Hydrogen/Chlorine Exchange Reactions of Gaseous Carbanions

Hao Chen and R. Graham Cooks

Department of Chemistry, Purdue University, West Lafayette, Indiana, USA

Eduardo C. Meurer and Marcos N. Eberlin*

Institute of Chemistry, State University of Campinas, UNICAMP, Campinas, Brazil

Gas-phase reactions of three typical carbanions CH_2NO_2^- , CH_2CN^- , and $\text{CH}_2\text{S}(\text{O})\text{CH}_3^-$ with the chloromethanes CH_2Cl_2 , CHCl_3 , and CCl_4 , examined by tandem mass spectrometry, show a novel hydrogen/chlorine exchange reaction. For example, reaction between the nitromethyl anion CH_2NO_2^- and carbon tetrachloride CCl_4 forms the ion CHClNO_2^- . The suggested reaction mechanism involves nucleophilic attack by CH_2NO_2^- at the chlorine of CCl_4 followed by proton transfer within the resulting complex $[\text{CH}_2\text{ClNO}_2 + \text{CCl}_3]^-$ to form CHClNO_2^- and CHCl_3 . Two other carbanions CH_2CN^- and $\text{CH}_2\text{S}(\text{O})\text{CH}_3^-$ also undergo the novel hydrogen/chlorine exchange reactions with CCl_4 but to a much smaller extent, their higher nucleophilicities favoring competitive nucleophilic attack reactions. Proton abstraction is the exclusive pathway in the reactions of these carbanions with CHCl_3 . While CH_2CN^- and $\text{CH}_2\text{S}(\text{O})\text{CH}_3^-$ promote mainly proton abstraction and nucleophilic displacement in reactions with CH_2Cl_2 , CH_2NO_2^- does not react. (J Am Soc Mass Spectrom 2005, 16, 2045–2051) © 2005 American Society for Mass Spectrometry

Nitromethyl, cyanomethyl, and dimethylsulfinyl carbanions (CH_2NO_2^- , CH_2CN^- , and $\text{CH}_2\text{S}(\text{O})\text{CH}_3^-$) are important reactive intermediates in organic chemistry. Due to the strong electron-withdrawing effect of the nitro, cyano and sulfinyl groups, the negative charge on carbon is delocalized and the stability of these carbanions is enhanced (Scheme 1). The nitromethyl anion CH_2NO_2^- is believed to be involved in the Henry or nitroaldol reaction, [1] a classic carbon–carbon coupling reaction between an alkylnitro compound bearing α hydrogens and a carbonyl compound. Dimethylsulfinyl carbanions have been used in innumerable synthetic studies since Corey and Chaykovsky reported the first preparation of the dimethylsulfinyl carbanion in dimethyl sulfoxide (DMSO) solution [2]. A recent NMR study [3] suggests that the dimethylsulfinyl carbanion $\text{CH}_2\text{S}(\text{O})\text{CH}_3^-$ is actually a tridentate nucleophile, i.e., it can behave as an O-, S-, or C-nucleophile in organic reactions. Because of this synthetic relevance, the study of the intrinsic chemistry of these carbanions in the gas phase is receiving increased attention. DePuy et al. [4] found that nitromethyl anion CH_2NO_2^- fails to undergo H/D exchange with deuterated methanol CH_3OD but exchanges both hydrogens with $\text{CF}_3\text{CH}_2\text{OD}$. Bartmess and coworkers

