Gas-Phase Carbene Radical Anions: New Mechanistic Insights

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Carbenes have been extensively studied for several decades, both experimentally and theoretically, because of their importance as intermediates in many organic reactions, their unique reactivity, and their low-lying singlet and triplet states.\(^1,2\) While neutral carbenes have received considerable attention, only a few studies have addressed the chemistry of the corresponding anions. These studies have produced both intriguing results and continuing controversy.

Simple halogen substituted carbenes (\(\cdot\)CHX, where X = F, Cl, and Br) have singlet ground states and the addition of an electron forms a \(\pi\)-radical anion.\(^3\) Several studies have addressed the electron and proton transfer reactions of these anions and have provided valuable thermodynamic information about the corresponding neutral carbenes.\(^4,7\) Nibbering and co-workers have investigated the reactivity of CHCl\(^-\) and CHBr\(^-\) with a series of neutral reagents that include methyl halides, whose reactions proceed via \(S_2\) substitution.\(^5,6\) In this work, we reinvestigate the reaction of CHCl\(^-\) with CH\(_2\)Cl to add additional reactions with CH\(_2\)Cl\(_2\), CHCl\(_3\), and CCl\(_4\). Our results show that the CHCl\(^-\) anion primarily reacts via \(S_2\) substitution and proton transfer, but additionally demonstrate that these reactions can proceed by insertion into a C–Cl bond to form an unstable intermediate, which eliminates either Cl\(_2\) or Cl\(^-\) + Cl\(^.\) Neutral and cationic carbenes are known to insert into single bonds;\(^1,2,9,10\) however, the results presented here are the first report of such gas-phase anion reactivity.

Kinetic data for the reactions of CHCl\(^-\) + CH\(_2\)Cl\(_n\) (\(n = 0–3\)) were collected using a tandem flowing afterglow-selected ion flow tube instrument, FA-SIFT.\(^1,2\) Reactant ions were formed in the source from electron impact on N\(_2\)O to produce O\(^.\) Bond to form an unstable intermediate, which eliminates either Cl\(_2\) or Cl\(^-\) + Cl\(^.\). Neutral and cationic carbenes are known to insert into single bonds,\(^1,2,9,10\) however, the results presented here are the first report of such gas-phase anion reactivity.

The CHCl\(^-\) anion reacts with CCl\(_4\) to form an unstable intermediate, which eliminates either Cl\(_2\) or Cl\(^-\) + Cl\(^.\). Neutral and cationic carbenes are known to insert into single bonds,\(^1,2,9,10\) however, the results presented here are the first report of such gas-phase anion reactivity.

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the carbene C atom and the carbene lone pair attacks the C atom of CHCl₃. Insertion of :CHCl forms the [CH₂ClCH₂Cl]⁺ intermediate, where the extra electron is localized on a Cl atom in a low-lying σ-type orbital. This intermediate is unstable, and eliminates Cl₂⁻; the overall reaction is sufficiently exothermic (ΔH ≈ −80 kcal mol⁻¹) such that Cl₂⁻ can dissociate into Cl⁻ and Cl⁻. Insertion of CH₃Cl into a C–C bond results in a Cl⁻ (82:18) and Cl₂⁻ (67:30:3) isotope distribution, while insertion of CH₂ClCl results in a Cl⁻ (57:43) and Cl₂⁻ (29:56:15) isotope distribution. These predictions are in agreement with the measured Cl⁻ and Cl₂⁻ isotope distributions for the reaction of CHCl⁻ with CH₂Cl₂; however, the occurrence of minor amounts of S₉2 substitution would influence the Cl⁻ isotope distribution. Despite this, the predicted distributions for an insertion–elimination mechanism provide the best agreement with experiment compared to other possible mechanisms. Furthermore, these results indicate that insertion occurs into a C–Cl bond rather than into a C–H bond. In solution carbenes typically insert into C–H bonds; however, in the gas-phase insertion into a C–Cl bond is favored since the addition of an extra electron increases the nucleophilicity of the Cl⁻ atom.

The reaction of CHCl⁻ with CH₂Cl₂ exclusively produces Cl⁻. These results are in excellent agreement with the work of Nibbering and co-workers, which show a slightly skewed Cl⁻ isotope distribution for the reaction of CH₃Cl⁻ with CH₂Cl₂ (3% deviation from the 35Cl:37Cl natural abundance of 76:24); however, we propose an alternate, energetically favorable mechanism to explain the skewed Cl⁻ isotope distribution. The authors propose that this reaction proceeds by two pathways, as shown in eq 4a and eq 4b. We agree that the primary path (4a) is a traditional S₉2 reaction to produce Cl⁻ and the CH₂ClCH₂Cl radical, where the displaced halide ion is produced with an isotopic distribution representative of the Cl⁻ atom natural isotope abundance. Additionally, it was suggested that this reaction proceeds by a minor second path (4b), where the anion abstracts a proton from methyl chloride prior to S₉2 substitution; the result of this pathway is the formation of Cl⁻ and CICl₂CH₂Cl.

