A Comparison of the Reactions of the Oxide Radical Anion ($O^{\cdot-}$) with Simple Aromatic Compounds at Atmospheric and at Reduced Pressure Conditions

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The reactions of oxide radical anions ($O^{\cdot-}$) with benzene and toluene under atmospheric pressure (APCI) and conventional chemical ionization (CI) conditions were compared. Hydrogen radical ($H^{\cdot}$) displacement by oxygen, yielding $[M - H + O]^{\cdot-}$, was observed in both the APCI and the CI source. However, the product, $[M - 2H]^{\cdot-}$, derived from dihydrogen radical ion ($H_2^{\cdot+}$) transfer which was observed in the CI spectra, was consistently absent under APCI conditions. This behavior is rationalized in terms of the higher pressures and chemical equilibrium associated with the APCI source. In addition to the formation of the a priori expected phenoxide isomers, the reaction of $O^{\cdot-}$ with toluene to yield the $[M - H + O]^{\cdot-}$ product generates a benzyloxy anion. Tandem mass spectrometry data from collision-induced dissociation and isotopic labeling with deuterium support a reaction mechanism initiated by α hydrogen abstraction for both the $H^{\cdot}$ and the $H_2^{\cdot+}$ transfer pathways. (*J Am Soc Mass Spectrom* 1994, 5, 367-376)

Since its discovery in the late 1960s by Field and Munson, chemical ionization (CI) has become prominent as an ionization technique in analytical mass spectrometry. In the ensuing decades a wide variety of CI reagent gases have been introduced. The predominant ionization scheme involves the use of Bronsted acids and bases which react with the analyte to form $[M + H]^+$ and $[M - H]^+$ ions, respectively [1]. Such reagent gases are very general in that they react with any substrate with the proper gas phase acidity or basicity. For purposes of structural characterization, however, the analytical chemist would ideally like to have available an array of CI reagent systems, each exhibiting a behavior indicative of some particular structural feature. While that goal remains far from being realized, there are some reagents which react in unique ways with certain types of compounds. An example of such a reagent for negative chemical ionization (NCI) is the oxide radical anion, $O^{\cdot-}$. In general $O^{\cdot-}$ reacts primarily via the five pathways shown in Scheme I [2]. Furthermore, the extent to which each pathway contributes to the product spectrum is highly dependent upon substrate structure. For instance the $[M - H + O]^{\cdot-}$ pathway is very important for aromatic substrates. One of the areas of greatest interest in $O^{\cdot-}$ as an NCI reagent has therefore been in

the field of environmental pollutant analysis [3-6]. In addition to its utility to the analytical chemist, $O^{\cdot-}$ has also been found to be an invaluable tool and an intriguing subject of investigation to the gas phase ion chemist. For instance, the range of ions whose gas phase chemistry can be studied has been broadened [7, 8] due to the very high gas phase basicity of $O^{\cdot-}$ ($PA = 382$ kcal/mol) [9]. This feature, for example, enables the investigator to generate highly energetic carbanion species for further study. The oxide radical ion is also an interesting target of study because it is an open shell ion. As a result, its reactivity with organic compounds is quite diverse.

One of the most interesting reactions exhibited by $O^{\cdot-}$ is the formal transfer of $H_2^{\cdot+}$ to form a new radical anion and H_2O . In suitably activated aliphatic substrates $O^{\cdot-}$ is known to abstract both hydrogens from

Scheme I. General pathways observed in the reaction of $O^{\cdot-}$ with organic compounds.

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the same carbon atom. This type of mechanism was first demonstrated by Goode and Jennings [10] in an ICR study using deuterium labeled ethylene, while in another ICR study of variously substituted ethylenes, Dawson and Jennings reported that substituents which reduced electron density at the $=CH_2$ group were found to enhance H_2^{+} transfer. Conversely, substituents which increased electron density at the $=CH_2$ group were found to suppress H_2^{+} transfer [11]. Dihydrogen ion transfer from aromatic compounds has also been found to be structure dependent. Benzenes, for instance, have been shown to lose H_2^{+} to yield the *o*-benzynes radical anion [12, 13] while alkyl benzenes such as toluene have been reported to lose both hydrogens from the α -carbon [2]. The ability to generate the *o*-benzynes radical anion in the gas phase is of particular utility because it has allowed researchers to determine the acidity of the phenyl radical and the heat of formation of *o*-benzynes [14]. The mechanism of dihydrogen transfer from an aromatic ring and the factors affecting it have been the subject of a recent report by Matimba et al. [15].

