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Allenic Anions. Structure and Inversion Barrier of H_2CCCH^-

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Abstract: Ab initio calculations have been performed on the allenic anion H_2CCCH^-. The structure is found to be bent, resembling allene, and the barrier to inversion is about 7 kcal. Substitution of H^- with Cl^- leads to a larger inversion barrier. Removal of the α-H^- from the allenic anion requires 94 kcal, but ionization of Cl^- from H_2CCCCl^- appears to be competitive with inversion. Some comparisons are made with the vinyl anion.

Introduction

Organic anions present an array of challenging chemical problems relating to their structures, interconversions, protonation energies, and formation. The difficulty underlying these problems is that the most fundamental information about anions is often hard to obtain. Recent experimental developments are just beginning to provide some firm understanding of the nature of simple organic anions. Laser photodetachment techniques of Lineberger[1-4] and co-workers have been quite successful in studying bound negative ions. With this approach, it has been possible not only to measure electron affinities of a parent neutral species, but also to determine the nature of the anion's ground electronic state and the anion's shape, which in many instances is similar to that of the neutral molecule, e.g., CH_2^-,[3] or to that of a neutral molecule isoelectronic with the anion. A new technique of Balle et al.[5] has made possible precise structural determinations of short-lived molecular complexes or weakly bound negative ions through the direct observation of microwave rotational transitions. However, basic understanding about anion reactions and formation may still require indirect study.

The allenic anion, $C_3H_3^-$, and related species have been of interest because of questions about structure, reactions, and interconversions. Early studies of Hennion and Maloney[6] on the solvolysis of $Cl(CH_3)_2CC\equiv CH$ and $(CH_3)_2C=C=CHCl$ suggested the existence of a resonance-stabilized carbene intermediate:

$$R_2C^+{-}C\equiv C^-: \leftrightarrow R_2C=C=C:$$

1

Kinetic evidence of Shiner and Wilson[7] confirmed the existence of this intermediate and showed that it was formed by deprotonation followed by a rate-controlling loss of the halide ion. Further evidence was provided by Hartzler[8] in studies of the synthesis of alkenylidenecyclopropanes. The usefullness of carbenes in synthetic work stimulated the interest in producing intermediates such as **1**. However, the allenic anions themselves seem to be useful synthetically. Anion formation from a propargyl system can be followed with alkylation to yield a specific substituted allene.[9] We may represent this as

$$RC\equiv CH_2R' \rightarrow [RC\equiv CHR']^- \xrightarrow{R''X} RR''C=\underset{\mathbf{2}}{C}=CHR'$$

With a proper choice of the substituents R, R′, and R″, the anion reacts entirely to produce an allene rather than an acetylene.[9] The anion could, of course, be produced from a halogen-substituted allene, too. Cumulene carbene intermediates with four-carbon chains have also been generated by Stang and Fisk[10] through deprotonation and then ionization of a halide substituent.

Recently, le Noble and co-workers[11] have considered the nature of allenic anion species by studying disubstituted adamantanes. Two questions arose in this work, the structure of an allenic anion and the barrier to conversion to the other configuration. In 1966, Shiner and Humphrey[12] had proposed a linear structure for halogenated allenic anions. On the basis of the allenyl hydrogen exchange rate in $(CH_3)_2CCCHBr$, they concluded that there would be some allylic resonance stabilization of the anion leading to the linear structure, while the transition state for Br^- removal was believed to be bent. le Noble and co-workers questioned this conclusion.[13] Measurement of activation volumes for carbene formation from an allenic chloride in comparison to measurements on an isomeric propargylic chloride[14] could be explained if the allenic anion were bent and not linear. Finally, in the recent work of le Noble et al.,[11] an inversion barrier of 22 kcal was reported for a chlorinated allenic anion on the basis of exchange rates. These workers went on to suggest that replacement of chlorine by hydrogen would yield a lower but nonzero inversion barrier; i.e., the anion would still be bent. Other direct studies appear to be in the offing using new methods for the gas-phase generation of specific isomers of anions, such as recently reported for $C_3H_3^-$.[15]