[5] observed that Claisen condensation products are formed in the reactions of CH_2NO_2^- , CH_2CN^- , and $\text{CH}_2\text{S}(\text{O})\text{CH}_3^-$ with $\text{HCO}_2\text{CH}=\text{CH}_2$ performed in an ion cyclotron resonance spectrometer (ICR). Grabowski and Zhang [6] examined the anion/molecule reactions of CH_2NO_2^- and CH_2CN^- with dimethyl disulfide. While nitromethyl carbanion reacted slowly but completely to give $\text{CH}_3\text{SCHNO}_2^-$ as the sole primary product ion, cyanomethyl carbanion also underwent substitution at sulfur. However, the reactivity of these carbanions towards halogenated compounds, especially haloalkanes, has seen little study although the gas-phase ion/molecule reactions with neutral halomethanes have been extensively investigated by Grabowski et al. [7], Knighton and Grimsrud [8], and Nibbering and coworkers [9, 10]. Products arising from dissociative electron-transfer (DET), $\text{S}_\text{N}2$ nucleophilic substitution, and proton abstraction reactions were observed.

In the condensed phase, the tetrahalogenated methanes such as CCl_4 are fairly unreactive toward the usual nucleophilic agents and are often used as inert media in organic synthesis. However, they are especially labile toward the halogenophilic attack [11]. For instance, the conversion of alcohols into the corresponding alkylchlorides using CCl_4 and PPh_3 proceeds with chlorine cation transfer from CCl_4 to PPh_3 to form an intermediate $[\text{Ph}_3\text{PCl}]^+\text{CCl}_3^-$ [12]. Examination of the reaction of the free carbanions as nucleophiles with haloalkanes is therefore desirable.

Hydrogen/chlorine exchange is quite a general phenomenon in condensed-phase reactions and it is of

Published online October 24, 2005

Address reprint requests to Dr. R. G. Cooks, Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907-1393, USA. E-mail: cooks@purdue.edu.

* Also at Institute of Chemistry, State University of Campinas, UNICAMP Campinas SP, Brazil. E-mail: eberlin@iqm.unicamp.br

Scheme 1

interest because it can offer a convenient means to prepare chlorination products. The most common hydrogen/chlorine exchange reaction is the photocatalyzed chlorination of hydrocarbons with Cl_2 gas, which involves $\text{Cl}^\cdot$ radical intermediates. However, nonradical hydrogen/chlorine exchange reactions of both negative and positive chlorine have been also reported. Exchange of halogen and hydrogen between organic halides such as *t*-butyl chloride and hydrocarbons such as 2-methylbutane under AlCl_3 catalysis was observed by Bartlett et al. [13]. The reaction was proposed to begin with the formation of an ionic intermediate $\text{Me}_3\text{C}^+\cdot\text{AlCl}_4^-$, subsequent deprotonation of 2-methylbutane by Me_3C^+ and then chloride Cl^- transfer from AlCl_4^- to the deprotonated 2-methylisobutane (Scheme 2). A similar hydrogen/chlorine exchange reaction between bicyclo [2,2,1]heptane and *t*-butyl chloride catalyzed by AlCl_3 was later reported by Schmerling, who found the chlorination product to be 2-chlorobicyclo [2,2,1]heptane rather than 1-chlorobicyclo [2,2,1]heptane because the tertiary carbonium ion is not stable (Scheme 3, eq 1) [14]. This kind of reaction has been extended to boron compounds. Zakharkin observed that refluxing carborane in CCl_4 or CHCl_3 under AlCl_3 catalysis gave mono-, di-, and trichlorocarboranes with chlorine replacing hydrogen atoms in the $\text{B}_{10}\text{H}_{10}$ moiety [15]. Kerrigan reported that the exchange of hydrogen and chlorine atoms occurs in the course of the interaction of boron trichloride and diborane to yield monochlorodiborane and dichloroborane (Scheme 3, eq 2) [16]. Kondo developed a method for detection of

intramolecularly hydrogen-bonded peptide NH groups based on a hydrogen/chlorine exchange reaction with reagents of positive chlorine, *t*-BuOCl or chlorine, and proposed a positive chlorine transfer mechanism [17].

