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Reactions of Phenoxide Ion in the Gas Phase

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Upon collisionally activated dissociation (CAD) phenoxide ion experiences fragmentation reactions in the gas phase that produce the daughter ions $[C_6H_3]^-$, $[C_5H_5]^-$, $[C_2HO]^-$, and $[C_3H_3]^-$. Based upon study of the anions derived from 2,3,4,5,6-pentadeuteriophenol (**2**), 4-deuteriophenol (**3**), 3,5-dideuteriophenol (**4**), and 2,4,6-trideuteriophenol (**5**), mechanisms for formation of the $[C_6H_3]^-$, $[C_5H_5]^-$, and $[C_2HO]^-$ ions have been proposed.

During the past two decades negative-ion chemical ionization mass spectrometry (NICI MS) has become a powerful tool for studying the chemistry of organic ions in the gas phase.[1-4] This technique also has assumed an increasingly important role in monitoring and identifying trace amounts of organic compounds.[4,5] Phenols easily form negative ions in the gas phase and, consequently, have been the subject of a number of NICI MS investigations.[6-14] Significantly lacking, however, is a knowledge of the basic fragmentation reactions of phenoxide ion. Study of these reactions is the topic of this paper.

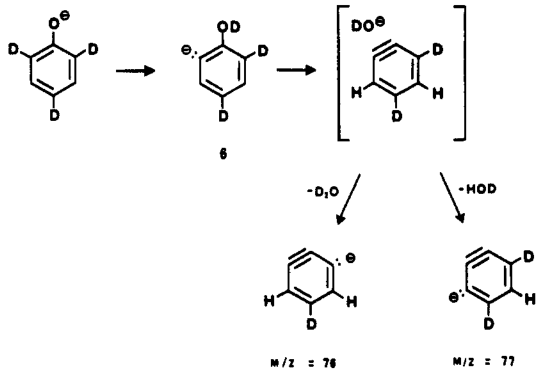
Phenol (**1**) is readily deprotonated under negative-ion chemical ionization conditions using ammonia as the reagent gas to give the corresponding anion $[M - H]^-$.[6] Although the cluster ion $[2M - H]^-$ also is easily formed,[6] no fragmentation of the $[M - H]^-$ ion is observed under these conditions. Collisionally activated dissociation (CAD) of the $[M - H]^-$ ion reveals reaction pathways that produce ions at m/z of 75, 65, 41, and 39 (Table I). Essential information about the structures of these ions is obtained from the CAD spectrum of $[C_6D_5O]^-$ (derived from the fully deuterated phenol **2**), which contains peaks for ions with m/z of 78 (replacing that at 75), 70 (replacing that at 65), and 42 (replacing those at 41 and 39) (Table I). These results suggest that phenoxide ion $[C_6H_5O]^-$ reacts to give anions with the formulas $[C_6H_3]^-$ ($m/z = 75$, loss of H_2O), $[C_5H_5]^-$ ($m/z = 65$, loss of CO), $[C_2HO]^-$ ($m/z = 41$, loss of C_4H_4), and $[C_3H_3]^-$ ($m/z = 39$, loss of C_3H_2O).

Table I. CAD of Anions from Phenols 1-5

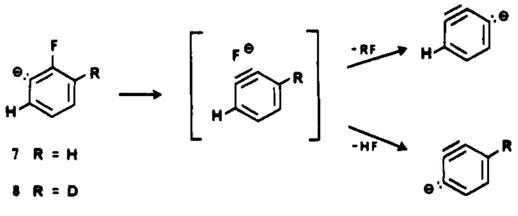
source compd	ion (m/z)	rel abund[a]	anion formula
1	75	1.82	$[C_6H_3]^-$
1	65	3.31	$[C_5H_5]^-$
1	41	1.24	$[C_2HO]^-$
1	39	2.61	$[C_3H_3]^-$
2	78	1.38	$[C_6D_3]^-$
2	70	3.90	$[C_5D_5]^-$
2	42	3.09	$[C_2DO]^-$ or $[C_3D_3]^-$
3	76	2.71	$[C_6H_2D]^-$
3	66	4.45	$[C_5H_4D]^-$
3	42	1.86	$[C_2DO]^-$
3	41	1.88	$[C_2HO]^-$
3	40	2.48	$[C_3H_2D]^-$
3	39	0.82	$[C_3H_3]^-$
4	77	1.50	$[C_6D_2H]^-$
4	76	1.51	$[C_6H_2D]^-$
4	67	4.75	$[C_5H_3D_2]^-$
4	41	1.68	$[C_2HO]^-$ or $[C_3D_2H]^-$
4	40	1.61	$[C_3H_2D]^-$
4	39	1.49	$[C_3H_3]^-$
5	77	1.20	$[C_6D_2H]^-$
5	76	1.01	$[C_6H_2D]^-$
5	68	3.79	$[C_5H_2D_3]^-$
5	42	2.64	$[C_2DO]^-$ or $[C_3D_3]^-$
5	41	2.82	$[C_2HO]^-$ or $[C_3D_2H]^-$