Ab initio studies of complex molecular systems cannot always treat all details of a chemical problem, such as interaction with solvent molecules. They can, though, provide a free-molecule limit description and can do so even for the most transient species. For instance, distinguishing whether a reaction proceeds through a carbene such as **1** or a propargylcarbene[16]

$$RC\equiv C \underset{\mathbf{3}}{-} \ddot{C} - R$$

or both may be aided by ab initio predictions. Such calculations have provided a prediction that the energy difference between the ground singlet state of H_2CCC: and the corresponding singlet

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state of propargylene is about 14 kcal,[17] and other calculations have indicated that triplet propargylene lies about 48 kcal below the singlet,[18,19] placing it 34 kcal below ground-state H_2CCC:. The results of electronic structure calculations yield relative energetics and from such energetics mechanisms may sometimes be deduced. For the simplest allenic anion, $C_3H_3^-$, however, there have been few ab initio studies. Hopkinson et al.[20] have reported self-consistent-field (SCF) results indicating that $C_3H_3^-$ does have a nonlinear, bent structure and predicting an inversion barrier of 6.6 kcal. If the "spare pair"[12] of electrons that stabilizes the bent structure through hybridization were removed from the anion, one expects that the resulting cation, H_2CCCH^+, is less likely to be bent. This, in fact, was the result obtained by Radom et al.[21] from minimal basis (STO-3G) SCF calculations.

A greater amount of theoretical data is available for C_2H_3 systems and comparison with them is useful if we view the structure of $C_3H_3^-$ as just deprotonated allene, and the structure of $C_2H_3^-$ as just deprotonated ethylene. The "spare pair" electrons in the diffuse highest lying occupied molecular orbital of $C_2H_3^-$ have a profound effect on the structure. The C–C–H bond angle for the lone proton is only about 110°[22] and several calculations have given the barrier to inversion via a linear structure as about 40 kcal.[22-24] Removing these two electrons changes the structural picture completely and for $H_3C_2^+$ the linear structure is a shallow minimum on the potential-energy surface.[25] The effect of lone-pair electrons on geometrical structure is seen for an even simpler molecule, CH_3; the cation and neutral species are planar while the anion is pyramidal.[26] However, in spite of the similarity of CH_3^-, $C_2H_3^-$, and $C_3H_3^-$, there are major differences among them in inversion energetics, and a definitive theoretical study of the allenic anion structure is called for. Energetics and reaction paths for anion–carbene pair formation are also examined as part of this study.

Theroretical Approach

Calculations were performed at several levels of treatment. Geometry searches were performed at the SCF level and final energetics were evaluated with correlated wave functions, using the method of self-consistent electron pairs[27,28] (SCEP). The SCEP method makes possible the variational treatment of all singly and doubly substituted correlating configurations relative to the closed-shell reference configuration. Closed-shell quadruply substituted configurations[29] have also been included to account for a share of the size-consistency error.[30] Carbon 1s-like orbitals were frozen to substitution in the SCEP calculations. The basis sets used were double-ζ (DZ) sets of Dunning-contracted functions[33] [carbon (9s5p/4s2p) and hydrogen (4s/2s)] and augmented DZ sets. For the chlorine atom, a similar quality set was used and consisted of the (11s7p/6s4p) contraction[34] of Huzinaga's primitive set[35] augmented with a set of d functions with exponent 0.606. The set used for most of the calculations was formed by augmenting these DZ sets with diffuse s functions on all centers. The exponents for these diffuse s functions were all 0.05 and this set is designated DZs. Diffuse 2p functions would probably be necessary for precise calculations of electron affinities,[34] but were found to have little effect on relative energies of the vinyl anion.[22] This was tested for the allenic anions by augmenting the DZs basis with diffuse 2p functions on carbon and chlorine centers. The exponent used was 0.07 for both types of centers. This basis, designated DZsp, consisted of 140 primitive functions and 76 contracted functions for H_2CCCCl^-. Poppinger and Radom have shown that inclusion of continuum functions in the basis sets used for anions may reduce a positive orbital energy of an occupied orbital to a physically correct value of zero, but will not improve and may worsen the structural predictions.[36] In all calculations reported here, the orbital energies of all occupied orbitals were negative, indicating that even at the SCF molecular orbital level a bound description for the extra electron of the anions is obtained. Contour plots were made with a modified version of the Jorgensen plotting program.[37]

