Gas-phase electrophilic addition promoted by \( \text{CH}_3\text{S}^+ = \text{CH}_2 \) ions on aromatic systems

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The gas-phase methylation reaction between \( \text{CH}_3\text{S}^+ = \text{CH}_2 \) and alkylbenzenes, aniline, phenol and alkyl phenyl ethers, which yields [M + CH]\(^+\) and \( \text{CH}_3\text{SH} \), has been studied by Fourier transform ion cyclotron resonance (FT-ICR) techniques and computational chemistry at the DFT level. The methylthiomethyl cation is less reactive than methoxymethyl and, unlike the latter, is unreactive toward benzene. The calculations suggest that reaction with toluene should proceed primarily by addition at the \( \text{para} \) and \( \text{ortho} \) positions resulting in a benzyl-type ion. Reaction with aniline-2,3,4,5,6-\( \text{d}_5 \) reveals that elimination of \( \text{CH}_3\text{SD} \) is kinetically favored by a factor of 5 over elimination of \( \text{CH}_3\text{SH} \). Experiments with \( \text{C}_6\text{H}_6\text{ND}_2 \) and theoretical calculations suggest that methylation at the nitrogen atom is energetically favorable and likely, but the observed results may reflect some H/D scrambling, which occurs after attack at a ring position. By comparison, reaction with phenol-2,3,4,5,6-\( \text{d}_5 \) reveals that methylation followed by elimination of \( \text{CH}_3\text{SD} \) is kinetically favored by a factor of 3.8 over elimination of \( \text{CH}_3\text{SH} \). For phenol, the theoretical calculations suggest that attack by \( \text{CH}_3\text{S}^+ = \text{CH}_2 \) at the \( \text{para} \) or \( \text{ortho} \) position is the only low-energy pathway for methylation. However, a low-energy pathway for hydrogen scrambling is predicted by the calculations originating from the exit complex, \( [\text{CH}_3\text{SH}^+ \cdot \cdot \cdot \text{CH}_2 = \text{C}_6\text{H}_5 = \text{OH}]^+ \), of reaction at a ring position. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: methylthiomethyl cation; aromatic electrophilic reactions; ion/molecule reactions

INTRODUCTION

The methoxymethyl cation, \( \text{CH}_3\text{O}^+ = \text{CH}_2 \), is a ubiquitous species in gas-phase ion chemistry whose reactivity has been explored by several research groups using a variety of experimental techniques.\(^1\)–\(^10\) Four types of ion–molecule reactions have been well established for the \( \text{CH}_3\text{O}^+ = \text{CH}_2 \) cation depending on the nature of the neutral organic substrate (M):\(^11\) (1) addition followed by elimination of methanol to yield an [M + CH]\(^+\) ion; (2) methylation leading to an [M + \( \text{CH}_3\text{H} \)]\(^+\) ion; (3) direct addition with the subsequent formation of an adduct ion; and (4) hydride abstraction to yield an [M – H]\(^+\) ion. This range of reactivity has made the methoxymethyl cation a useful and specific reagent for chemical ionization.\(^12\)–\(^14\)

Considerably less is known about the gas-phase ion chemistry of the methylthiomethyl cation, \( \text{CH}_3\text{S}^+ = \text{CH}_2 \), or similar \( \text{RS}^+ = \text{CH}_2 \) cations, even though they are common fragments in the mass spectrum of thioethers.\(^15\) While similarities might be expected between the ion chemistry of \( \text{CH}_3\text{O}^+ = \text{CH}_2 \) and that of \( \text{CH}_3\text{S}^+ = \text{CH}_2 \), it has been shown that significant differences can be observed in the reactivity of these ions with conjugated dienes under the typical conditions of a pentaquadrupole mass spectrometer.\(^16\)

One of the most intriguing reactions of the \( \text{CH}_3\text{O}^+ = \text{CH}_2 \) cation is its ability to promote the electrophilic addition of a methylene unit to benzene followed by elimination of methanol.\(^17\) Preliminary experiments in our laboratories have revealed that \( \text{CH}_3\text{S}^+ = \text{CH}_2 \) is a weaker gas-phase electrophile, which prompted us to undertake an experimental and theoretical characterization of electrophilic reactions promoted by these ions in simple aromatic systems. Such a study is timely in view of the comprehensive study recently published on the gas-phase nitration of benzene,\(^18\) a reaction that is the classical prototype of aromatic electrophilic substitution. The present investigation of the gas-phase reactions of \( \text{CH}_3\text{S}^+ = \text{CH}_2 \) represents an extension of our earlier work on the reactivity of isomeric \( \text{C}_2\text{H}_5\text{S}^+ \) ions.\(^19\) In this case, the study has been extended to substrates such as phenol and aniline that display two possible sites for electrophilic addition and thus provide an interesting assessment between attack at a ring position as opposed to attack at the heteroatom.