The present study investigates the ion/molecule reactions of three typical carbanions CH_2NO_2^- , CH_2CN^- , and $\text{CH}_2\text{S}(\text{O})\text{CH}_3^-$ with the chloromethanes CH_2Cl_2 , CHCl_3 , and CCl_4 , and reports on a novel gas-phase hydrogen/chlorine exchange reaction between nitromethyl anion CH_2NO_2^- and tetrachloromethane CCl_4 . The reaction mechanism probably involves nucleophilic attack of CH_2NO_2^- to a chlorine of CCl_4 followed by proton transfer within the resulting complex $[\text{CH}_2\text{ClNO}_2 + \text{CCl}_3^-]$ to form CHClNO_2^- and CHCl_3 .

Experimental

Ion/molecule reactions were carried out on a Finnigan TSQ-70 triple quadrupole mass spectrometer (Thermo Finnigan, San Jose, CA). The mass-selected reactant ions CH_2NO_2^- , CH_2CN^- , and $\text{CH}_2\text{S}(\text{O})\text{CH}_3^-$ were generated by negative chemical ionization (CI) of the neutrals CH_3NO_2 , CH_3CN , and $\text{CH}_3\text{S}(\text{O})\text{CH}_3$, respectively, using isobutane as the buffer gas. Ion/molecule reactions were performed by mass selection of the precursor ion of interest in Q1, reaction with neutral reagent in Q2, and product ion mass analysis using Q3 to monitor product ions. The collision energy, given as the voltage difference between the ion source and the collision quadrupole, was nominally 0 eV for ion/molecule reactions and 10 eV for collision-induced dissociation (CID). All compounds were commercially available and used without further purification.

Scheme 2

Scheme 3

Table 1. Major ionic products of the ion/molecule reactions between carbanions and chloromethanes

Reagents		Products (<i>m/z</i>)				
Ions (<i>m/z</i>)	Neutral	H/Cl exchange	Chlorine abstraction	Proton abstraction	Nucleophilic substitution (<i>S_N2</i>)	Other ions
CH ₂ NO ₂ [−] (60)	CH ₂ Cl ₂	— ^a	—	—	—	—
	CHCl ₃	—	—	CCl ₃ [−] (117)	—	42,46
	CCl ₄	CHCINO ₂ [−] (94)	CCl ₃ [−] (117)	—	—	42 ^b
CH ₂ CN [−] (40)	CH ₂ Cl ₂	—	—	CHCl ₂ [−] (83)	Cl [−] (35)	—
	CHCl ₃	—	—	CCl ₃ [−] (117)	—	—
	CCl ₄	CHCICN [−] (74) ^b	CCl ₃ [−] (117)	—	Cl [−] (35)	—
CH ₂ SOCH ₃ [−] (77)	CH ₂ Cl ₂	—	—	CHCl ₂ [−] (83)	Cl [−] (35)	49,61
	CHCl ₃	—	—	CCl ₃ [−] (117)	—	—
	CCl ₄	CHCIS(O)CH ₃ [−] (111) ^b	CCl ₃ [−] (117)	—	Cl [−] (35) ^b	49,61

^aNot observed.^bVery weak.

Optimized geometries and energies of idealized conformations were obtained by density functional theory (DFT) calculations using the B3LYP/6-311G(d,p) basis set as implemented in Gaussian 2003 program [18]. The zero-point vibrational energies were scaled by a factor of 0.9806 [19, 20] and incorporated into the final total energy calculations.

Results and Discussion

Table 1 summarizes the results of the reactions of the three carbanions with the chloromethanes CH₂Cl₂, CHCl₃, and CCl₄. Figure 1a displays the product ion mass spectrum for reactions of nitromethyl anion CH₂NO₂[−] of *m/z* 60 with CCl₄. The main product ion is

Figure 1. Product ion mass spectra for ion/molecule reactions of: (a) CH₂NO₂[−] of *m/z* 60 and (b) CD₂NO₂[−] of *m/z* 62 with CCl₄ at nominally 0 eV collision energy.

