, followed by rate determining C—O bond cleavage. The $[C_6H_6O]^{+\cdot}$ ions formed at these energies possess, within the limits of detection, only the phenol structure. The trend in kinetic energy release values F>Cl>Br (Table 1) can be understood by examining the excess energy (E^*) for these threshold $[C_6H_6O]^{+\cdot}$ ions. An estimate of E^* can be made using Eqn (1).

$$A([C_{6}H_{6}O]^{+}) = \Delta H_{f}([C_{6}H_{6}O]^{+}) - \Delta H_{f}(C_{6}H_{5}OCH_{2}CH_{2}X) + \Delta H_{f}(C_{2}H_{3}X) + E^{*}$$
(1)

The $\Delta H_{f}([C_{6}H_{6}O]^{+})$ was calculated from the ionization energy of phenol as determined by photoionization.²² The $\Delta H_f(C_2H_3X)$ values were taken thermochemical determinations.22 The from $\Delta H_{\rm f}(C_6H_5OCH_2CH_2X)$ values were estimated by the group additivity method of Benson.²³ The appearance energies, measured by the semilog method,²⁴ and the calculated values of the excess energy E^* , are tabulated in Table 8. The increase of $E^{\overline{*}}$ from X = Br to X = F is in agreement with the increase in the kinetic energy release values in the same order. The threshold excess energy of $88 \text{ kJ} \text{ mol}^{-1}$ for $[C_6H_6O]^{++}$ ions generated from 2-phenoxyethyl bromide is smaller than the energy difference of 109 kJ mol^{-1} between dienone and phenol ions.¹⁴ This is consistent with the observation that only phenol ions are formed at threshold energies.

Table 8. Heats of formation, ionization energies, appearance energies of $[C_6H_6O]^{+-}$ and threshold excess energy, E^* , for various 2-phenoxyethyl halides in kJ mol⁻¹

Compound	ΔH [°] _f (M)	I(M)	A([C ₆ H ₆ O] ⁺⁻)	$\Delta H_{f}^{\circ}(C_{2}H_{3}X)$	E*°
C ₆ H ₅ OH	99.2 ^b	824 ^ь			
C _e H _e OCH ₂ CH ₃	84.9 ^b	787 [⊳]	1033 [⊳]	52.3 ^b	171
C _e H _s OCH ₂ CH ₂ F	-251.5	833	1079	−117.2 ^b	222
C,H,OCH,CH,CH	-105.0	820	1042	35.6 ^b	176
C ₆ H ₅ OCH ₂ CH ₂ Br	54.8	812	937	71.1 ^b	88

 $^{\rm e}E^{\rm *}$ calculated assuming that $[{\rm C_6H_6O}]^{\rm +-}$ has the phenol structure as described in text.

^b Literature values. See Ref. 22.

Region 3. These are stable $[C_6H_6O]^+$ ions observed at m/z 94 in the mass spectrum. Collisional activation results can be interpreted to show that the majority of the ions possesses the phenol structure. Formation of these $[C_6H_6O]^+$ radical cations is accompanied by a small primary hydrogen isotope effect, and from this observation, we suggest the onset of a new mechanism which is now competitive with the direct 1,2 and 1,3 hydrogen transfer to oxygen.

Additional information about these $[C_6H_6O]^+$ ions is available from the ICR study.¹⁸ Irrespective of whether the 2-phenoxyethyl bromides and chloride are labelled with deuterium in the α or β position, the stable $[C_6H_5DO]^+$ ions which are formed at these energies exhibit both transfer of H and D to a base. This result has been interpreted to indicate a significant fraction of dienone structure (b); however, an equally valid explanation is to represent these ions as a mixture of phenol structures, i.e. $[C_6H_4DOH]^+$ and $[C_6H_5OD]^+$. The CA spectra of $[C_6H_5DO]^+$ from α d_2 - and β - d_2 -phenoxyethyl chloride and bromide show loss of OD and OH, which confirm the presence of $[C_6H_5OD]^+$ and $[C_6H_4DOH]^+$ structures as stable ions.

The mechanism which is in accord with these data and is shown in Scheme 1 (reaction D) first involves a rate determining 1,5 hydrogen shift to the aromatic ring to give a dienone-type intermediate, followed by transfer to oxygen and fast C—O bond cleavage. The absence of any ortho-H/ α -H exchange process in the molecular ions of phenetole and of the phenoxyethyl halides prior to or during formation of $[C_6H_6O]^+$ ions is in agreement with a rate determining 1,5 hydrogen shift.