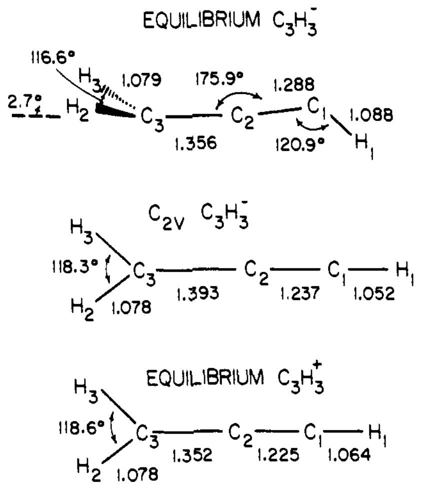

Figure 1. The optimized structures of equilibrium $C_3H_3^-$, $C_3H_3^-$ constrained to be planar (C_{2v} symmetry), and equilibrium $C_3H_3^+$.

Table I. Net Atomic Charges of H_2CCCH^- Based on Mulliken Populations

	equilibrium $C_3H_3^-$		C_{2v} $C_3H_3^-$		$H^- + H_2C_3$:	
atom[a]	SCF	SCEP	SCF	SCEP	SCF	SCEP
H_1	+0.097	+0.095	+0.169	+0.152	−1.000	−1.000
C_1	−0.766	−0.772	−0.726	−0.680	−0.073	−0.119
C_2	+0.099	+0.111	+0.133	+0.113	−0.257	−0.157
C_3	−0.586	−0.580	−0.714	−0.713	−0.037	−0.075
H_2 (or H_3)	+0.078	+0.073	+0.069	+0.064	+0.183	+0.175

[a] Atom designations are from Figure 1. The DZs basis was used.

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(30) The size-consistency error is the difference in the sum of independent fragment energies and the total system energy in the separated limit when all are treated at the same level of substitution in the configuration expansion. Variational treatments short of a full configuration expansion are not strictly size consistent. The size-consistency error, however, will often amount to only a very subtle effect. Detailed discussions are in ref 31 and 32.

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Table II. $C_3H_3^-$ and $C_2H_3^-$ Energetics[a]

		equilibrium structure (1)	C_{2v} inversion structure (2)	$E_2 - E_1$, kcal	H^- + carbene (3)	$E_3 - E_1$, kcal
$C_3H_3^-$	SCF	−115.192 05	−115.184 25	4.9	−115.046 36	91.4
	SCF/DZsp	−115.196 70	−115.191 19	3.5		
	SCEP	−115.451 41	−115.440 05	7.1	−115.301 32	94.2
$C_2H_3^-$	SCF	−77.337 17[b]	−77.276 77[b]	37.9[b]	−77.229 48	67.6
	SCEP	−77.527 30[b]	−77.463 07[b]	40.3[b]	−77.412 01	72.3

[a] Energies of the structures are in au while energy differences relative to the equilibrium structure are in kcal. Where not indicated the DZs basis was used. [b] From ref 22.

