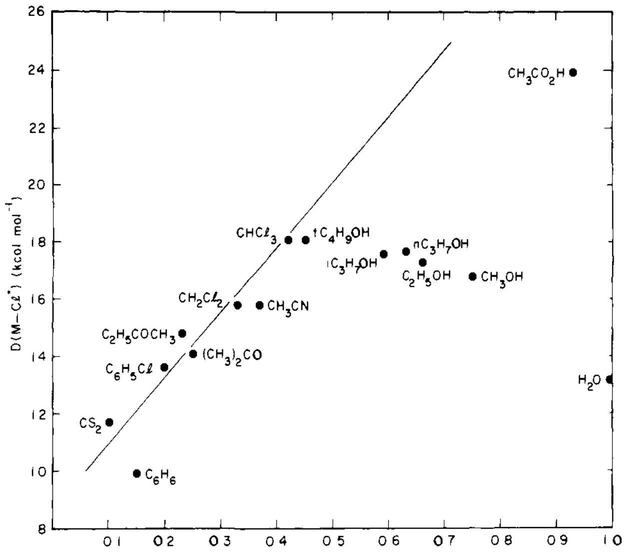

Figure 4. Variation of gas-phase chloride-binding energies with the Swain acity parameter, *A*.

solution and gas-phase solvatory abilities appears to be quite clearly a function of molecular size. The large size and structural complexity of the higher alcohols makes it much more difficult to have more than a few solvent molecules interacting with a single anion, whereas the small size of the water molecule makes multiple interactions with a single anion much more feasible. In cases such as this, the single molecule solvation energies do not give a realistic depiction of bulk solvating ability.

Conclusion

We have demonstrated that a qantitative scale of chloride ion binding energies for a wide variety of Brønsted acids has been established. The variation of chloride-binding energies with gas-phase acidities has shown that chloride binds protic substrates with far more electrostatic character than does the fluoride ion. Also, unlike the fluoride ion, a consistent variation of chloride affinity with gas-phase acidity does not hold for complex alcohols because of multiple binding site interactions which are far more favorable for Cl^- than for F^-. A comparison of chloride affinities with solution phase anion solvation ability ("acity") reveals a good correlation for nonpolar and dipolar aprotic solvents but an inverse correlation for protic, hydroxylic solvents. These, and related data from our laboratory, are being used to provide a basis for understanding molecular factors effecting the solvation process.

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Registry No. $ClCO_2CH_3$, 79-22-1; $ClCO_2^-$, 88015-38-7; Cl^-, 16887-00-6; HCl, 7647-01-0; HF, 7664-39-3; HCN, 74-90-8; H_2O, 7732-18-5; NH_3, 7664-41-7; CH_3F, 593-53-3; CH_3CN, 75-05-8; CH_3Cl, 74-87-3; CH_2Cl_2, 75-09-2; $CHCl_3$, 67-66-3; $CHFCl_2$, 75-43-4; CHF_2Cl, 75-45-6; CHF_3, 75-46-7; CH_3CF_2H, 75-37-6; CH_2FCF_2H, 430-66-0; C_6H_5Cl, 108-90-7; *o*-$C_6H_4F_2$, 367-11-3; *m*-$C_6H_4F_2$, 372-18-9; *p*-$C_6H_4F_2$, 540-36-3; SO_2, 7446-09-5; HCO_2H, 64-18-6; $MeCO_2H$, 64-19-7; MeCHO, 75-07-0; Me_3CCHO, 630-19-3; Me_2CO, 67-64-1; MeEtCO, 78-93-3; Et_2CO, 96-22-0; PF_3, 7783-55-3; MeOH, 67-56-1; EtOH, 64-17-5; PrOH, 71-23-8; *i*-PrOH, 67-63-0; *n*-BuOH, 71-36-3; FCH_2CH_2OH, 371-62-0; $ClCH_2CH_2OH$, 107-07-3; $(CH_2F)_2CHOH$, 453-13-4; CF_3CH_2OH, 75-89-8; $(CF_3)_2(CH_3)COH$, 1515-14-6; $(CF_3)_2CHOH$, 920-66-1; *t*-BuOH, 75-65-0; C_4H_5N, 109-97-7; $CF_3CH_2NH_2$, 753-90-2; CF_3CF_2H, 354-33-6; *t*-C_4H_9F, 353-61-7; *t*-C_4H_9Cl, 507-20-0; C_6H_6, 71-43-2.