Table 2. B3LYP/6-311G(d,p) calculated energies for molecules and cations in the hydrogen/chlorine exchange reaction

Species	Energy (Hartrees ^a)	Zero-point energy (Hartrees)	Corrected energy ^b (Hartrees)	ΔE (kcal/mol)
CH ₂ NO ₂ [−] (1)	−244.4874087	0.035501	−244.4525964	— ^c
CCl ₄ (2)	−1878.9771155	0.009216	−1878.968078	—
HCCl ₃ (3)	−1419.3755056	0.019787	−1419.356102	—
CHCINO ₂ [−] (4)	−704.1206603	0.027217	−704.0939713	—
H• (5)	−0.5021559	0.000000	−0.5021559	—
CCl ₃ • (6)	−1418.7166789	0.007007	−1418.709808	—
CCl ₃ [−] (7)	−1418.7973556	0.004786	−1418.792662	—
CH ₂ CINO ₂ (8)	−704.6910491	0.041223	−704.6506258	—
[CH ₂ NO ₂ + CCl ₄] (9)	−2123.4913040	0.045643	−2123.446546	—
[CH ₂ CINO ₂ + CCl ₃ [−]] (10)	−2123.5146422	0.046468	−2123.469076	—
[CHCINO ₂ [−] + CHCl ₃] (11)	−2123.5183855	0.047170	−2123.472131	—
[CH ₂ CINO ₂ [•] + CCl ₃ •] (12)	−2123.4364868	0.044162	−2123.393182	—
(3+4) − (1+2)	—	—	—	−18
(4 + 5 + 6) − (1 + 2)	—	—	—	+72
(7 + 8) − (1 + 2)	—	—	—	−14
(9) − (1 + 2)	—	—	—	−16
(10) − (1 + 2)	—	—	—	−30
(11) − (1 + 2)	—	—	—	−32
(12) − (1 + 2)	—	—	—	+17

^a1 Hartree = 627.51 kcal/mol^bCorrected E = E + 0.9806 × Zero-point E^cNot applied

that of *m/z* 94 with an isotopologue of *m/z* 96 of one third the abundance corresponding to CHCINO₂[−]. The assignment of this ion was confirmed by observing the ion CDCINO₂[−] of *m/z* 95 in the spectrum shown in Figure 1b for which the isotopologue carbanion CD₂NO₂[−] of *m/z* 62 was used. The fragmentation behavior of the product ion CH³⁵CINO₂[−] of *m/z* 94 upon collision with argon under 10 eV collision energy was used for its further characterization. This process yields just one fragment ion, Cl[−] of *m/z* 35, see the inset in Figure 1a, possibly by loss of the neutral carbene: CHNO₂ and in a good agreement with the formation of Br[−] of *m/z* 79 from the CID of CH⁷⁹BrNO₂[−] of *m/z* 138 generated by negative chemical ionization of CH₂BrNO₂ using isobutane as the buffer gas.

To form CHCINO₂[−] from the reaction of CH₂NO₂[−] and CCl₄, the neutral product could be either a neutral molecule of chloroform CHCl₃ or two radicals: H• plus •CCl₃. The latter possibility can be excluded since this pathway is predicted to be endothermic by 72 kcal mol^{−1} by DFT calculations at the B3LYP/6-311G(d,p) level. Loss of neutral chloroform is, however, favorable in energy, that is, it is exothermic by 18 kcal mol^{−1}. Table 2 summarizes the calculated energies of the species in the reaction. It can be seen that the formal hydrogen/chlorine exchange between CH₂NO₂[−] and CCl₄ occurs, as shown in the net reaction (eq 3). The ions of *m/z* 117, 119, and 121 in Figure 1a are attributable to the different isotopologues of CCl₃[−], and another ion of *m/z* 42 likely arises from the dissociation of the reactant ion CH₂NO₂[−] by the loss of H₂O.