[a] Relative abundance of the corresponding phenoxide ion = 100.

Scheme I



Scheme II



7 R = H

8 R = D

Additional information about the formation of the $[C_6H_3]^-$ ion, the most massive of the phenoxide daughter ions, came first from the study of 4-deuteriophenol (**3**). CAD of the anion from **3** revealed that the deuterium atom in the para position remained attached to the carbon framework during loss of the elements of H_2O; that is, $[C_6H_2D]^-$ was formed (Table I). Study of the ion from 3,5-dideuteriophenol (**4**) also was informative since it showed that, in addition to the loss of the oxygen atom,

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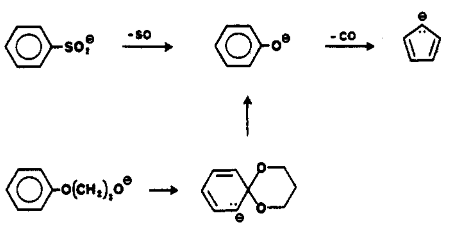
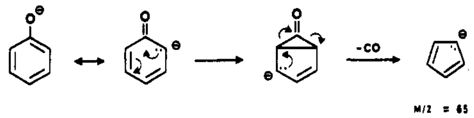
Scheme III



Scheme IV

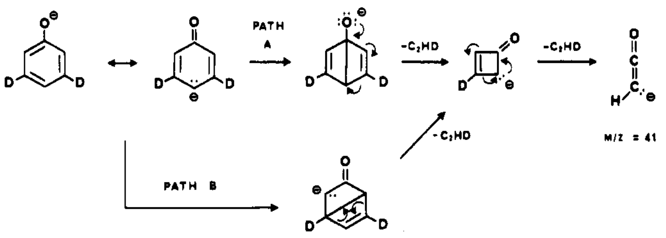


there was essentially equal probability of loss of either two ortho hydrogen atoms (to give an ion with $m/z = 77$) or an ortho hydrogen atom and a meta deuterium atom (to give an ion with $m/z = 76$). CAD of the anion from 2,4,6-trideuteriophenol (**5**) gave the same result (Table I); that is, it also produced ions that had lost either two ortho substituents or one ortho and one meta substituent.

The information about the $[C_6H_3]^-$ ion obtained from compounds **3**–**5** can be explained by a process that begins with the negatively charged oxygen atom abstracting a deuterium from the ortho position on the aromatic ring. This reaction is then followed by elimination of DO^- to form a complex from which D_2O or HDO loss produces the observed ions (Scheme I, ion from **5** used as an example). This process is analogous to a reaction observed by Gronert and DePuy,[15] who found that the *o*-fluorophenyl anion (**7**) reacted in the gas phase to generate $[C_6H_3]^-$. From the study of **8**, a deuterated analog of **7**, these authors proposed that a complex was formed which had essentially equal probability of expelling HF or DF (Scheme II). Chowdhury and Harrison[16] also have observed the formation of the $[C_6H_3]^-$ ion from reaction of **7**; however, in this case **7** was generated by fragmentation of the enolate anion derived from *o*-fluoroacetophenone. In light of the parallel between the reactions of the *o*-fluorophenyl anion **7** (Scheme II) and the *o*-hydroxyphenyl anion **6** (Scheme I), loss of the elements of water from phenoxide ion to give $[C_6H_3]^-$ appears to be a second reaction, closely related to the first, for generation of a deprotonated benzyne.