EXPERIMENTAL

Experiments were carried out in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer operating at a magnetic field of 1.0 T and provided with a one-region 15.75 cm\(^3\) cubic cell. Ionization, ion selection, ion–molecule reactions and detection take place in this cell. The general
operating conditions of this spectrometer have been previously described in our work related to the identification of triplet CH$_3$S$^+$ and C$_2$H$_4$S$^+$ cations.\textsuperscript{19,20}

The CH$_3$S$^+$$\rightarrow$CH$_2$ ions were directly generated by electron ionization at a nominal energy of 13 eV from (CH$_3$)$_2$S or CH$_2$SC$_2$H$_4$ at nominal pressures of 1.5–3 × 10$^{-8}$ Torr. Our previous work\textsuperscript{19} has shown that electron ionization results, in both cases, in a mixture of isomeric [C$_2$H$_6$S]$^+$ ions. The [C$_2$H$_6$S]$^+$ (m/z 61) ions were then isolated by a sequence of short, frequency-swept, ejection pulses to remove all unwanted primary and secondary ions (formed before ion isolation). An alternative procedure was also used in some cases to generate the CH$_3$S$^=$CH$_2$ isomer exclusively. This was based on obtaining CH$_3$O$^=$CH$_2$ by electron ionization from dimethoxymethane followed by ion–molecule reaction with (CH$_3$)$_2$S.

CH$_3$O$^=$CH$_2$ \rightarrow (CH$_3$)$_2$S \rightarrow CH$_3$S$^+$CH$_2$ + (CH$_3$)$_2$O \quad (1)

Unfortunately, this latter procedure is not always convenient because the CH$_3$O$^=$CH$_2$ ions themselves react with the aromatic substrates.

Ion–molecule reactions of CH$_3$S$^+$$\rightarrow$CH$_2$ with different neutral substrates were studied at different partial pressures up to total pressures of 1.5 × 10$^{-7}$ Torr. No attempts were made to measure the absolute rate constants because of the simultaneous reaction of the reagent ion with its neutral precursor and with the aromatic substrate. Reactions were typically followed up to 10 s of trapping times.

Reagents were obtained from Aldrich and used without further purification. Samples were thoroughly degassed and subjected to several freeze, pump and thaw cycles prior to their introduction in the high vacuum system of the spectrometer. Mass spectra of these samples obtained by running the FT-ICR spectrometer with continuous ionization and short trapping times revealed no detectable impurities. Deuterated toluene-d$_8$, aniline-d$_6$, and phenol-d$_5$ were obtained from Isotec, St. Louis, MO, USA. N,N-Dideuteroaniline, C$_6$H$_5$ND$_2$, was prepared by mixing aniline with excess D$_2$O, but exchange at the metal walls of the spectrometer prevented full deuteration.

**THEORETICAL CALCULATIONS**

Theoretical calculations at the DFT level were carried out in order to map out the potential energy surface for the reactions involving CH$_3$S$^+$$\rightarrow$CH$_2$ and C$_x$H$_y$X, with X = H, CH$_3$, NH$_2$ and OH, as well as some similar reactions with CH$_3$O$^+$$\rightarrow$CH$_2$. Structures for all energy minima and transition state structures were obtained by full geometry optimization using the B3LYP hybrid density functional\textsuperscript{21,22} with the 6-311++G(d,p) basis set. Electronic energies for these stationary points and transition states were computed at the B3LYP/6-311++G(d,p) level. Vibrational frequencies were also calculated to characterize local minima on the potential energy surfaces, first-order saddle points, and to obtain zero-point energies (ZPEs). All calculations reported in this study were performed with the Gaussian03 suite of programs.\textsuperscript{23}