Results and Discussion

The optimized structures obtained for the C_3H_3 systems studied are shown in Figure 1. (The DZ rather than DZs basis was used for the cation.) The equilibrium structure of the allenic anion is similar to that obtained by Hopkinson et al.,[20] who used a 4-31G basis set at the SCF level, but the larger DZs basis gives the C–C bond lengths as about 0.02 Å longer than their result. A minor structural feature is the nonplanarity of the H_2CCC fragment. A linear structure of the anion could be represented as

$$\mathrm{H_2C^-{—}C{\equiv}C{—}H}$$

4

The methylene carbon in this configuration would resemble CH_3^-, which is nonplanar. Energetically, **4** might not have a large role in determining the structure because, at the equilibrium pyrimidal angle of 17.5° for CH_3^-, the energy stabilization is only 1.5 kcal below the planar form.[26b] Table I gives the net atomic charges and in the equilibrium allenic anion the methylene carbon (C_3) has a net charge of −0.58, but the terminal carbon (C_1) has a charge of −0.77. Also, the difference of 0.068 Å between the two C–C bond lengths is about half the difference expected between carbon triple and single bonds. Thus, **4** does not have the dominant role in describing the bonding in the anions; the negative charge is delocalized. The small deviation from linearity of the carbon chain is probably due to some s–p hybridization as is distorted allene.[38]

The conversion from one configuration of the allenic anion to an equivalent configuration may occur in several ways.[11] The bent anion may simply invert through a linear form, or it may internally rotate, or it may ionize and then recombine. If the allenic anion is viewed as a deprotonated allene, internal rotation seems unfavorable since the barrier to internal rotation on the singlet state energy surface of allene is about 50 kcal.[38-40] Therefore, we restricted attention to inversion and ionization energetics.

If the anion is constrained to have planar C_{2v} symmetry, the second structure in Figure 1 has the lowest energy. The atomic charges have shifted in this inversion structure so that the −0.68 charge on C_1 is less than the −0.71 charge on C_3. The difference in the carbon bond lengths is now 0.156 Å, more typical of the difference between single and triple bond lengths. The fact that the energy difference given in Table II between this structure and the equilibrium structure is only 7.1 kcal shows that **4** does stabilize the linear configuration. With the diffuse 2p functions, the barrier is lowered by 1.4 kcal. For the vinyl anion the inversion barrier is quite high because with only two carbons there is no structure analogous to **4** which provides an easy path for inversion. In carbenes, the zwitterionic form

$$\mathrm{H_2C^+{—}C{\equiv}C^-}$$

5

is responsible for the large dipole moment[17,18] of propadienylidene. For even-numbered cumulene carbenes an alternating single and triple bond form is not possible and so the dipole moment of H_2CCCC: is not much different from that of H_2CCC:.[17] A reasonable generalization of this idea applied to anions of the form H_2CCH^-, H_2CCCH^-, H_2CCCCH^-, etc., would be that even-numbered carbon systems will have large inversion barriers while odd-numbered carbon systems will not because of stabilization from an acetylenic form. Stang and Fisk[10] point out that allenylidene carbenes may be stabilized by resonance with an acetylene form

$$\mathrm{H_2C{=}C{=}C{=}C{:}\qquad H_2C{=}C^+{—}C{\equiv}C^-}$$

6

but that the ionic contribution may be small because of the relatively high energy of vinyl cations. For the anion H_2CCCCH^-, an analogous acetylenic structure would not be expected to have any importance.

Table III. Net Atomic Charges[a] of H_2CCCCl^- from Mulliken Populations

atom[b]	bent structure[c]	linear structure[c]
Cl	−0.382	−0.299
C_1	−0.300	−0.337
C_2	−0.056	+0.207
C_3	−0.428	−0.728
H_2 (or H_3)	+0.083	+0.079
total energy	−574.093 93	−574.064 57

[a] From SCF wave functions, DZs basis. [b] Atom designations follow those of Figure 1. [c] Structures were taken to be the equilibrium and C_{2v} structures in Figure 1, but with a Cl–C_1 bond length of 1.75 Å, which was chosen from comparison of some carbon–chlorine bond lengths.[44]

Removing two electrons from the allenic anion yields $C_3H_3^+$ with a planar C_{2v} equilibrium structure as shown in Figure 1. There is no lone pair of electrons on C_1 and so the lone proton is collinear with the carbons. The difference in the C–C bond lengths in this system is 0.127 Å. Thus, while the cation looks primarily like a single–triple bond system, there must still be some resonance involving the double–double bond carbene form. Indeed, there is no longer a negative charge on the methyl carbon to push it away from the C_{2v} carbene structure. Therefore, the likelihood of having a linear equilibrium structure will be enhanced by diminishing the negative charge on C_1 in some combination with an increase in the negative charge on C_3.