Generation and Identification of Four Stable Isomeric $[C_3H_3]^+$ Ions by Direct Dissociative Ionization or by Charge Reversal of Anions

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Abstract: Examination of collisional activation mass spectra showed that pure [cyclopropenium]$^+$ was generated by only metastably fragmenting precursor ions, $[C_4H_6]^{+\cdot}$, $[C_3H_3Br]^{+\cdot}$, and $[C_3H_3Cl]^{+\cdot}$. Pure $[CH_2{=}C{=}CH^+]$ could be produced from the dissociative ionization of $[CH{\equiv}CCH_2I]$ in the ion source and among metastably fragmenting ions. The ions $[CH_2{=}CH{-}C{:}^+]$ and $[CH_3C{\equiv}C^+]$ were generated by collisionally induced charge inversion of the corresponding anions. The latter were produced by dissociative electron capture and by reaction of OH^- with cyclopropene and $CH_3C{\equiv}CD$, respectively. Although $[CH_2{=}CH{-}C{:}^+]$ exists in a potential well, $[CH_3C{\equiv}C^+]$ ions produced by the above method lie close to their dissociation limit. $[CH_2{=}C{=}CH^+]$ and $[CH_2{=}CH{-}C{:}^+]$ ions generated by charge reversal rearrange to similar mixtures of [cyclopropenium]$^+$ and $[CH_2{=}C{=}CH^+]$ within a time of ca. 8 μs. The fragmentations $[C_3H_5]^+ \rightarrow [C_3H_3]^+ + H_2$ and $[C_5H_5]^+ \rightarrow [C_3H_3]^+ + C_2H_2$ produce composite metastable peaks. The high and low kinetic energy release components therein were shown to result from the generation of [cyclopropenium]$^+$ and $[CH_2{=}C{=}CH^+]$, respectively.

Two isomeric $[C_3H_3]^+$ ions have been experimentaly observed, the cyclopropenium and propargyl cations. The heat of formation, $\Delta H_f°$, of the former has been well established by a variety of measurements[1] as 255 ± 1 kcal mol^{-1} and that of the latter as 281 ± 2 kcal mol^{-1}.[1,2] These experimental values have adequately been reproduced by ab initio calculations[3] where the difference in their $\Delta H_f°$ values was found to be 31 kcal mol^{-1}. Previous calculations[4] indicated that two other structures were stable below the dissociation of lowest energy requirement to $[C_3H]^+ + H_2$

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Table I. Collisional Activation Mass Spectra[a] of Propargyl Cations [CH_2=C=CH^+] Generated by Dissociative Ionization of CH≡C–CH_2I and by Charge Reversal

origin of $[C_3H_3]^+$ ion	translational energy, kV	*m/z* 38	37	36	27	26	25	24	14	13	12
$[HC{\equiv}CCH_2I]^{+\cdot}$	8	52	40	8	1	37	45	17	28	39	33
$[HC{\equiv}CCH_2I]^{+\cdot}$	6	54	40	6	1	39	44	15	32	39	29
$[HC{\equiv}CCH_2I]^{+\cdot}$	4	57	38	5	2	42	43	13	38	38	24
$[HC{\equiv}CCH_2I]^{+\cdot}$	2	61	38	2	3	43	43	12	41	38	20
metastable $[HC{\equiv}CCH_2I]^{+\cdot}$	1.9	60	40	1	3	41	43	12	41	38	20
$[CH_2{=}C{=}CH]^-$ [b]	8	57	38	5	1	40	44	15	36	37	26