**RESULTS AND DISCUSSION**

[C$_2$H$_6$S]$^+$ (m/z 61) ions generated by electron ionization from different precursors usually give rise to an isomeric mixture of CH$_3$S$^=$CH$_2$, CH$_3$C(H)SH$^+$ and triplet CH$_3$CH$_2$S$^+$ ions.\textsuperscript{19} They can be conveniently distinguished in FT-ICR experiments by the ability of CH$_3$C(H)SH$^+$ to transfer a proton to substrates of higher proton affinity than thioacetaldehyde, and of triplet CH$_3$CH$_2$S$^+$ to undergo fast charge transfer to substrates with ionization energies lower than the recombination energies of the thioethoxy radical cation. Thus, in several of our studies competitive reactions occur from these isomeric ions with the aromatic substrates. High level theoretical calculations suggest that CH$_3$S$^+$$\rightarrow$CH$_2$ and CH$_3$C(H)SH$^+$ are unlikely to undergo unimolecular isomerization\textsuperscript{24} on the time scale of FT-ICR experiments, but little is known about the possibility of isomerization induced by bimolecular processes.

Figure 1 illustrates the reactivity of the mixture of isomeric [C$_2$H$_6$S]$^+$ ions, obtained by electron ionization from (CH$_3$)$_2$S, with the parent neutral. Figure 2 illustrates the kinetics of the different processes with the CH$_3$C(H)SH$^+$ leading to formation of (CH$_3$)$_2$SH$^+$ (m/z 63), triplet CH$_3$CH$_2$S$^+$ leading to formation of (CH$_3$)$_2$S$^+$ (m/z 62), while the unreactive fraction of m/z 61 is attributed to the CH$_3$S$^+$ = CH$_2$ ion.

**Reaction with benzene**

Unlike the methoxymethyl cation,\textsuperscript{27} CH$_3$S$^+$ = CH$_2$ is unreactive toward benzene within the time scale of our experiment. This difference in reactivity is well illustrated by the calculated energy surfaces for the reaction of the two ions.

Figure 3 shows the calculated energy surface for the methylene group addition to benzene promoted by CH$_3$O$^+$ = CH$_2$. This energy profile reveals the typical double well potential that is common to many ion–molecule reactions. The calculations suggest that the reaction proceeds by initial aromatic addition of the electrophile to yield a radical cation. Thus, in several of our studies competitive reactions occur from these isomeric ions with the aromatic substrates. High level theoretical calculations suggest that CH$_3$S$^+$$\rightarrow$CH$_2$ and CH$_3$C(H)SH$^+$ are unlikely to undergo unimolecular isomerization\textsuperscript{24} on the time scale of FT-ICR experiments, but little is known about the possibility of isomerization induced by bimolecular processes.

![Figure 1. FTMS spectrum obtained after 5 s of reaction time of isolated [C$_2$H$_6$S]$^+$ ions, obtained by 20 eV electron ionization from (CH$_3$)$_2$S at 4 × 10$^{-8}$ Torr, with their neutral precursor.](image-url)
exit side of the reaction, the system forms a stable complex between the benzyl ion, \( C_6H_5CH_2^+ \), and the nascent CH$_3$OH molecule (identified as C2), prior to dissociation into the final separated products as shown below.

\[
CH_3O^+ + C_6H_6 \rightarrow C_6H_5CH_2^+ + CH_3OH \quad (2)
\]

\[\Delta H^\circ (0 K, \text{calcd}) = -14.6 \text{ kcal mol}^{-1}\]

The calculated pathway for the reaction leads to the formation of the benzyl cation (P1) and methanol. Figure 3 also displays a qualitative outline of the barrier for isomerization of benzyl ion to the more stable tropylium ion structure (P2) as the final ionic product. This isomerization is unlikely in this case because the barrier for such a process has been estimated to be in the range of 65–69 kcal mol$^{-1}$.