For the purpose of developing O^- as an NCI reagent, the reactions of O^- with simple six-membered ring aromatic compounds were carried out by Bruins et al. [2] in the CI source of a double focusing mass spectrometer. Again, the contribution of each pathway in Scheme I was found to be dependent upon the structure of the neutral reactant. For instance benzene and pyridine produce only dihydrogen transfer ($[M - 2H]^-$) and hydrogen atom displacement ($[M - H + O]^-$) products. Introduction of an alkyl substituent, however, makes $H^\cdot$ and H^+ transfer competitive with H_2^{+} transfer and $H^\cdot$ displacement. Deuterium labeling of alkylbenzenes suggests that proton transfer involves loss of hydrogen from the alkyl substituent, whereas $[M - H + O]^-$ formation involves displacement of a ring hydrogen.

Another systematic investigation of the reactions of O^- with six-membered ring (benzene and pyridine) and five-membered ring (furan, pyrrole, thiophene, and cyclopentadiene) aromatic compounds using the flowing afterglow (FA) technique has recently been reported by Guo et al. [16]. Both benzene and pyridine were shown to react only by dihydrogen transfer and hydrogen atom displacement. Hydrogen atom displacement in the five-membered rings, however, was relatively unimportant. In fact, with the exception of thiophene, none of these compounds produced $[M - H + O]^-$. This result was rationalized by the authors to be due to the higher acidity of the C_5 aromatics as well as the tendency of the carbons to be more electron rich than those in the C_6 aromatics (thus inhibiting oxygen atom addition).

It is clear from the above that much of our knowledge regarding the reactivity of O^- comes from FA and ion cyclotron resonance experiments. On the other hand, the effective use of any CI reagent requires a good understanding of its reactivity under conditions

typical of analytical mass spectrometry. As a consequence, a number of investigators have further examined the CI behavior of O^- [6, 17]. In this article we compare the reactions of O^- with simple aromatic systems, benzene and toluene, under atmospheric pressure and conventional (~ 1 torr) chemical ionization conditions. Of special interest has been the structural characterization of the isomeric phenoxide ions produced by the displacement of $H^\cdot$ by O^- in toluene. To that effect we capitalized on the power of triple quadrupole mass spectrometry and the comparison of collision-induced dissociation (CID) spectra of "standard" phenoxide ions with those produced from the reaction of O^- with toluene. Deuterium labeled toluene analogues were also used to probe the reaction mechanisms.

Experimental

Atmospheric Pressure Ionization Experiments

The atmospheric pressure chemical ionization experiments were performed on a Sciex TAGA6000 triple quadrupole mass spectrometer equipped with a corona discharge atmospheric pressure chemical ionization (APCI) source. The method of sample introduction, while somewhat crude, was suitable for our purposes. About 10 μ L of the liquid sample (benzene, toluene, or benzyl alcohol) was loaded onto a piece of cotton or Kimwipe which was packed inside a piece of glass tubing. In the case of solid samples (cresols), a small grain of analyte was placed within the packing. The glass tubing was then placed in line with the carrier gas stream. Thus, as the carrier gas passed over the packing, the analyte was carried into the APCI source where the discharge needle was held at -4 kV. In our experiments the carrier gas consisted of a 2.5 L/min flow of N_2 and a 20 mL/min flow of N_2O which were teed into a common line. The nitrogen served to thermalize the electrons by electron capture and subsequent electron detachment, while N_2O was the source of O^- reagent ions. Other species present in the reagent ion mixture were predominantly O_2^- at m/z 32 and $O^-(N_2O)$ at m/z 60. In this case O_2^- is believed to be a consequence of the atmospheric environment in which at least trace amounts of oxygen are present. The CID experiments were performed by attenuating the precursor beam to 30% using argon as the collision gas and a collision energy of 80 eV. In addition, the resolution of Q1 was reduced so as to maximize the transmission of the precursor beam into the collision chamber.

