Gas-Phase Carbene Radical Anions: New Mechanistic Insights

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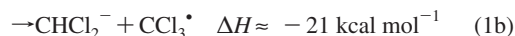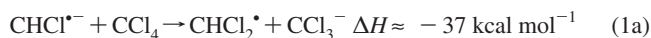
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Carbenes have been extensively studied for several decades, both experimentally and theoretically, because of their importance as intermediates in many organic reactions, their unique reactivity, and their low-lying singlet and triplet states.[1,2] 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 (:CHX, where X = F, Cl, and Br) have singlet ground states and the addition of an electron forms a π-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 $CHCl^{\bullet-}$ and $CHBr^{\bullet-}$ with a series of neutral reagents that include methyl halides, whose reactions proceed via S_N2 substitution.[7,8] In this work, we reinvestigate the reaction of $CHCl^{\bullet-}$ with CH_3Cl in addition to reactions with CH_2Cl_2, $CHCl_3$, and CCl_4. Our results show that the $CHCl^{\bullet-}$ anion primarily reacts via S_N2 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 $Cl_2^{\bullet-}$ or $Cl^- + Cl^{\bullet}$. Neutral and cationic carbenes are known to insert into single bonds;[1,2,9–11] however, the results presented here are the first report of such gas-phase anion reactivity.

Kinetic data for the reactions of $CHCl^{\bullet-} + CH_nCl_{4-n}$ ($n = 0-3$) were collected using a tandem flowing afterglow-selected ion flow tube instrument, FA-SIFT.[12] Reactant ions were formed in the source from electron impact on N_2O to produce $O^{\bullet-}$, which then reacts with CH_3Cl via $H_2^{\bullet+}$ abstraction to form $CHCl^{\bullet-}$.[7,13] Reactant ions of a single isotopomer were mass-selected and injected into a reaction flow tube where they were thermalized to ∼298 K by collisions with He buffer gas (0.5 torr, ∼10^4 cm s^{-1}). Minor amounts of Cl^- ions, produced from collision-induced dissociation of $CHCl^{\bullet-}$, were also present; the presence of these fragment ions was considered in the data analysis. Measured flows of neutral reagents were introduced at various distances along the reaction flow tube and the depletion of reactant ion and the formation of product ions were analyzed by a quadrupole mass filter coupled to an electron multiplier. Reaction rate constants, branching ratios, and efficiencies are presented in Table 1, along with the product ion isotope distributions, which were determined by alternately SIFT-injecting both isotopomers of the reactant ion. Neutral reagents were purchased from commercial sources and used without further purification. The reported reaction efficiencies are the measured rate constants divided by the calculated collision rate constants (eff = k/k_{col}), which were calculated from parametrized trajectory collision rate theory.[14]

The $CHCl^{\bullet-}$ anion reacts with CCl_4 to primarily produce CCl_3^- and a trace amount of $CHCl_2^-$, as shown in eq 1a and 1b.

$$CHCl^{\bullet-} + CCl_4 \rightarrow CHCl_2^{\bullet} + CCl_3^- \quad \Delta H \approx -37 \text{ kcal mol}^{-1} \quad (1a)$$

$$\rightarrow CHCl_2^- + CCl_3^{\bullet} \quad \Delta H \approx -21 \text{ kcal mol}^{-1} \quad (1b)$$

The formation of these products is consistent with attack on chlorine causing displacement of CCl_3^- or chlorine atom transfer to form $CHCl_2^-$; for both pathways, electron transfer can occur before the initial products separate. Similar reactivity has been reported for the reactions of other open and closed shell anions with CCl_4.[15–17] As predicted by this mechanism, the CCl_3^- ion is produced with an isotope distribution that reflects the natural Cl atom abundance in CCl_3 (44:42:13:1); hence this distribution does not change for different reactant ion isotopomers. In contrast, the $CHCl_2^-$ product isotope distribution is skewed toward the reactant ion isotopomer.