Figure 4 shows the calculated energy diagram for the reaction of CH$_3$S$^-$ with benzene. The general features of the energy surface are similar, but the initial arenium complex is calculated to be considerably less stable (only 6.4 kcal mol$^{-1}$ below the reagents) than for the case of CH$_3$O$^+═CH$_2$. More important, the TS on this double well potential surface is now predicted to be 4.6 kcal mol$^{-1}$ above the energy of the reagents. Although energy barriers calculated by DFT methods must often be viewed with some caution, our calculations suggest that the rate constant for the
Gas-phase methylenation by $\text{CH}_3\text{S}^+\rightleftharpoons\text{CH}_2$ ions

Our theoretical calculations are again useful for understanding the energy surface for this reaction and for visualizing the preferred ring positions of attack. The energy surface is similar to those shown in Figs 3 and 4 and it is outlined in Fig. 6 for pathways originating from attack at either the para or ortho position of toluene. The para and ortho positions are the most favorable pathways, although attack at the meta position is also estimated to yield a stable arenium ion complex as shown in Table 2. Thus, it is possible that addition of a CH$_2$ group promoted by CH$_3$S$^+\rightleftharpoons$CH$_2$ ions at thermal energies can actually proceed at all three ring positions but preferentially at the para position.

A comparison between Figs 4 and 6 reveals that the methyl group of toluene has a pronounced effect on the stability of the initial arenium ions (C1) and in lowering the barrier for proton migration to the sulfur atom.

**Table 1.** Calculated Mulliken atomic charges (in atomic units) for the CH$_3$O$^+\rightleftharpoons$CH$_2$ and CH$_3$S$^+\rightleftharpoons$CH$_2$ cations. $\Delta$ is the difference between the atomic charges in both ions

<table>
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<th>CH$_3$S$^+\rightleftharpoons$CH$_2$</th>
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**Figure 5.** FTMS spectrum obtained after 3 s of reaction between CH$_3$S$^+\rightleftharpoons$CH$_2$ ions and toluene-$\alpha$,\,$\alpha$,$\alpha$-$d_3$ as the aromatic substrate. The spectrum shown in Fig. 5 clearly reveals that all the deuterium atoms are retained in the ionic product, C$_8$H$_6$D$_3^+$ ($m/z$ 108).

**Figure 6.** Calculated energy surface and relevant structures calculated at the B3LYP/6-311++G(d,p)/B3LYP/6-311++G(d,p) level considering the energy of the reagents, CH$_3$S$^+\rightleftharpoons$CH$_2$ and the aromatic substrate, as zero energy.

**Table 2.** Relative energy (in kcal mol$^{-1}$ with ZPE included) of the initial intermediate arenium ion complex resulting from addition of CH$_3$S$^+\rightleftharpoons$CH$_2$ to different ring positions and at the heteroatom. Calculations were performed at the B3LYP/6-311++G(d,p)/B3LYP/6-311++G(d,p) level considering the energy of the reagents, CH$_3$S$^+\rightleftharpoons$CH$_2$ and the aromatic substrate, as zero energy.

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**Reaction with alkylbenzenes**

A dramatic difference occurs upon reacting CH$_3$S$^+\rightleftharpoons$CH$_2$ ions with alkylbenzenes. For simple alkyl groups, the prototype reaction (3) (R = alkyl) proceeds to completion rapidly (in less than 5 s) under our experimental conditions.

\[
\text{H}_3\text{C} = \text{CH}_2 + R\text{CH}_2 \rightarrow \text{CH}_2^+ + \text{CH}_3\text{SH} (3)
\]

Methylenation at a ring position was established by using toluene-$\alpha$,\,$\alpha$,$\alpha$-$d_3$ as the aromatic substrate. The spectrum shown in Fig. 5 clearly reveals that all the deuterium atoms are retained in the ionic product, C$_8$H$_6$D$_3^+$ ($m/z$ 108).

**Table 1.** Calculated Mulliken atomic charges (in atomic units) for the CH$_3$O$^+\rightleftharpoons$CH$_2$ and CH$_3$S$^+\rightleftharpoons$CH$_2$ cations. $\Delta$ is the difference between the atomic charges in both ions

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**Figure 5.** FTMS spectrum obtained after 3 s of reaction between CH$_3$S$^+\rightleftharpoons$CH$_2$ ions and toluene-$\alpha$,\,$\alpha$,$\alpha$-$d_3$ at 8 x 10$^{-8}$ Torr. The product ions at $m/z$ 62 and $m/z$ 63 are due to the reaction of the other isomeric $m/z$ 61 ions with their neutral precursor as illustrated in Fig. 1.