Negative Chemical Ionization Experiments

All of the NCI experiments were performed using a VG Quattro triple quadrupole mass spectrometer and a conventional chemical ionization source. All of the benzene spectra, full scan and CID, were obtained by

introducing benzene via the reference inlet. For the full scan spectra of the toluenes (d_0 , d_1 , and d_3) the analyte was introduced via the gas chromatograph (Hewlett Packard, 5890A). The CID spectra, however, were obtained by introducing the analyte through the reference gas inlet. The source temperature was 180 °C and the reagent gas was N_2O . While an N_2 buffer was found to be essential for maintaining a stable discharge in APCI it was not found necessary for operation under NCI. Therefore, nitrogen was deleted from the reagent gas mixture. In addition to $O^{--}(m/z\ 16)$, the reagent gas produced ionic species at $m/z\ 26, 30, 32, 42$, and 46 . Based on observations reported in the literature [18, 19] the ions at $m/z\ 30, 32$, and 46 are believed to correspond to NO^- , O_2^- and NO_2^- , respectively. The identity of the others, however, is unknown. The source pressure was adjusted to maximize the intensity of $m/z\ 16$. Finally, CID was performed using argon as the collision gas and a 110 eV collision energy.

Chemicals

The reagent gases were high purity and purchased from MedTech Gases (Medford, MA). The benzene and toluene were spectroscopic grade and purchased from J. T. Baker. The reference methyl phenols and benzyl alcohol were purchased from Aldrich Chemical Co. (Milwaukee, WI). The α, α, α - d_3 -toluene (99%) was acquired from A. Idelson, ICON Isotopes (Mount Marion, NY). All of the above were used as received. The α - d_1 -toluene was synthesized by the reaction of benzyl magnesium chloride (Aldrich Chemical Co., Milwaukee, WI) and D_2O (99.8%, Cambridge Isotope Labs, Woburn, MA) followed by simple distillation after which the only remaining contaminant, benzyl alcohol (OD) was at a level of less than 0.1%. Given the much higher boiling point of benzyl alcohol (208 °C) relative to toluene (110 °C), this level of contamination was believed to be acceptable for the APCI experiments where no chromatographic method would be used.

Results and Discussion

Reactions of O^{--} with Benzene

The reaction of O^{--} with benzene under APCI and NCI conditions was examined first because of the overall greater structural simplicity of the system and availability of relevant thermochemical data. The O^{--}/NCI

and $O^{--}/APCI$ spectra of benzene are compared in Figure 1. The ionic products formed are summarized in Table 1. While our NCI results are consistent with the results of NCI and FA experiments reported previously [2, 16], there is a significant discrepancy between the APCI data and those same reports. The APCI data differ in that there is no evidence for a dihydrogen radical ion transfer. This is remarkable, given the fact that this pathway has been shown to be quite competitive under both CI and FA conditions. For example, even though the ratio of $m/z\ 76$ to $m/z\ 93$ tends to vary depending upon reaction conditions, ratios from 2:1 to 1:2 have been reported [2, 16]. Although the energetics of the dihydrogen transfer pathway ($\Delta H_{rxn} = -9.5$ kcal/mol) are not as favorable as those for the $H^\cdot$ displacement pathway ($\Delta H_{rxn} = -32.9$

Figure 1. (a) O^{--}/NCI spectrum of benzene; (b) $O^{--}/APCI$ spectrum of benzene.

Table 1. Ionic products observed upon reaction of O^{--} with benzene under NCI and APCI conditions.

Technique	Reaction Products	Mass-to-Charge Ratio Products
Negative	$[M - 2H]^{--} + H_2O$	$m/z\ 76$
chemical ionization	$[M - H + O]^{--} + H^\cdot$	$m/z\ 93$
Atmospheric pressure	$[M - H + O]^{--} + H^\cdot$	$m/z\ 93$
chemical ionization		

kcal/mol), the former has been shown to be competitive because of kinetic factors [16].