Substitution of the lone proton by chlorine changes the atomic net charges considerably as shown in Table III, and, unlike the proton in the parent allenic anion, chlorine is negatively charged. As le Noble et al.[11] point out, this would at first imply an increased role for the structure

$$\mathrm{H_2C{=}C{=}C{=}Cl^-}$$

7

But the energies given in Table III show an inversion barrier of about 18.4 kcal (17.8 kcal with the DZsp basis), close to the 22-kcal experimental value.[11] Clearly, the chlorine-substituted allenic anion has a much *larger* inversion barrier than the unsubstituted ion. With the withdrawal of negative charge by chlorine, the stability of the allene structure is greater than that which could result from pyramidalizing the CH_2 end of the anion. As suggested above by the comparison with $C_3H_3^+$, the likelihood of a linear structure will be enhanced, in part, by increase in the negative charge on C_3. Comparing the substituted and unsubstituted anions, it is seen that chlorine substitution reduces the charge of this carbon from −0.59 to −0.43. The negative charge

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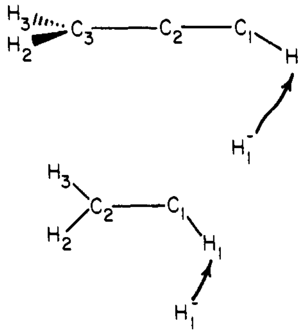

Figure 2. Qualitative representation of the minimum energy approach of H^- to propadienylidene and vinylidene.

on C_1 is also reduced by chlorine substitution but this is accomplished by shifting the charge to the chlorine rather than back through the carbene fragment, something that would improve the prospects of a linear structure. The lone pair of electrons is apparently hybridizing with the available chlorine orbitals. The chlorine d orbitals show only small population and very little change in going from the bent to the linear structure. However, the chlorine p orbitals in the molecular plane in the linear form increase in population by about one-half of an electron when the anion is bent. This seems to be the source of the stabilizing hydridization of the lone-pair electrons.

The rate-controlling step in the base-promoted solvolysis of halogenated allenes is the ionization of the halogen.[7,8] We investigated the loss of hydride from the allenic anion in the free-molecule limit. Comparison calculations on the loss of hydride from the vinyl anion to produce vinylidene were also performed. Structures were optimized for a number of fixed hydride–carbene distances and no barrier was found: the energy increases smoothly. As shown in Table II, the vinyl anion was found to be about 72 kcal more stable than H^- and vinylidene. Previously, it has been found[22,41] that, as H^- approaches, acetylene trans distorts. A barrier of about 16 kcal is encountered and the equilibrium vinyl anion is about 26 kcal more stable than H^- and acetylene. With a DZ basis, SCEP calculations give a value of 46 kcal for the energy difference between vinylidene and acetylene,[42] which is consistent with the inferred energy difference obtained here, 72 minus 26 kcal. It is not too surprising, then, that no barrier is encountered in adding hydride to vinylidene because the 40 or 46 kcal[42] instability of vinylidene relative to acetylene puts this reaction well above the barrier for the hydride addition to acetylene. It is interesting that addition of hydride to propadienylidene yields 94 kcal or about 20 kcal more than addition to vinylidene. This seems to be a consequence, once again, of the importance of a zwitterionic resonance structure in odd-numbered carbon systems which is being enhanced with addition of hydride.