**Reaction with aniline**

The reactions of CH$_3$S$^+\rightleftharpoons$CH$_2$ with aniline, C$_6$H$_5$NH$_2$, is of potential interest because the reagent ion can in principle attack the ring positions, the heteroatom, or
both sites. Ion–molecule reactions of CH$_3$O$^+$=CH$_2$ with NH$_3$ and CH$_3$NH$_2$ are known to proceed by methylene insertion to yield the corresponding protonated imines, CH$_2$NH$_2$ and CH$_3$NH=CH$_2$, respectively, with rate constants comparable to the collision rate constants. The mechanism for the NH$_3$ reaction has been previously explored by computational chemistry and the calculated energy surface is similar to those presented in Figs 3, 4 and 6.

Similar reactions have also been observed in our laboratories with CH$_3$S=CCH$_2$ as the reagent ion. The mixture of [C$_2$H$_5$S] isomeric ions reacts rapidly with aniline to yield C$_6$H$_5$NH$_2$C= by charge transfer (presumably from triplet C$_2$H$_5$S$^+$) and C$_5$H$_5$NH$_2$$^+$ by addition–elimination from CH$_3$S$^+$=CH$_2$. It is this reaction that needs to be better understood. For example, reaction of CH$_3$S=CCH$_2$ with aniline-2,3,4,5,6-d$_5$ (99\% D) provides in principle the possibility of comparing the relative ease of electrophilic attack at ring positions as opposed to attack at the heteroatom. The resulting spectrum, shown in Fig. 7, reveals the formation of C$_6$H$_5$D$_5$N$^+$ (m/z 110) with elimination of CH$_3$SD and C$_7$H$_3$D$_5$N$^+$ (m/z 111) with elimination of CH$_3$SH in a 5.1 ± 0.3 ratio (uncorrected for $^{13}$C contribution). By comparison, reaction of CH$_3$S=CCH$_2$ with C$_6$H$_5$ND$_2$ (≈80\% D) yields C$_7$H$_6$D$_2$N$^+$ (m/z 108), C$_7$H$_7$DN$^+$ (m/z 107) and C$_7$H$_8$N$^+$ (m/z 106). The product distribution suggests that CH$_3$SH is essentially the only neutral eliminated in the formation of the three product ions because the relative abundance of the observed products closely reflects the isotopic deuterium atom purity of the aniline sample measured by mass spectrometry. The significance of these results can be explored further with the help of theoretical calculations.

Theoretical calculations are helpful for visualizing the energy surface involving possible attack at ring positions and at the nitrogen center, as well as possible mechanisms for hydrogen–deuterium scrambling. The relative stability of the initial complexes C1 resulting from addition of CH$_3$S=CCH$_2$ to the different ring positions and to nitrogen are given in Table 2. It is clear from our calculated values that initial addition to the para and ortho position, or to the nitrogen atom, is greatly preferred over attack at the meta position. Figure 8 shows the full reaction energy diagram for the CH$_3$S=CCH$_2$/aniline reaction considering attack at the para position of the ring (reaction 4a), whereas Fig. 9 shows the energy diagram for attack on nitrogen (reaction 4b).

Although the calculations reveal that addition of the reagent ion to nitrogen is slightly more stable than addition at the para ring position, the calculated energy barriers for elimination of CH$_3$SH clearly favor reaction at the ring.
The calculated energy diagrams presented in Figs 8 and 9 and in Table 2 suggest that reactions are energetically possible at all the ring positions and at the nitrogen atom. Unfortunately, the experiments with deuterated anilines are inconclusive for determining the relative extent of reaction at ring positions and at the heteroatom center. Two different mechanisms can be envisioned to contribute to the results obtained with C₆D₅NH₂ and C₆H₅ND₂:

1. The first possibility is that attack does occur directly at one or more ring positions and at the nitrogen center but a likely isotope effect accounts for a decrease in CH₃SD elimination;