The possibility that $C_6H_4^-$ ions were being lost because of quenching by neutral impurities was considered in light of the known tendency of $C_6H_4^-$ to react with O_2 and CO_2 to form neutral orthoquinone and a benzoate anion, respectively [14]. While direct detection of the orthoquinone neutral is obviously impossible, an experiment was conducted in which CO_2 was added to the reagent gas stream in order to determine if there was any $C_6H_4^-$ available for quenching. A benzoate product ion of m/z 121, however, was not observed. This result suggests that either the dihydrobenzene anion is not being formed under APCI conditions or it is too short lived to undergo reaction with CO_2 . While the possibility of quenching by O_2 cannot be definitively eliminated, it was considered unlikely in view of the results of the CO_2 experiment. An alternative rationale for the absence of a dihydrogen transfer product is based on the effect of the instrumental conditions under which these reactions took place. It may be argued that indeed $C_6H_4^-$ is formed, but the unique atmospheric pressure, multi-collision environment of the APCI source allows the redistribution of products along the more exothermic pathway. While the differences in activation barrier for the discrete steps of each pathway are presumably small, the barrier for disruption of the $[C_6H_4^- \dots H_2O]$ ion-neutral complex is significantly higher than that of the $[C_6H_5O^- \dots H]$ ion-neutral complex [16]. Thus the reverse reaction in the $H^\cdot$ displacement pathway may be less competitive than that for the dihydrogen transfer pathway, leading to exclusive formation of $[M - H + O]^-$ under APCI conditions.

Reactions of O^- with Toluene

By virtue of the methyl substituent on the aromatic ring, toluene is expected to exhibit a higher degree of chemical complexity, thus introducing the possibility of two additional reaction pathways. These are $H^\cdot$ and H^+ transfer to yield OH^- and the benzyl anion ($PhCH_2^-$) respectively. The O^-/NCI and the $O^-/APCI$ spectra of toluene are compared in Figure 2. Consistent with the report by Bruins et al. [2] all four possible products are observed under O^-/NCI , as indicated in Table 2. Also shown in Table 2 are the ionic species

Figure 2. (a) O^-/NCI spectrum of toluene; (b) $O^-/APCI$ spectrum of toluene.

produced under $O^-/APCI$, where the only processes observed are the $H^\cdot$ displacement and H^+ transfer reactions. Notable again is the absence of products from the H^+ and H_2^+ transfer reactions (m/z 91 and m/z 90) under APCI conditions. An experiment similar to that performed with benzene was again carried out in order to assess the possibility of $[M - 2H]^-$ quenching by neutral impurities. The $O^-/APCI$ spectrum of toluene in the presence of CO_2 is shown in Figure 3. Little or no methyl substituted benzoate ion (m/z 134) was detected, again suggesting that the dihydrogen ion transfer pathway is not operative or that the intermediate is too short-lived to react with CO_2 . Of particular interest, however, are the peaks at m/z 91 and 135, which correspond to the masses of a

Table 2. Ionic products observed upon reaction of O^- with toluene under NCI and APCI conditions

Technique	Reaction Products	Mass-to-Charge Ratio Products
Negative chemical ionization	$[M - H]^- + OH^-$	m/z 17
	$[M - 2H]^- + H_2O$	m/z 90
	$[M - H]^- + OH^\cdot$	m/z 91
	$[M - H + O]^- + H^\cdot$	m/z 107
Atmospheric pressure chemical ionization	$[M - H]^- + OH$	m/z 17
	$[M - H + O]^- + H^\cdot$	m/z 107

Figure 3. O^{-} /APCI spectrum of toluene in the presence of CO_2 .

benzyl anion and phenylethanoate ($PhCH_2CO_2^{-}$), respectively. The ion at m/z 135 supports the formation of $PhCH_2^{-}$ via proton transfer followed by quenching with CO_2 . Furthermore, it suggests that the reaction of $PhCH_2^{-}$ with CO_2 is competitive with reversion back to O^{-} and toluene while the reaction of $[M - 2H]^{-}$ with CO_2 is not. Finally, it is unknown why the benzyl anion itself is observed in the presence of CO_2 . It can be reasoned, however, that it is the result of unimolecular decomposition of phenylethanoate. The process of $PhCH_2^{-}$ addition to CO_2 followed by unimolecular decomposition of the adduct can be viewed as diverting some of the proton transfer product away from the pathway leading back to reactants.