Scheme 4 proposes a mechanism for this novel hydrogen/chlorine exchange reaction. CH₂NO₂[−] is initially attracted to neutral CCl₄ to form a transient complex [CH₂NO₂[−] + CCl₄] and this complexation releases 16 kcal mol^{−1} (Table 2). A subsequent intermolecular transfer of Cl⁺ from CCl₄ to CH₂NO₂[−] (i.e., nucleophilic attack on chlorine of CCl₄ by CH₂NO₂[−]) occurs to produce a second complex [CH₂CINO₂ + CCl₃[−]] and this step is also thermodynamically favorable, that is, it is exothermic by as much as 30 kcal mol^{−1}. The possibility of Cl[−] transfer in the initial complex can be excluded on Coulombic grounds. Another alternative pathway of chlorine radical transfer is also unlikely since the calculations show that the formation of the complex [CH₂CINO₂[•] + CCl₃•] is endothermic by +17 kcal mol^{−1}. The remaining possibility, Cl⁺ transfer, is considered likely. In the literature, intermolecular chlorine cation transfer was also previously proposed to occur in the condensed phase from a *N*-chloroanilinium ion to an aniline [21] and from CCl₄ to PPh₃ [12] as mentioned earlier. In the case being discussed, a subsequent intermolecular proton transfer takes place within the second complex [CH₂CINO₂ + CCl₃[−]] to form a third complex [CHCINO₂[−] + CHCl₃] and the hydrogen/chlorine exchange products, CHCINO₂[−] and CHCl₃, thus arise from the dissociation of the third complex. The exothermicity of the formation of the third complex [CHCINO₂[−] + CHCl₃] from CH₂NO₂[−] and CCl₄ is 32 kcal mol^{−1}. Overall, in this reaction, the exchange of chlorine and hydrogen is stepwise and occurs via three ion-neutral intermediate complexes, in a mechanism very similar to that reported for the hydrogen/deuterium exchange in the gas phase [22]. Interestingly, no further H/Cl exchange occurs to

Scheme 4

form $\text{CCl}_2\text{NO}_2^-$, probably because with one more electron-withdrawing Cl atom, CHClNO_2^- is less nucleophilic than CH_2NO_2^- . Note that as Scheme 4 shows, energy barriers might exist in the conversion from the initial complex to the second complex and from the second to the third complex. The latter two complexes are stabilized by hydrogen bonding (Scheme 4).

Another product ion, CCl_3^- of m/z 117, is also observed in the spectrum of Figure 1a, and this ion is probably formed by direct attack on a chlorine atom of CCl_4 by CH_2NO_2^- . The exothermicity for the formation of CCl_3^- from reactants CH_2NO_2^- and CCl_4 is $-14 \text{ kcal mol}^{-1}$. Direct nucleophilic attack on a halogen atom in an organic compound by an anion has been described for both condensed- [11, 23] and gas-phase reactions [24]. For example, α -chlorination to the carbonyl compounds effected by CCl_4 in basic media involves the nucleophilic attack on a Cl atom of the CCl_4 by the intermediate carbonyl anion and the reactivity increases with decreased delocalization of its negative charge [23]. Nibbering et al. reported that nucleophilic attack on a chlorine atom is the exclusive reaction of the allyl anion with CF_3Cl in the gas phase [24].

As seen from the discussion above, the carbanion CH_2NO_2^- is further functionalized via a simple reaction with CCl_4 . Potentially, this reaction could find synthetic applications in solution since the $\text{CH}_2\text{ClNO}_2^-$ may subsequently undergo a Henry/nitroaldol reaction. In the gas-phase reaction between OH^- and CCl_4 to form Cl^- and CCl_3^- performed in a FT-ICR mass spectrometer, Nibbering and coworkers observed hydrogen/chlorine exchange products of OCl^- and CHCl_3 as the minor products [25].