2. A second possibility arises from a scrambling mechanism involving the ring deuterium atoms with the nitrogen protons, or vice versa in the case of C₆H₅ND₂. Proton migration from an initial complex resulting from attack at a ring position such as complex C1 in Fig. 8, or para- (thiomethoxymethyl)aniline protonated at the para ring carbon, seems unlikely. While our calculations reveal that the proton can undergo ring-walk to the meta, ortho and ipso carbon position (relative to the NH₂ group) through energy barriers calculated to be just below the energy of the reactants, migration of the proton from the ipso ring position to the NH₂ group involves a barrier of over 14 kcal mol⁻¹. This contention is consistent with the view that ring-protonated and nitrogen-protonated anilines are distinct species in the gas phase. A second mechanism for scrambling can result from the loose ion–molecule complex C2 (Fig. 8). The nascent CH₃SH(D) is expected to be relatively free (calculated C–S distance is 2.89 Å) and able to explore the energy surface prior to final separation into products. In this respect, we find that CH₃SH can exchange protons with the nitrogen protons of the ionic species [CH₂=CH₂–NH₂]⁺ of the complex through the transition state shown in Fig. 10, located 1.2 kcal mol⁻¹ below the energy of the original reactants.

In summary, the combination of experimental and theoretical results for aniline suggests that attack by CH₃–S⁺=CH₂ at the ring is preferred over attack at nitrogen. The data also suggest that attack at nitrogen is likely but a significant isotope effect that would favor CH₃SH over CH₃SD elimination makes it difficult to estimate the extent of attack at nitrogen. Furthermore, the extent of attack at nitrogen, if any, is further complicated by the possibility of hydrogen–deuterium scrambling promoted in the exit complex of the reaction that originally takes place by attack of the electrophile at a ring position.

**Reaction with phenol and alkyl phenyl ethers**

Methylation promoted by CH₃S⁺=CH₂, with subsequent CH₃SH elimination, is also observed to be a facile reaction with substrates such as C₆H₅OC₂H₅ and C₆H₅OH, as illustrated in Fig. 11.

Figure 11 shows the kinetics of the mixture of isomeric m/z 61 ions with phenetole, C₆H₅OC₂H₅. The main reaction product, C₆H₅O₂⁺ (m/z 135), is the result of methylene addition presumably at a ring position because the eventual elimination of CH₃SH from possible addition at the oxygen atom requires a double hydrogen migration. The other products can be identified, as in the case of aniline, to protonation of phenetole, (C₆H₅OC₂H₅)H⁺ (m/z 123), and charge exchange to yield C₆H₄O=C₂H₅⁺ (m/z 122). These two ionic products are formed by CH₃C(H)SH⁺ and triplet CH₃(CH₂)S⁺, respectively.

Figure 12 shows a spectrum obtained after 1 s of reaction between isolated [C₆H₅S]⁺ ions (obtained by electron ionization from CH₃SC₂H₅) and phenol. In this case, CH₃S⁺=CH₂ reacts with the parent neutral by hydride abstraction (m/z 75) and with phenol by methylene group addition to yield C₆H₅O⁺ (m/z 107). Further studies with...
Figure 11. Kinetic plot of the reaction products of isomeric [C2H5S]+ ions (m/z 61) with C6H5OC2H5 at a total pressure of 1.5 x 10^{-7} Torr. Methylation by CH3S=CH2 yields m/z 135, whereas C6H5OC2H5^+ (m/z 122) is attributed to the reaction of triplet CH3CH2S=CH2 yields (m/z 135) with C6H5OC2H5 at a total pressure of 1.5 x 10^{-7} Torr. Methylation by CH3S=CH2 yields m/z 135, whereas C6H5OC2H5^+ (m/z 122) is attributed to the reaction of triplet CH3CH2S=CH2 yields (m/z 135) with C6H5OC2H5^+ (m/z 123) to reaction of CH3C(H)=SH^+ or protonated thioacetaldehyde ions.

phenol-2,3,4,5,6-d5 revealed that reaction with CH3S=CH2 yields both C7H3D4O^+ (m/z 111) with loss of CH3SD, and C7H2D5O^+ (m/z 112) with loss of CH3SH. The ratio (C7H3D4O^+)/(C7H2D5O^+) has been measured to be 3.8 ± 0.3.

The results with phenol prompted us to examine the potential energy surface for the methylene addition reaction and to explore two possible reaction pathways.

The structure of the final product ions of reactions (5a) and (5b) is of considerable interest in view of the recent characterization of C7H3O^+ ions by IR spectroscopy showing that hydroxytropylium ions do not interconvert readily to hydroxybenzyl cations under ICR conditions. The structure of the final product ions of reactions (5a) and (5b) is of considerable interest in view of the recent characterization of C7H3O^+ ions by IR spectroscopy showing that hydroxytropylium ions do not interconvert readily to hydroxybenzyl cations under ICR conditions.In view of the recent characterization of C7H3O^+ ions by IR spectroscopy showing that hydroxytropylium ions do not interconvert readily to hydroxybenzyl cations under ICR conditions.