Position of Oxygen Incorporation in the Formation of $C_7H_7O^{-}$ Product Ions CID Experiments

In addition to expanding the range of reaction types observed, the presence of a methyl group on the benzene ring also introduces the possibility of selectivity in terms of the position of oxygen incorporation. CID was used in order to determine the structure(s) of the H^{-} displacement product ($C_7H_7O^{-}$) of m/z 107. Our strategy involved a comparison of the CID spectrum of the ion produced from the reaction of O^{-} with toluene to the CID spectra of $C_7H_7O^{-}$ reference ions of known structure. Three obvious structural possibilities for the $C_7H_7O^{-}$ ion were the *o*-, *p*-, and *m*-methylphenoxide (CH_3PhO^{-}) isomers. A fourth possibility, the benzyl-oxide ion ($PhCH_2O^{-}$) was also considered although a priori it was deemed less likely since it is energetically less favorable ($\Delta H_{rxn} [O^{-} + PhCH_3 \rightarrow PhCH_2O^{-} + H] = -5.8$ kcal/mol; $\Delta H_{rxn} [O^{-} + PhCH_3 \rightarrow p-CH_3PhO^{-}] = -15.7$ kcal/mol) [20]. Nevertheless, this possibility was also investigated.

The CID spectra of the four $C_7H_7O^{-}$ reference ions generated in the gas phase by proton abstraction from *o*-, *p*-, *m*-cresol and from benzylalcohol are shown in

Figure 4. CID spectra of the m/z 107 ion produced by O^{-} /APCI of (a) 2-methylphenol, (b) 3-methylphenol, (c) 4-methylphenol, and (d) benzyl alcohol.

Figure 4a-d. The spectra of the meta and para isomers show the greatest similarity. For instance, they are both dominated by the peaks at m/z 92 (loss of CH_3) and m/z 41 (fragmentation through the aromatic ring). Although minor in relative intensity, the peaks at m/z 64 and 77 in the spectrum of the para isomer, however, provide a basis for the differentiation of these two isomers. The spectrum of the ortho isomer, on the other hand, is characterized by the intense peaks at m/z 41, 64, and 92. The intensity of m/z 64 makes the presence of the ortho isomer clearly identifiable. Significantly, the loss of 15 daltons in the CID spectra of m/z 107 helps identify the presence of a methyl group on the precursor ion. Finally, the CID spectrum of m/z 107 from benzyl alcohol is totally dominated by the m/z 77 fragment ion which is presumably formed via the elimination of $CH_2=O$ as shown in Scheme II. In addition, because the m/z 77 peak is of relatively minor intensity in the spectra of the phenoxide isomers, its presence can be diagnostic of the benzyl-oxide isomer.

The CID spectrum of the m/z 107 ion produced by reaction of toluene with O^{-} is shown in Figure 5. The four most abundant ions in the spectrum are found at m/z 92, 77, 64, and 41. For purposes of comparison with the reference spectra, emphasis was placed on the presence and relative abundance of these particular fragment ions. It is apparent from Figures 4 and 5 that the APCI reaction of toluene with O^{-} produced a

Scheme II. Proposed mechanism for the collision induced expulsion of CH_2O from the benzoxide ion.

Figure 5. CID spectrum of the m/z 107 ion produced by O^- /APCI of toluene.

mixture of methylphenoxide and benzyloxide isomers. The formation of a benzyloxide anion is supported by the high intensity of the m/z 77 peak shown in Figure 5. This is somewhat unexpected in view of previous reports that, under NCI conditions, only ring hydrogens are displaced in the H^+ displacement pathway [1, 2].

Because of the unusual nature of the benzyloxide reaction product, it was of interest to estimate the relative extent of its formation. This was done using the principle of linear superposability of CID spectra. This concept is based on the assumption that the spectrum produced by a mixture is simply a linear superposition of the spectrum of each individual isomer in the mixture. The approach has long been used for the analysis of organic mixtures by electron impact (EI) mass spectrometry (see, for example, Ref. [21]). It is important to note that there have been some questions regarding the reliability of linear superposability for CID spectra [22]; however, there have also been reports in which the reliability has been reinforced by neutralization-reionization experiments [23]. In addition, this experiment was performed with the under-

standing that differences in precursor ion internal energy can be important at low collision energies. Therefore the result is merely an estimate. However, at the very least we felt that such an analysis of the CID data obtained from the isomeric mixture might provide some insight into the relative propensity for formation of a benzyloxide ion versus a methylphenoxide ion.