We also examined the reactions of carbanions CH_2CN^- of m/z 40 and $\text{CH}_2\text{S(O)CH}_3^-$ of m/z 77 with CCl_4 . To our surprise, unlike CH_2NO_2^- , both CH_2CN^- and $\text{CH}_2\text{S(O)CH}_3^-$ form fairly weak hydrogen/chlorine exchange products CHClCN^- of m/z 74 and CHClS(O)CH_3^- of m/z 111 with CCl_4 . Instead, Cl^- and CCl_3^- were observed in both cases. The formation of Cl^- could be due to either dissociative electron-transfer

since cyanomethyl radical has a lower electron affinity (1.5 eV) [26] than CCl_4 (2.0 eV) [27] or from the nucleophilic displacement of CCl_4 ($\text{S}_{\text{N}}2$ mechanism) because CH_2CN^- is also a good nucleophile towards formation of C—C bonds. However CCl_4^- , a common intermediate in typical dissociative electron of CCl_4 transfer [8], was not observed, indicating that the nucleophilic substitution $\text{S}_{\text{N}}2$ reaction might indeed be responsible for the formation of Cl^- . Due to the presence of competitive nucleophilic substitutions, the hydrogen/chlorine exchange reactions of CH_2CN^- and $\text{CH}_2\text{S(O)CH}_3^-$ with CCl_4 are prevented. This can be rationalized by the different electron-withdrawing effect of the substitution groups of the three carbanions. Because nitro group has a larger electron-withdrawing effect than cyano and sulfinyl groups [28], the nucleophilicity of CH_2CN^- and $\text{CH}_2\text{S(O)CH}_3^-$ toward CCl_4 is therefore higher than that of CH_2NO_2^- . This rationale is also supported by experimental evidence that another competitive reaction with the hydrogen/chlorine exchange, the direct nucleophilic chlorine attack of CCl_4 by CH_2CN^- or $\text{CH}_2\text{S(O)CH}_3^-$, forms an abundance of CCl_3^- signals as the main product in the reaction of CH_2CN^- or $\text{CH}_2\text{S(O)CH}_3^-$ with CCl_4 , analogous with the observation of intermediate phenylchloroacetonitrile PhCHClCN in the chlorination of phenylacetonitrile PhCH_2CN by CCl_4 in the presence of sodium hydroxide [29]. The distinct reactivity toward CCl_4 can be used to differentiate CH_2NO_2^- from CH_2CN^- and $\text{CH}_2\text{S(O)CH}_3^-$.

All three carbanions have similar reactivity towards chloroform (CHCl_3) and form exclusively CCl_3^- of m/z 117 by proton abstraction, as Figure 2 exemplifies for the reaction of CH_2NO_2^- and CHCl_3 . This reactivity is analogous with the reaction of O^- with CHCl_3 [9, 10]. However, when CH_2Cl_2 is chosen as the neutral reactant, both proton abstraction and nucleophilic displacement are observed to form CHCl_2^- , m/z 83, and Cl^- , m/z 35, in the reaction with CH_2CN^- and $\text{CH}_2\text{S(O)CH}_3^-$ while CH_2NO_2^- is inert. Again, these results suggest that the nucleophilicity of CH_2NO_2^- is the lowest among the three carbanions.

Figure 2. Product ion mass spectrum for ion/molecule reaction of CH_2NO_2^- of m/z 60 with CHCl_3 at nominally 0 eV collision energy

Conclusions

Investigation on the gas-phase ion/molecule reactions of three typical carbanions with chloromethanes shows that CH_2NO_2^- reacts efficiently via a novel hydrogen/chlorine exchange pathway with CCl_4 to yield CHClNO_2^- and CHCl_3 likely via a complex in which chlorine cation transfer and subsequent proton transfer occurs. By contrast, CH_2CN^- and $\text{CH}_2\text{S}(\text{O})\text{CH}_3^-$ have much lower hydrogen/chlorine exchange reactivities with CCl_4 due to the presence of competitive nucleophilic attack on both carbon and chlorine of CCl_4 . The conversion of CH_2NO_2^- into CHClNO_2^- via this simple H/Cl exchange reaction might be worthy of extension to the investigation of carbon–carbon bond formation reaction by further reacting CHClNO_2^- with electrophiles such as aldehydes. All three carbanions react with CHCl_3 via proton abstraction. For the reactions of CH_2CN^- and $\text{CH}_2\text{S}(\text{O})\text{CH}_3^-$ with CH_2Cl_2 , both proton abstraction and nucleophilic displacement products are predominant owing to the high nucleophilicity of these carbanions.