The reactions of $CHCl^{\bullet-}$ with $CHCl_3$ and CH_2Cl_2 primarily occur via proton transfer (eq 2a and eq 3a) to produce CCl_3^- and $CHCl_2^-$, respectively. As expected, the isotope distributions of these product ions are not altered upon changing the reactant ion isotopomer.

$$CHCl^{\bullet-} + CHCl_3 \rightarrow CH_2Cl^{\bullet} + CCl_3^- \quad \Delta H \approx -25 \text{ kcal mol}^{-1} \quad (2a)$$

$$\rightarrow CHCl_2^{\bullet} + CHCl_2^- \quad \Delta H \approx -16 \text{ kcal mol}^{-1} \quad (2b)$$

$$CHCl^{\bullet-} + CH_2Cl_2 \rightarrow CH_2Cl^{\bullet} + CHCl_2^- \quad \Delta H \approx -8 \text{ kcal mol}^{-1} \quad (3a)$$

The reaction of $CHCl^{\bullet-}$ with $CHCl_3$ (eq 2b) additionally proceeds by anion attack on Cl to produce $CHCl_2^-$ (analogous to eq 1a). The isotope distribution of this product ion changes when the reactant ion isotopomer is changed, consistent with thermoneutral electron transfer within the product ion−molecule complex. An intriguing result of these reactions is the formation of $Cl_2^{\bullet-}$ and Cl^- ions, and that changing the $CHCl^{\bullet-}$ isotopomers affects the isotope distributions of both of these product ions. For example, when $CH^{37}Cl^{\bullet-}$ is allowed to react with $CHCl_3$, all three isotopomers of $Cl_2^{\bullet-}$ are detected, however the isotope distribution is skewed to reflect incorporation of ^{37}Cl. Likewise although both Cl^- isotopes are detected, $^{37}Cl^-$ exceeds the natural abundance. These observations suggest that these products must result from a mechanism that partially scrambles the reactant ion and neutral reagent Cl atoms.

The formation of both $Cl_2^{\bullet-}$ and Cl^- is consistent with an insertion−elimination mechanism, shown for the reaction of $CHCl^{\bullet-}$ with $CHCl_3$. Presumably the first step of this reaction
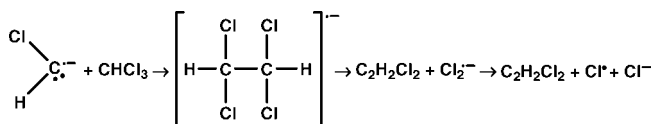
involves the formation of a $\sigma-\pi$ complex, where the singly occupied π orbital of the anion overlaps with the C−Cl σ bond of the neutral species to transfer an electron. Neutral :CHCl then inserts into the Cl−C bond in a concerted step, which proceeds through a three-centered transition state where the Cl atom of $CHCl_3$ attacks
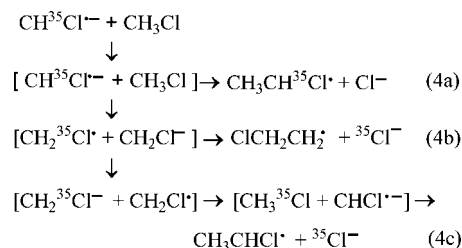
Table 1. Reaction Rate Constants (10^{-10} cm^3 s^{-1}), Efficiencies, and Product Ion Branching Ratios for the Reactions of CH^{35}Cl$^{\bullet-}$ with CH$_n$Cl$_{4-n}$ ($n = 0-3$) and Product Ion Isotope Distributions for the Reactions of CH^{35}Cl$^{\bullet-}$ and CH^{37}Cl$^{\bullet-}$ with CH$_n$Cl$_{4-n}$ ($n = 0-3$)

CH$_n$Cl$_{4-n}$	k (efficiency)	ionic products	branching fraction[a]	product ion isotope distributions[b]	
				injection of CH^{35}Cl$^{\bullet-}$	injection of CH^{37}Cl$^{\bullet-}$
CH$_3$Cl	2.62 ± 0.10 (0.176)	Cl$^-$	1.00	78:22	70:30
CH$_2$Cl$_2$	11.8 ± 0.4 (0.468)	Cl$^-$	0.10	78:22	68:32
		Cl$_2$$^{\bullet-}$	trace	73:22:5	26:57:17
		CHCl$_2$$^-$	0.90	57:37:6	57:37:6
CHCl$_3$	11.3 ± 0.4 (0.568)	Cl$^-$	0.05	81:19	59:41
		Cl$_2$$^{\bullet-}$	trace	71:25:4	28:55:17
		CHCl$_2$$^-$	0.15	60:35:5	49:44:7
		CCl$_3$$^-$	0.80	44:43:12:1	45:42:12:1
CCl$_4$	9.26 ± 0.12 (0.723)	CHCl$_2$$^-$	trace	68:28:4	8:64:28
		CCl$_3$$^-$	1.00	45:41:13:1	44:42:13:1