In order to improve the precision of the mass spectral data, several repeat scans of the CID spectra of the reference anions and of the m/z 107 ion produced from toluene were taken. The four most intense peaks, m/z 92, 77, 64, and 41 in the CID spectra of the reference ions and the isomer mixture were used for our semiquantitative calculation. Good reproducibility is apparent as indicated by the reconstructed CID spectra shown in Table 3. In order to simplify the analysis, it was assumed that the ion of m/z 64 in the spectrum of the toluene reaction product originated solely from the *o*-methylphenoxide isomer. Based on the intensity of m/z 92 relative to m/z 64 in the reference spectrum of the *o*-methylphenoxide, the amount of m/z 92 contributed by that isomer in the CID spectrum from toluene is estimated to be about 27%. By difference, the amount of m/z 92 due to the combined contributions of the *m*- and *p*-methylphenoxide isomers is 73%. While this does not allow us to distinguish the individual contributions of the *m*- and *p*-isomers, it can be stated that the ratio of *o*-methylphenoxide to the combined *m*- and *p*-methylphenoxides is approximately 1:3. In determining the contribution of the benzyloxide isomer to the spectrum in Figure 5, two scenarios were considered. In the first, it was assumed that the remaining methylphenoxide contribution was only due to the *p*-isomer. The combined contributions of *o*- and *p*-methylphenoxides to the ion current at m/z 77 can then be determined by the relative ratio of m/z 77 to m/z 92 in the reference spectra. By difference, a contribution from benzyloxide of 84% is obtained and a minimum ratio of benzyloxide to *o*-methylphenoxide of 21:1 is obtained. A second scenario in which the remaining methylphenox-

Table 3. Reconstructed CID spectra of m/z 107 ions produced by the reaction of O^- with toluene and reference compounds

Precursor	Product Ions			
	m/z 41	Normalized Intensity (RSD ^a)		m/z 92
		m/z 64	m/z 77	
Toluene ($C_7H_7O^-$)	54.6 (11)	30.2 (13)	57.4 (10)	100
2-Methylphenoxide (2- CH_3 - PhO^-)	85.2 (3)	100	7.72 (9)	89.3 (2)
3-Methylphenoxide (3- CH_3 - PhO^-)	21.7 (1)	6.46 (2)	.861 (6)	100
4-Methylphenoxide (4- CH_3 - PhO^-)	22.1 (1)	3.38 (7)	9.82 (3)	100
Benzyl Alcohol ^b ($PhCH_2O$)	.093	.072	100	.17

^aRelative standard deviation.

^bNo RSD data available for benzyl alcohol.

ide contribution is only due to the *m*-isomer was considered. An analysis similar to the one described above results in a benzyloxyde contribution to m/z 77 of 96% and a maximum ratio for benzyloxyde to *o*-methylphenoxide of 25:1. Because the ratio of *o*-methylphenoxide to the combined *m*- and *p*-isomers is 1:3, it would thus appear that benzyloxyde formation is favored over total methylphenoxide formation by a factor of 5 to 6. At this point no rationale could be provided for this predominance of the benzyloxyde isomer. However, the results discussed below from isotopic labeling experiments using α,α,α - $[^2H]_3$ -toluene and α - $[^2H]_1$ -toluene are consistent with oxygen incorporation at the benzylic carbon. In addition, they support an $H^\cdot$ displacement mechanism which is initiated by benzylic hydrogen abstraction.

Reactions of O^- with Deuterium Labeled Toluenes

α,α,α - $[^2H]_3$ -toluene. We examined first the reaction of α,α,α - $[^2H]_3$ -toluene (d_3 -toluene) with O^- under APCI conditions. Based on the APCI results obtained with unlabeled toluene, product ions of m/z 18 (OD^-), and m/z 109 ($[M - D + O]^-$) were expected. Remarkably, no products indicative of any reaction of O^- with the labeled toluene were observed. Two ions of still undetermined origin at m/z 119 and m/z 59 were observed consistently. CID of the former ion yielded fragments of m/z 59 while CID of the latter ion yielded fragments of m/z 44 and 15. Neither of these fragmentation processes appear to be associated with an aromatic structure. The absence of OD^- and the lack of evidence for $[M - H + O]^-$ and $[M - D + O]^-$ pathways indicates that

1. Nucleophilic aromatic substitution (S_NAr) is not operative
2. $C_7H_7O^-$ formation (benzyloxyde and methylphenoxides) occurs via initial benzylic hydrogen abstraction