The fact (ICR evidence) that a 1,5 hydrogen shift occurs for the phenoxyethyl halides and not for phenetole might to some extent be due to an electrostatic repulsion between the electronegative oxygen and the halogen atom which will be beneficial to this hydrogen shift. However, the increase of the 1,5 hydrogen shift in the order, F, Cl, Br suggests that the increase in radii of these atoms is the dominating factor in promoting the reaction. This may be understood quite well, if the molecular ions populate the rotamer d, shown below, to a large extent: A model of



this rotamer has shown that the hydrogen atoms from the methylene group, adjacent to the halogen atom, are ideally situated to be transferred to the *ortho* positions of the phenyl ring via a 1,5 hydrogen shift.

Furthermore, the intermediate formed by the initial 1,5 shift of a hydrogen to the *ortho* position can be stabilized via an interaction such as that depicted in structure *e*. By virtue of this interaction in structure *e*,



the halogen atom may act as the catalyst for the 1,3 hydrogen transfer from the *ortho* methylene group to the oxygen atom to eventually yield phenol ions. This is analogous to the 'catalysed' 1,3 hydrogen shift which occurs in the enolic ions of *o*-hydroxy-acetophenone, generated by elimination of C_2H_4 from the molecular ions of *o*-hydroxy-butyrophenone.²⁵

Region 4. Based on the kinetic energy release measurements discussed earlier and presented in Tables 5 and 6, it is clear that the majority of the metastable $[C_6H_6O]^{+\cdot}$ ions, which originate from even higher energy states of the molecular ions, have predominantly the phenol structure.

Region 5. The highest energy regime pictured in Fig. 1 is made up of the stable fragments from $[C_6H_6O]^+$; i.e. $[C_5H_6]^+$ and $[C_5H_5]^+$. We have no information on the nature of the original $[C_6H_5OCH_2CH_2X]^+$ precursors of these fragments.

CONCLUSION

Based on all the experimental results to date, we believe a coherent and internally consistent picture of the rearrangement reaction in phenoxyethyl halides has emerged. The formation of $[C_6H_6O]^+$ from molecular ions having a relatively low internal energy occurs by 1,2 and 1,3 hydrogen shifts to oxygen followed by a rate determining C-O bond cleavage to yield the phenol radical cation. For molecular ions having higher internal energies, a new mechanism becomes competitive involving a rate determining 1,5 hydrogen shift, followed by a 1,3 hydrogen shift from the ortho methylene group to oxygen and rapid C-O bond cleavage to yield a phenol radical cation. The hydroxyl hydrogen of the phenol is either the original ortho hydrogen or one of the alkyl hydrogen atoms. This interpretation is in agreement with the original ICR study¹⁸ and recent CA study.¹⁴

No indications have been found for a direct C—O bond cleavage after the 1,5 hydrogen shift generating 2,4-cyclohexadienone ions. Therefore, this reaction, if present, must be a minor process in the metastable time frame of 10^{-6} to 10^{-5} s. This is not inconsistent with the CA study,¹⁴ which has indicated that only 10 to 30% 2,4-cyclohexadienone ions are present in the *total* fraction of stable [C₆H₆O]⁺⁺ ions.

More generally, it should be noted that metastable kinetic energy release measurements can be a basis for developing a detailed picture of the potential energyreaction coordinate relation along which ions decompose. However, other methods, like ICR and CA, are essential to complete the mechanistic picture as has been shown in the present study.

EXPERIMENTAL

Mass spectrometry

Mass spectra were obtained with an AEI MS-5076 and a Hitachi RMU-6D double focusing instrument with source and inlet temperatures at 200 °C. Metastable ion studies were made using the defocusing techniques of accelerating voltage scans. Kinetic energy release was calculated from the peak width at half height, with these values being corrected for the energy distribution of the main ion beam. Since beginning this study, the geometry of the Hitachi instrument has been reversed and the kinetic energy release values have been remeasured by the mass analysed ion kinetic energy (MIKES) technique. Typical conditions for both normal and MIKES geometry are ionizing energy 70 eV, emission 100 µA, ion accelerating voltage 3.7 kV (MIKES 5.5-6.5 kV) and β slit width 0.2 mm.

Field ionization kinetic experiments were performed

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on a Varian MAT 711 double focusing mass spectrometer equipped with a combined EI/FI/FD source.26

Ionization and appearance energies were determined using the semilog method.²⁴ Only the region of the ionization efficiency curve below 10% of the 30 eVion current was used. The electron energy scale was standardized using benzene and furan, introduced simultaneously with the sample, for each determination. In order to minimize error due to sample depletion, measurements were recorded as the ionizing energy was lowered and again as it was raised.

Materials

The synthesis of all compounds studied has been described previously.14,18

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