As in the case of aniline, a ring-walk mechanism for proton mobility from the para position to the meta, ortho and ipso (relative to the OH group) positions is calculated to have energy barriers that are accessible at typical ion thermal energies for 298 K for para-(thiomethoxymethyl)phenol protonated at the para ring carbon (resulting from initial addition of the methylthiomethyl cation at the para position of phenol). However, the transition state that would allow

by direct addition to the oxygen atom. Nevertheless, there is a pronounced favoring for attachment at the para or ortho position and the lowest energy barrier pathway is elimination of CH3SH after attack at the para position (Fig. 13).

The energy profile for the reaction initiated by attack at the OH group reveals a positive energy barrier, and within the accuracy of our calculations this pathway would not be easily observed under thermal ICR experiments. Thus, it was necessary to explore again the possibility that formation of both C7H3D4O^+ (m/z 111) and C7H2D5O^+ (m/z 112) in the case of ring-deuterated phenol could originate from a hydrogen–deuterium scrambling mechanism. Recent work on the gas-phase infrared spectrum of protonated phenol, C6H5O^+, clearly identified oxonium-type ions (oxygen protonation) and carbenium-type ions (ring protonation at either the ortho or para position) as distinct species. Theoretical calculations at the B3LYP/6-311G(2df,2pd) level revealed that the barrier for proton scrambling from the ring to the oxygen atom is about 27 kcal mol^{-1}.

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for hydrogen scrambling between the ipso carbon and the OH group is calculated to be 31 kcal mol$^{-1}$ above the energy of the reactants. This barrier, even allowing for generous estimates of errors by DFT methods, essentially eliminates the possibility that hydrogen--deuterium scrambling could be important under the conditions of our experiment with phenol-d$_5$.

Hydrogen--deuterium scrambling can also occur from the exit ion–molecule complex C2 shown in Fig. 13 resulting from attack of CH$_3$S$^+$ + CH$_2$ at either the para or ortho position, namely [CH$_3$SH$^-$.CH$_2$=C$_6$H$_5$.OH$^+$], as previously discussed for aniline. The loose CH$_3$SH is found to be able to exchange protons with the OH group through the transition state shown in Fig. 14 that is located 14 kcal mol$^{-1}$ below the energy of the reactants.

Thus, we can conclude from our experimental results with C$_6$D$_5$OH and from our theoretical calculations that methylation takes place exclusively at the para and ortho ring positions of phenol. Furthermore, the observed elimination of both CH$_3$SH and CH$_3$SD in the case of C$_6$D$_5$OH can be attributed to an H/D scrambling mechanism that occurs after attack of the CH$_3$S$^+$ + CH$_2$ at a ring position and proceeds through the transition state illustrated in Fig. 14.

**CONCLUSIONS**

Our results indicate that the methylthiomethyl cation can readily promote gas-phase addition of a methylene group to the aromatic ring of alkylbenzenes, aniline, phenol and ethers with elimination of CH$_3$SH resulting in the formation of an [M + CH$_2$]$^+$ ion. These reactions bear strong resemblance to the well-known reactions in condensed phases that are used to methylthiomethylate these same substrates.$^{38,39}$ In the case of aniline and phenol, insertion of a methylene group occurs preferentially at the para position of the aromatic ring according to theoretical calculations. For aniline, the experimental data and the results of theoretical calculations suggest that addition at the nitrogen atom with subsequent formation of an iminium type ion is very likely.

Our results also indicate that the thiomethoxymethyl cation is less electrophilic than the corresponding methoxymethyl cation. Further evidence of the decrease in reactivity is observed by deactivating toluene with an electron-withdrawing substituent. For example, experiments with para-fluorotoluene reveal that CH$_3$O$^+$ + CH$_2$ is capable of methylene addition whereas no reaction is observed with CH$_3$S$^+$ + CH$_2$ within our experimental conditions.

Finally, the actual isomeric composition of the final products of the different reactions studied in this work is an interesting problem that opens the possibility for some challenging studies in the newly developed area of IR spectroscopy of ions.

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