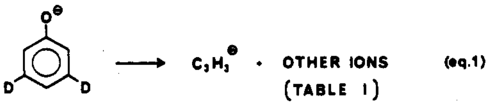
Formation of the $[C_5H_5]^-$ ion from phenoxide ion could be anticipated from the work of Bowie and Stringer,[17] who observed the appearance of an ion with m/z of 65 in the CAD spectrum of $[C_6H_5SO_2]^-$ and, in a later study from the same research group,[18] in the CAD spectrum of $[C_6H_5O(CH_2)_3O]^-$. In each case phenoxide ion was proposed as an intermediate (Scheme III) and, in the latter study, ^{13}C labeling of the ipso carbon atom in the aromatic ring provided convincing evidence of CO loss. When the results from these two studies[17,18] are combined with the findings from collisionally activated dissociation of the anions from phenols **1** and **2**, CO loss from phenoxide ion to give the cyclopentadienyl anion seems firmly established. A mechanism for this process is proposed in Scheme IV.

Scheme V



Reactions of the deuterated phenols **3**–**5** proved to be quite informative about the mechanism for generation of the oxygen-containing ion $[C_2HO]^-$ ($m/z = 41$). When the anion from 3,5-dideuteriophenol (**4**) experienced collisionally activated dissociation, an ion with m/z of 41 (but none with m/z of 42) was observed, while CAD of the anion from 2,4,6-trideuteriophenol (**5**) gave ions with m/z of 42 and 41 (Table I). Since compound **4** produced no ions with m/z of 42, an oxygen-containing ion derived from **4** must have the formula $[C_2HO]^-$; thus, only ortho or para hydrogen atoms can become part of such an ion.[19] The two mechanisms shown in Scheme V are consistent with this observation. Reaction by path A requires incorporation of either ortho or para hydrogen atoms into $[C_2HO]^-$, while reaction by path B predicts only ortho hydrogen atoms will be present in this ion. A choice between these two pathways was made by CAD of the anion from 4-deuteriophenol (**3**), which gave anions at $m/z = 42$ $[C_2DO^-]$ and 41 $[C_2HO]^-$. Only reaction by path A (Scheme V) is consistent with this result.[20]

The fragmentation of phenoxide ion into $[C_3H_3]^-$ is a reaction which does not allow a clear mechanistic interpretation from the data available. The difficulties in interpretation can be appreciated by considering that 3,5-dideuteriophenol (**4**) produces a significant amount of the $[C_3H_3]^-$ ion (eq 1). Such an ion either is formed from a quite complex process or, more probably, is the resulting of "scrambling" of the deuterium label during its formation, a reaction which would render the study of the deuterated compounds **3**–**5** incapable of providing the necessary information for understanding how this ion is produced.



In summary, the experiments and observations on the anions derived from phenols **1**–**5** provide evidence that four major reaction pathways are available to phenoxide ion in the gas phase. When the data generated from these anions are combined with information on analogous processes in the literature, a basis exists for proposing mechanisms for formation of the daughter ions $[C_6H_3]^-$, $[C_5H_5]^-$, and $[C_2HO]^-$. A similar mechanistic proposal for generation of the remaining daughter ion $[C_3H_3]^-$ cannot be made from the data available, due probably to hydrogen–deuterium exchange during its formation.

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(18) Eichinger, P. C. H.; Bowie, J. H.; Hayes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4224. Also reported in this paper in the CAD spectrum of $[C_6H_5O]^-$ is a small peak corresponding to an ion with $m/z = 64$. (This peak actually appears as a shoulder on the much larger peak at $m/z = 65$.) The ion responsible for the peak at $m/z = 64$ was not considered in the present study since its abundance was so small that its formation did not represent a significant reaction pathway.

(19) Another consequence of the lack of ions at m/z of 42 is that there was no general "scrambling" of the deuterium label prior to CAD of the parent ion or during formation of the $[C_2HO]^-$ ion.