Acknowledgments

The authors acknowledge support from the National Science Foundation (CHE04-12,782), the U.S. Department of Energy, Office of Basic Energy Sciences, and the Brazilian research foundations CNPq and FAPESP.

References

- Palomo, C.; Oiarbide, M.; Mielgo, A. Unveiling Reliable Catalysts for the Asymmetric Nitroaldol (Henry) Reaction. *Angew. Chem. Int. Ed.* **2004**, *43*, 5442–5444.
- Corey, E. J.; Chaykovsky, M. J. Methylsulfinylcarbanion. *J. Am. Chem. Soc.* **1962**, *84*, 866–867.
- Buncel, E.; Park, K.-T.; Dust, J. M.; Manderville, R. A. Concerning the Denticity of the Dimethylsulfinyl Anion in Meisenheimer Complexation. *J. Am. Chem. Soc.* **2003**, *125*, 5388–5392.
- Stewart, J. H.; Shapiro, R. H.; Depuy, C. H.; Bierbaum, V. M. Hydrogen–Deuterium Exchange Reactions of Carbanions with Water- d_2 in the Gas Phase. *J. Am. Chem. Soc.* **1977**, *99*, 7650–7653.
- Bartmess, J. E.; Hays, R. J.; Caldwell, G. The Addition of Carbanions to the Carbonyl Group in the Gas Phase. *J. Am. Chem. Soc.* **1982**, *103*, 1338–1344.
- Grabowski, J. J.; Zhang, L. Dimethyl Disulfide: Anion–Molecule Reactions in the Gas Phase at 300 K. *J. Am. Chem. Soc.* **1989**, *111*, 1193–1203.
- Rinden, E.; Maricq, M. M.; Grabowski, J. J. Gas-Phase Ion–Molecule Reactions of the Nitric Oxide Anion. *J. Am. Chem. Soc.* **1989**, *111*, 1203–1210.
- Knighton, W. B.; Grimsrud, E. P. Gas-Phase Electron-Transfer Reactions Between Selected Molecular Anions and Halogenated Methanes. *J. Am. Chem. Soc.* **1992**, *114*, 2336–2342.
- Staneke, P. O.; Groothuis, G.; Ingemann, S.; Nibbering, N. M. M. Competing Electron Transfer, Proton Abstraction, and Nucleophilic Substitutions in Gas-Phase Reactions of (Radical) Anions with Chloro- and Bromomethanes. *J. Phys. Org. Chem.* **1996**, *9*, 471–486.
- Staneke, P. O.; Kauw, J.; Born, M.; Ingemann, S.; Nibbering, N. M. M. Low Pressure Gas-Phase Reactions of the Atomic Oxygen Radical Anion with Halomethanes Studied Using Fourier Transform Ion Cyclotron Resonance. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 124–132.
- Zefirov, N. S.; Marhon'kov, D. I. X-Phylic Reactions. *Chem. Rev.* **1982**, *82*, 615–624.
- Slagle, J. D.; Huang, T. T.-S.; Franzus, B. Mechanism of Triphenylphosphine-Tetrachloromethane-Alcohol Reaction: Pericyclic or Clustered Ion Pairs? *J. Org. Chem.* **1981**, *46*, 3526–3530.
- Bartlett, P. D.; Condon, F. E.; Schneid, A. Exchanges of Halogen and Hydrogen Between Organic Halides and Isoparaffins in the Presence of Aluminum Halides. *J. Am. Chem. Soc.* **1944**, *66*, 1531–1539.