[a] The errors for the product ion branching fractions are ±30%. [b] The error associated with the product ion isotope distributions is ±0.05 for Cl$^-$ and Cl$_2$$^{\bullet-}$ and ±0.02 for CHCl$_2$$^-$ and CCl$_3$$^-$. The natural abundance isotope distributions are Cl$^-$ (76:24), Cl$_2$$^{\bullet-}$ (57:37:6), CHCl$_2$$^-$ (57:37:6), and CCl$_3$$^-$ (44:42:13:1).

the carbene C atom and the carbene lone pair attacks the C atom of CHCl$_3$. Insertion of :CHCl forms the [CHCl$_2$CHCl$_2$]$^{\bullet-}$ intermediate, where the extra electron is localized on a Cl atom in a low-lying σ-type orbital. This intermediate is unstable, and eliminates Cl$_2$$^{\bullet-}$; the overall reaction is sufficiently exothermic ($\Delta H \approx -80$ kcal mol^{-1}) such that Cl$_2$$^{\bullet-}$ can dissociate into Cl$^\bullet$ and Cl$^-$. Insertion of :CH^{35}Cl into a Cl−C bond results in a Cl$^-$ (82:18) and Cl$_2$$^{\bullet-}$ (67:30:3) isotope distribution, while insertion of :CH^{37}Cl results in a Cl$^-$ (57:43) and Cl$_2$$^{\bullet-}$ (29:56:15) isotope distribution. These predictions are in agreement with the measured Cl$^-$ and Cl$_2$$^{\bullet-}$ isotope distributions for the reaction of CHCl$^{\bullet-}$ with CHCl$_3$. The predictions fall slightly outside of the experimental error bars for reaction of CHCl$^{\bullet-}$ with CH$_2$Cl$_2$; however, the occurrence of minor amounts of S$_N$2 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.[18] 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$^{\bullet-}$ with CH$_3$Cl 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 CH^{35}Cl$^{\bullet-}$ with CH$_3$Cl (3% deviation from the ^{35}Cl:^{37}Cl natural abundance of 76:24);[7] 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 S$_N$2 reaction to produce Cl$^-$ and the CH$_3$CH^{35}Cl$^\bullet$ radical, where the displaced halide ion is produced with an isotope 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 S$_N$2 substitution; the result of this pathway is the formation of ^{35}Cl$^-$ and ClCH$_2$CH$_2$$^\bullet$.

$$CH^{35}Cl^{\bullet-} + CH_3Cl$$
$$\downarrow$$
$$[\,CH^{35}Cl^{\bullet-} + CH_3Cl\,] \rightarrow CH_3CH^{35}Cl^\bullet + Cl^- \quad (4a)$$
$$\downarrow$$
$$[CH_2{}^{35}Cl^\bullet + CH_2Cl^-] \rightarrow ClCH_2CH_2^\bullet + {}^{35}Cl^- \quad (4b)$$
$$\downarrow$$
$$[CH_2{}^{35}Cl^\bullet + CH_2Cl^\bullet] \rightarrow [CH_3{}^{35}Cl + CHCl^{\bullet-}] \rightarrow$$
$$CH_3CHCl^\bullet + {}^{35}Cl^- \quad (4c)$$

Instead, we propose a mechanism (eq 4c) in which the chlorine atoms are scrambled by two proton exchanges. In this process, CH^{35}Cl$^{\bullet-}$ and CH$_3$Cl 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 CH^{35}Cl$^{\bullet-}$ with CH$_3$Cl, is endothermic (~15 kcal mol^{-1}) and consumes most of the complexation energy; thus it seems unlikely that the S$_N$2 reaction of CH$_2$^{35}Cl$^\bullet$ with CH$_2$Cl$^-$ (eq 4b) could proceed past an S$_N$2 reaction barrier despite the fact that the overall reaction is exothermic. Instead, back transfer of a proton to form [CH$_3$^{35}Cl + CHCl$^{\bullet-}$] restores the complexation energy, scrambles the Cl atoms, and allows for an S$_N$2 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$^{\bullet-}$ with CHCl$_3$ 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.

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