A mechanism consistent with benzyloxyde and methylphenoxide ion formation via initial $H^\cdot$ abstraction by O^- is proposed in Scheme III. The mechanism hinges on extensive chemistry occurring within an ion-neutral complex. Evidence for this type of behavior is well documented in studies of gas phase ion chemistry [24-27]. Generation of $C_7H_7O^-$ is envisioned to be initiated by transfer of a benzylic hydrogen atom to O^- . It is proposed that the resultant benzyl radical may interact directly with the OH^- ion to form benzyloxyde. Alternatively, it may rearrange to form a seven-membered ring into which oxygen can eventually be incorporated. While only the formation of the *o*-methylphenoxide isomer is illustrated in Scheme III, formation of the *m*- and *p*-isomers is envisioned to proceed via a series of 1,2 $H^\cdot$ migrations. It is thus possible that when the benzylic carbon is perdeuterated, the increased barrier to $D^\cdot$ transfer may completely suppress the $H^\cdot$ displacement pathway. While

Scheme III. Proposed mechanism for the formation of benzyloxyde and *o*-methylphenoxide isomers via initial α -hydrogen abstraction.

the energetics are unknown, it can be speculated that the activation barriers are in general lower for methylphenoxide ion formation via the mechanism in Scheme III (which involves benzylic hydrogen abstraction) than they are for a nucleophilic aromatic substitution (S_NAr) mechanism (which involves disruption of aromaticity). Hence, under APCI conditions methylphenoxide ion production appears to occur exclusively via initial α -hydrogen transfer. Finally, if $H^\cdot$ ($D^\cdot$) displacement is, as argued, no longer competitive, the question of why dihydrogen transfer is not observed still remains. Evidence is shown below which suggests that this process, unlike the analogous reaction for benzene, is also initiated by benzylic hydrogen transfer.

As shown in Figure 6, the effect of perdeuteration of the methyl group is less dramatic under NCI condi-

Figure 6. O^- /NCI spectrum of α,α,α - d_3 -toluene.

tions. With the exception of the perplexing absence of m/z 18 (due to D^+ transfer), the results are very informative. For example, signals at m/z 110 and 109 corresponding respectively to H^+ and D^+ displacement are observed. The presence of ions at m/z 110 and 109 in this case suggests that, under NCI, perdeuteration of the methyl group does not completely suppress H^+ displacement. This is in contrast to the behavior exhibited under APCI. Moreover, the presence of m/z 110 ($[M - H + O]^-$) suggests that the S_NAr mechanism is followed to a certain extent. The heated source may make both pathways, S_NAr and initial D^+ transfer, more accessible; hence the different behavior under NCI and APCI.

The CID spectrum of m/z 109, presumably $[M - D + O]^-$, is shown in Figure 7a. The general features of the spectrum are similar to those observed upon collision-induced fragmentation of the $[M - H + O]^-$ ion from unlabeled toluene, shown in Figure 7b. This pattern indicates a mixture of methylphenoxide and benzyloxide isomers. Of particular interest is the ion at m/z 92 in Figure 7a which corresponds to the loss of a dideuteromethyl radical ($CD_2H^{\cdot}$) from a methyl phenoxide product. This is analogous to the loss of $CH_3^{\cdot}$ in Figure 7b. The clean loss of 17 u from $[M - D + O]^-$, however, is consistent with initial deuterium abstraction followed by some type of rearrangement

whereby a ring hydrogen is transferred to the α -carbon. The next region of interest includes the ions m/z 77, 78, and 79. The loss of 32 u, yielding m/z 77, corresponds to $CD_2=O$ and is consistent with a benzyloxide product resulting from the direct incorporation of oxygen onto the benzylic carbon. Moreover, the fragment at m/z 78 suggests that oxygen incorporation onto the benzylic carbon also occurs after some degree of hydrogen rearrangement. Finally, the fragment at m/z 79 may be the result of further hydrogen/deuterium (H/D) exchange at the α -carbon prior to oxygen incorporation. This is not totally clear, however, because m/z 79 is also present in the CID spectrum of $[M - H + O]^-$ from unlabeled toluene.