14. Schmerling, L. The Exchange of Hydrogen and Chlorine Between Biocyclo(2,2,1)Heptane and *t*-Butyl Chloride. *J. Am. Chem. Soc.* **1946**, 68, 195–196.
15. Zakharkin, L. I.; Okhlobystin, O. Y.; Semin, G. K.; Babushkina, T. A. Exchange of Hydrogen for Chlorine in the Carborane-Carbon Tetrachloride or Chloroform System under the Action of Aluminum Chloride. *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya* **1965**, 10, 1913–1914.
16. Kerrigan, J. V. The Interaction of Boron Trichloride with Diborane. *Inorg. Chem.* **1964**, 3, 908–910.
17. Kondo, M.; Nishi, I.; Okamoto, K.; Kato, T.; Izumiya, N. Studies on Detection of Intramolecular Hydrogen Bonds by Hydrogen–Chlorine Exchange Method. Peptides, Synthesis, Structure, Function. *Proceedings of the 7th American Peptide Symposium*; Madison, Wisconsin, 1981; pp 291–294.
18. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 2003*; Gaussian Inc.: Wallingford, CT.
19. Scott, A. P.; Radom, L. Harmonic Vibrational Frequencies: An Evaluation of Hartree-Fock, Moller-Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors. *J. Phys. Chem.* **1996**, 100, 16502–16513.
20. Faustov, V. I.; Baskir, E. G.; Biryukov, A. A. Thermal Isomerization of Acetylnitrene: A Quantum-Chemical Study. *Rus. Chem. Bull. Int. Ed.* **2003**, 52, 2328–2333.
21. Paul, D. F.; Haberfield, P. Chlorination of Anilines. Bimolecular Acid-Catalyzed Rearrangement of *N*-Chloroanilines. *J. Org. Chem.* **1976**, 41, 3170–3175.
22. Depuy, C. H. An Introduction to the Gas Phase Chemistry of Anions. *Int. J. Mass Spectrom.* **2000**, 200, 79–96.
23. Morel, G.; Seux, R.; Foucaud, A. Halogenation of Various α -Carbonyl Carbanions by Carbon Tetrachloride. *Bull. Soc. Chim. France* **1975**, 7/8, 1865–1870.
24. Staneke, P. O.; Groothuis, G.; Ingemann, S.; Nibbering, N. M. M. The Interplay Between Electron Transfer and Attack on Halogen in Gas-Phase Reactions of Negative Ions with Fluoro-Chloromethanes and Fluoro-Bromomethanes. *Int. J. Mass Spectrom.* **1995**, 149/150, 99–110.
25. Staneke, P. O.; Groothuis, G.; Ingemann, S.; Nibbering, N. M. M. Competing Electron Transfer, Proton Abstraction, and Nucleophilic Substitutions in Gas-Phase Reactions of (Radical) Anions with Chloro- and Bromomethanes. *J. Phys. Org. Chem.* **1996**, 9, 471–486.
26. Moran, S.; Ellis, H. B.; Defrees, D. J.; Mclean, A. D.; Ellison, G. B. Carbanion Spectroscopy: CH_2CN^- . *J. Am. Chem. Soc.* **1987**, 109, 5996–6003.
27. Disper, H.; Lacmann, K. Negative Ion Formation in Collisions Between Potassium and Fluoro- and Chloromethanes: Electron Affinities and Bond Dissociation Energies. *Int. J. Mass Spectrom. Ion Phys.* **1978**, 28, 49–67.
28. Buncl, E.; Dust, J. M. *Carbanion Chemistry: Structures and Mechanisms*; Oxford University Press and American Chemical Society: Washington DC and New York, 2003; p 41.
29. Jonczyk, A.; Kwast, A.; Makosza, M. Reactions of Organic Anions. 89. Reactions of Carbon Tetrachloride with Carbon Acids in Catalytic Two-Phase System. *J. Org. Chem.* **1979**, 44, 1192–1194.