As suggested by Shiner and Humphrey[12] and le Noble et al.,[13] the path for loss of H^- or Cl^- will be bent relative to the carbon skeleton because of sp hybridization. Our search for the minimum potential energy path supports this idea for both the propadienylidene–hydride pair and the vinylidene–hydride pair. Qualitative representations of these paths are given in Figure 2.

The ionization of Cl^- from H_2CCCCl^- requires remarkably less energy than ionization of H^- from the unsubstituted ion. From the total energy given in Table III and the energy of Cl^- infinitely separated from propadienylidene (−574.065 87 au, DZs basis), the energy to remove the halide ion is only 17.6 kcal. This can be viewed as a free-molecule "barrier" to the ionization–recombination reaction. Thus, this reaction now seems to be competitive with inversion. The low energy for removing Cl^- relative to removing H^- is surely due to chlorine's better ability to carry a negative charge.

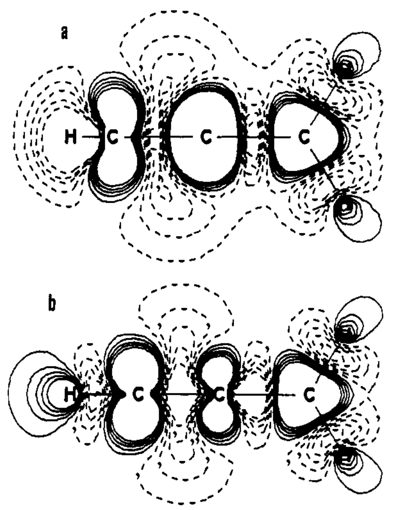

Figure 3. Electron density difference (SCEP less SCF) contour plots for H_2CCCH^- in the equilibrium structure (a) and the C_{2v} planar structure (b). Dotted lines are contours in regions where electron density is reduced because of correlation and solid lines correspond to regions where the density is increased.

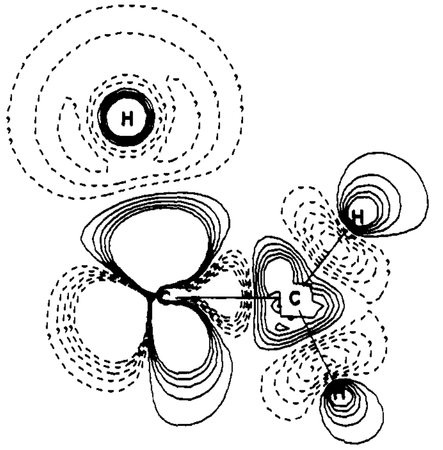

Figure 4. Electron density difference (SCEP less SCF) contour plot for the approach of H^- to vinylidene.

The effect of electron correlation on the energetics of the allenic anion is small and it is encouraging that the conclusions of this work could rest as well on uncorrelated SCF calculations. However, our understanding of correlation effects, of any size, obviously is the key to ascertaining their importance beforehand in other applications. One way of isolating correlation effects is to look at the change in the electron-density distribution when correlation effects are included.[43] Such plots of the density difference are given in Figure 3 for the allenic anion. The typical pattern for these plots for equilibrium systems is the removal of density between centers and the buildup in density on the centers. Figures 3a and 3b show no major differences from this pattern and thus the net correlation effect on energetics is small.[43] However, as in Figure 3a, the effect of correlation is to reduce the diffuseness of the electron distribution by diminishing density not only between atomic centers but also in the outer regions of the molecule. If we take this redistribution as the means of stabilizing the anionic structure via correlation, then we can see that this is happening to a lesser extent in the planar structure (Figure 3b). As discussed earlier, some negative charge is shifted toward the CH_2 end of the anion in the planar or inversion form. In this form, correlation appears to do less in reducing the dif-

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fuseness of the electron distribution and it makes a lesser contribution to the total energy: the inversion barrier is raised slightly due to correlation effects.