(20) The formation of the $[C_2HO]^-$ from phenoxide ion represents the formal loss of C_4H_4. Loss of these elements has been observed from other aromatic compounds and has been attributed to loss of cyclobutadiene.[21] Such a loss cannot be taking place from phenoxide ion because it is inconsistent with the ions formed from CAD of **5**.

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Experimental Section

General Procedures. Mass spectra were obtained using a Finnigan TSQ-45 triple quadrupole mass spectrometer under the following conditions: source temperature, 120 °C; ammonia gas pressure, 0.35 Torr; electron energy, 70 eV; electron multiplier 1300–1500 V. The collision cell pressure was 1.3 mTorr, and the collision energy was 30 eV. ^{13}C NMR spectra were obtained at 75 MHz in $CDCl_3$ with TMS as an internal standard.

Compounds 1–5. Compounds 1 and 2 were purchased from the Aldrich Chemical Co. Compounds 4 and 5 were prepared by hydrogen–deuterium exchange according to the method of Epp, Boyd, and Berchtold,[22] using phenols 2 and 1, respectively, as the starting materials. The fully proton decoupled ^{13}C NMR spectrum of compound 4 contained singlet resonances at 155.40 (ipso carbon atom), 120.55 (para carbon atom), and 115.26 (ortho carbon atoms) ppm and a low-intensity triplet (meta carbon atoms) at 129.41 ppm. The fully proton-decoupled ^{13}C NMR spectrum for compound 5 contained singlet resonances at 155.25 (ipso carbon atom) and 129.52 (meta carbon atoms) ppm and low-intensity triplet resonances at 120.59 (para carbon atom) and 115.17 (ortho carbon atoms) ppm. Compound 3 was prepared by irradiation of *p*-chlorophenol in CD_3OD as described by Muller, Parlar, and Korte.[23] The fully proton-decoupled ^{13}C NMR spectrum of compound 3 had singlet resonances at 155.59 (ipso carbon atom), 129.50 (meta carbon atoms), and 115.28 (ortho carbon atoms) ppm and a low-intensity triplet (para carbon atom) at 120.59 ppm.

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From *p*-Dimethoxybenzene toward Crown Benzenophanes: 1,3,10,14-Tetraoxa[3.5]paracyclophane

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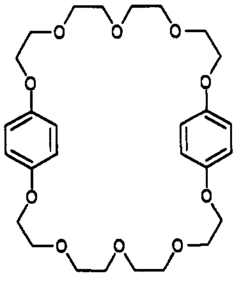
The title compound tetraoxa[3.5]paracyclophane (**6**) has been prepared and studied in order to investigate the evolution of spectroscopic properties in going from the monomer unit *p*-dimethoxybenzene (**9**) via the noncyclic bichromophoric reference compound **3b** to **6**. The X-ray structural analysis of **6** shows that the distance between the two aromatic carbon atoms linked to the smaller bridge is shorter than the van der Waals distance. The resulting electronic interaction is reflected by the perturbation of the UV spectrum of **6** (in particular by a distinct hypochromic effect) and in its charge-transfer complexes with TCNE and TCNQ, as compared to **9** and **3b**. The fluorescence quantum yields show significant quenching as compared to **9**. This process is related to the formation of a new, structureless red-shifted band with a maximum at 26 670 cm^{-1}, comparable to that of the excimer of **9**. From a Stern–Volmer plot the self-quenching rate constant of the latter, $k_q \approx 1.2 \times 10^9$ mol^{-1} s^{-1} is derived.

Introduction

Crown ethers continue to attract interest as synthetic organic host molecules. Among a plethora of recent examples, the dibenzocrown ether BBO_5O_5 (B = benzene), studied by Stoddard and co-workers, encapsulates a molecule of paraquat. This was the prototype for preparing new catenanes and rotaxanes with great potential for various applications in molecular electronics.[1] Formally, this compound may also be regarded as belonging to the paracyclophane family, whose first members show special spectroscopic and chemical properties because of the close proximity of their aromatic subunits.[2] However, the free ligand BBO_5O_5 can undergo considerable con-



BBO_5O_5

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