In the O^- /NCI spectrum of d_3 -toluene there are also signals at m/z 91 and 92 corresponding to D_2^+ and HD^+ transfer. Evidence for these pathways is consistent with the APCI data which suggest that dihydrogen transfer from toluene does not involve abstraction of the aromatic ring hydrogens. This is also in agreement with the isotope labeling experiments (reported but not shown) of Bruins et al. [2] which indicate hydrogen removal from the benzylic carbon. The ion at m/z 93 is therefore believed to be due to D^+ as opposed to H_2^+ transfer. In addition, the presence of m/z 92 suggests that both hydrogens are not directly removed from the benzylic carbon. Instead, it is consistent with initial α -H transfer followed by isomerization to a seven-membered ring. If dihydrogen transfer does follow this pathway, then it would be expected, under APCI, to be affected in the same way as H^+ displacement upon perdeuteration of the α -carbon. Indeed, this is what is observed.

α -[2H] $_1$ -toluene. In light of the complete suppression of APCI reactivity upon perdeuteration of the methyl group it was deemed appropriate to evaluate the behavior of α -[2H] $_1$ -toluene (d_1 -toluene) under both O^- /APCI and O^- /NCI conditions (Figures 8a and b).

Based on the information obtained from the APCI spectrum of unlabeled and d_3 -labeled toluene, a single product $[M - H + O]^-$ of m/z 108 was expected under O^- /APCI conditions. While this ion was, indeed, observed the spectrum also contained a peak at m/z 107. It is not clear, however, whether the latter ion was actually related to toluene since the spectra obtained on that particular occasion contained numerous $OH^-(H_2O)_n$ clusters extending up to m/z 215 ($n = 11$). It is therefore possible that m/z 107 corresponds to a cluster where $n = 4$. This hypothesis is further supported by the O^- /NCI spectrum of d_1 -toluene, shown in Figure 8b, where a clean signal at m/z 108 indicates the occurrence of only H^+ displacement. Based on the previous NCI evidence that α - D^+ displacement and S_NAr are competitive (Figure 7a) and the lack of evidence for D^+ displacement in the present spectrum, exclusive H^+ displacement from the α -carbon is proposed. Furthermore, if α - D^+ displacement is shown not to be competitive with α - H^+ displacement under NCI

Figure 7. (a) CID of m/z 109 produced by O^- /NCI of α, α, α - d_3 -toluene; (b) CID of m/z 107 produced by O^- /NCI of toluene.

Figure 8. (a) O^{--} /APCI spectrum of α - d_1 -toluene; (b) O^{--} /NCI spectrum of α - d_1 -toluene.

conditions, it is not likely to be competitive in the "cold" APCI source. Therefore, the NCI data further support the assertion that m/z 107 in the APCI spectrum of α - d_1 -toluene is $OH^-(H_2O)_5$ and not $[M - D + O]^-$.

Conclusions

The comparative use of APCI and NCI in conjunction with CO_2 quenching, isotope labeling, and CID experiments has enabled us to investigate in some detail the reactions of O^{--} with simple aromatic compounds. The results of such experiments illustrate the effect of reduced and atmospheric pressure environments on the behavior of a chemical ionization system and have shed light on the mechanism by which H_2^{+} is transferred and H^+ is displaced in the reaction of O^{--} with toluene.

For example, the product mass spectra observed upon reaction of O^{--} with benzene and toluene under APCI conditions are markedly different from those produced using other instrumental techniques (NCI, FA, ion cyclotron resonance). Specifically, the dihydrogen transfer product ion ($[M - 2H]^-$) is conspicu-

ously absent in the APCI mass spectrum. The absence of $[M - 2H]^-$ (and $[M - H]^-$ in the case of toluene) is rationalized on the basis of kinetic arguments. That is, collision rates and residence times under APCI are such that competitive reverse reactions can be observed.

Data from CID experiments and isotope labeling experiments have also been presented which suggest extensive formation of the benzyloxide isomer of $[M - H + O]^-$ in addition to the expected methylphenoxide isomers in the reactions of O^{--} with toluene. A mechanism which accounts for the production of benzyloxide has been proposed. The mechanism involves initial α -hydrogen abstraction followed by rearrangement to a seven-membered ring intermediate. The results of the isotope labeling experiments also suggest that a similar mechanism may be involved in the pathway leading to dihydrogen transfer from toluene.

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