Figure 4 is a density difference plot for one point on the minimum-energy path of the H$^-$ plus vinylidene reaction. Again, correlation pulls in the diffuse electron density of the hydride. The beginning of charge transfer in the formation of the vinyl anion is therefore likely to be predicted incorrectly at the SCF molecular orbital level.

The inversion barriers of allenic anions are low in comparison to vinyl anions because of the role of an acetylenic structure in the odd-numbered carbon system. But this also means that the inversion barrier is sensitive to substitution because substitution can control the role of the acetylenic structure. Halogen substitution increases the height of the barrier. As a result, ionization of a halogen-substituted allenic anion followed by re-formation of the carbene–anion pair may be more competitive with inversion than for the unsubstituted anion. The net effect of electron correlation seems to be small throughout.

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Isotope Exchange Reactions of OH$^-$ or OD$^-$ with Hydrogen and Water

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Abstract: Exchange between gaseous hydroxyl ion and hydrogen and water has been investigated by using two mass spectrometers and two modes of ionization. Exchange of OH$^-$ and D_2 is a relatively slow reaction (collision efficiency = 2.9×10^{-2}), and its rate constant exhibits a small negative temperature coefficient, $k = CT^{-0.7}$. The exchange of OD$^-$ with H_2 is 30% slower than OH$^-$ + D_2, the difference becoming less as the temperature increases. Exchange of OD$^-$ with H_2O is fast (collision efficiency $\sim$1). Exchange of OD$^-$ with CH_4 and i-C_4H_{10} has also been examined, but these reactions are very slow ($k \leq 3 \times 10^{-13}$ cm^3/molecule·s) and may well be zero.

A number of investigations of the OH$^-$ negative chemical ionization mass spectrometry of various compounds have recently been made.[1-5] In these studies, unusual and interesting reactions of gaseous anions have been observed, and we plan to make studies using deuterium labeling to elucidate their mechanisms. However, since with a high-pressure chemical ionization apparatus the gaseous anions being investigated will suffer many collisions with gas molecules during the period of their residence in the ionization chamber, the stability of the labels with respect to exchange with the gas molecules must first be investigated before the mechanistic studies utilizing labels can properly be undertaken. We have made such investigations, using two mass spectrometers each operated in a different mode (continuous ionization in one and pulsed, time-resolved ionization in the other). We find that hydroxyl anion (OH$^-$/OD$^-$) exchanges with gaseous hydrogen (H_2/D_2). We here report our results.

Perhaps the first study of hydrogen–deuterium exchange under chemical ionization conditions was that of Hunt, McEwen, and Upham,[6] who pointed out that active hydrogens in positive ions would exchange with D_2O at 1 Torr pressure. The phenomenon was suggested as an analytical technique to determine the numbers of active hydrogens in small samples. Lin and Smith[7] have shown that the number of active hydrogens in positive ions can be determined by using ND_3, and Hunt, Sethi, and Shabinowitz[8] have shown that exchange occurs with active hydrogens in negative ions and that the number of active hydrogens can be determined by using a variety of deuterated reagent gases.

More general studies of exchange in positive ions have been made by Freiser, Woodin, and Beauchamp,[9] Martinsen and Buttrill,[10] and Hunt, Gale, and Sethi.[11] General studies of exchange in negative ions have been made by DePuy, Shapiro, and co-workers.[12-14]

To summarize these studies, it is found that both for positive and negative ions certain hydrogens in the ions will exchange with certain deuterated reagents. Under some conditions and for some compounds, multiple exchange occurs. Both Hunt and co-workers[8] and DePuy, Shapiro, and co-workers[13,14] point out that in positive ions the occurrence of exchange depends upon the relative strengths of the base initiating the exchange and the conjugate base of the protonated ion undergoing the exchange, and in negative ions the exchange analogously depends upon the relative acidities of the acid promoting the exchange and the conjugate acid of the anion undergoing the exchange. The exchange will not occur in positive ions if the difference in basicities is too great or in negative ions

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