CH₃Cl⁻ + CH₂Cl₂
[ CH₃Cl⁺ + CH₂Cl⁺ ] → CH₃CH₂Cl⁻ + Cl⁻ (4a)
[ CH₃Cl⁺ + CH₂Cl⁺ ] → ClIClCH₂Cl⁻ + Cl⁻ (4b)
[ CH₃Cl⁺ + CH₂Cl⁺ ] → [CH₃Cl⁺ + CHCl⁻] → CH₂ClCHCl⁺ (4c)

Instead, we propose a mechanism (eq 4c) in which the chlorine atoms are scrambled by two proton exchanges. In this process, CH₃Cl⁻ and CH₂Cl₂ enter a long-lived ion•dipole complex which typically contains ~15–20 kcal mol⁻¹ excess energy. The first step of the exchange, the proton transfer reaction of CH₃Cl⁻ with CH₂Cl₂, is endothermic (~15 kcal mol⁻¹) and consumes most of the complexation energy; thus it seems unlikely that the S₉2 reaction of CH₃Cl⁻ with CH₂Cl₂ (eq 4b) could proceed past an S₉2 reaction barrier despite the fact that the overall reaction is exothermic. Instead, back transfer of a proton to form [CH₃Cl⁺ + CHCl⁻] restores the complexation energy, scrambles the CI⁻ atoms, and allows for an S₉2 reaction to occur. Equation 4c produces different isotopomers of the reactants and products in 4a through an energetically favorable mechanism.

These isotopic studies have shown that carbene anions can act as prototypical anions in that they undergo proton transfer and substitution reactions with chloromethanes. In addition to these classic transformations, the product ion isotope distributions for the reaction of CHCl⁻ with CH₂Cl₂ provide convincing support for the occurrence of an insertion–elimination mechanism, analogous to neutral carbene processes. While it has been shown that such character is associated with carbene cations,¹¹ this is the first report of such reactivity for carbene anions.

Acknowledgment. The authors thank Prof. Charles H. DePuy and Prof. Tarek Sammakia for valuable discussions. This work was supported by NSF (Grant CHE-0647088) and AFOSR (Grant FA9550-06-1-006).

References

(18) Insertion into a C–H bond results in a Cl⁻ (88:12) and Cl₂⁻ (76:24) isotope distribution for the reaction of CH₃Cl⁻ and a Cl⁻ (38:62) and Cl₂⁻ (0:76:24) isotope distribution for the reaction of CH₃Cl⁻.

JA801819B

| CH₃Cl⁻ | k (efficiency) | ionic product | branching fraction | injection of CH₃Cl⁻ | injection of Cl⁻ | product ion isotope distributions²
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<td>CHCl₃</td>
<td>2.62 ± 0.10 (0.176)</td>
<td>Cl⁻</td>
<td>1.00</td>
<td>78:22</td>
<td>70:30</td>
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<td>CH₂Cl₂</td>
<td>11.8 ± 0.4 (0.648)</td>
<td>Cl⁻</td>
<td>0.10</td>
<td>78:22</td>
<td>68:32</td>
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<tr>
<td>CCl₄</td>
<td>9.26 ± 0.12 (0.723)</td>
<td>Cl⁻</td>
<td>1.00</td>
<td>68:28</td>
<td>8:64:28</td>
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Table 1. Reaction Rate Constants (10⁻¹⁰ cm³ s⁻¹), Efficiencies, and Product Ion Branching Ratios for the Reactions of CH₃Cl⁻ with CH₃Cl₁₈ (n = 0–3) and Product Ion Isotope Distributions for the Reactions of CH₃Cl⁻ and CH₃Cl₁₈ with CH₃Cl₁₈ (n = 0–3).

CH₃Cl⁻ + CHCl₃
[ CH₃Cl⁺ + CHCl⁺ ] → CH₃CH₂Cl⁻ + Cl⁻ (4a)
[ CH₃Cl⁺ + CHCl⁺ ] → ClIClCH₂Cl⁻ + Cl⁻ (4b)
[ CH₃Cl⁺ + CH₂Cl⁺ ] → [CH₃Cl⁺ + CHCl⁻] → CH₂ClCHCl⁺ (4c)

CH₃Cl⁻ + CH₂Cl₂
[ CH₃Cl⁺ + CH₂Cl⁺ ] → CH₃CH₂Cl⁻ + Cl⁻ (4a)
[ CH₃Cl⁺ + CH₂Cl⁺ ] → ClIClCH₂Cl⁻ + Cl⁻ (4b)
[ CH₃Cl⁺ + CH₂Cl⁺ ] → [CH₃Cl⁺ + CHCl⁻] → CH₂ClCHCl⁺ (4c)