[a] Relative abundances normalized to Σ = 100 within each group of ions. At 8 kV the relative abundance of the C_3, C_2, and C_1 groups was ca. 100:5:1, respectively, and at 2 kV it was 100:2:1. Charge-stripping peaks have been omitted. Variation with acceleration voltage is small. At 8 kV *m/z* 37^{2+}:*m/z* 38^{2+}:*m/z* 39^{2+} was 1:31:68; at 2 kV it was <0.5:28:72. [b] Generated by dissociative electron capture or reaction of CH_2=C=CH_2 with OH^-; charge reversal in the second field free region of the ZAB-2F mass spectrometer.

(ca. 378 kcal mol^{-1}),[5-7] namely [CH_2=CH—C:$^+$] the prop-2-en-1-yl-3-ylidene cation in its allylic form, ΔH_f° = 325 kcal mol^{-1}, and the 1-propynyl cation, [$CH_3C{\equiv}C^+$], $\Delta H_f \simeq$ 368 kcal mol^{-1}. Although the cyclopropenium and propargyl cations generated by dissociative ionization are distinguishable by means of their reactivities, for example propargyl cations undergo reaction with acetylene to form $C_5H_5^+$ but cyclopropenium ions do not,[8] they are less easy to identify by means of their collisional activation (CA) mass spectra[9] where the *m/z* 14:*m/z* 13 ratio (0.85 and 0.42, respectively) provides the only distinctive feature.

An alternative method of generating positive ions is collisionally to induce charge inversion of an anion, a method pioneered some years ago by Bursey et al.[10] This reaction for high-velocity ions is a vertical process[11] and provided that geometric differences between the negative and positive ions are not large (i.e., the Franck–Condon factors are similar for both species) the instantaneously formed cations retain the structure of the anion. Autoejection[12] and autoionization[1] time scales decrease rapidly with increasing internal energy and so superexcited negative ions have very short lifetimes, ca. 10^{-15}–10^{-16} s. The dissociation behavior of the new cation will in turn be structure characteristic, and the charge inversion CA mass spectrum might be expected to compare closely with that for the corresponding positive ions generated by direct electron impact. Thus for example $[C_3H_3]^+$ ions of structure [$CH_3C{\equiv}C^+$] could be generated by charge reversal of [CH_3-C≡C]$^-$ ions. DePuy et al.[13] showed that reaction of OH^- with propyne produces [CH_2=C=CH]$^-$ and [$CH_3C{\equiv}C$]$^-$ by abstraction of H from each end of the alkyne. Thus reaction of OH^- with $CH_3C{\equiv}CD$ would yield the desired anion having *m/z* 39. In this paper we report a detailed investigation of the collisionally induced fragmentations of a variety of $[C_3H_3]^+$ and $[C_3H_3]^-$ ions.

Results and Discussion

The Propargyl Cation [CH_2=C=CH^+]. It was earlier shown that propargyl cations were generated by loss of I· from ionized propargyl iodide.[2] Table I shows the CA mass spectrum of $[C_3H_3]^+$ ions produced in the ion source and via metastable fragmentation in the first field free region of a V.G. Micromass ZAB-2F mass spectrometer (see Experimental). The CA mass spectrum of the metastably generated $[C_3H_3]^+$ ions (which have low excess internal energy) is identical with that of ion source generated $[C_3H_3]^+$ ions (having a *wide* range of internal energies) having the *same translational energy* as the metastable ions. This result indicates that propargyl cations do not rearrange to cyclopropenium to any significant extent on the time scale of these experiments (10^{-5} s). The CA mass spectrum for ions having 8-kV translational energy agree adequately with those reported earlier.[9] Note how sensitive the *m/z* 14:*m/z* 12 ratio is to translational energy; at the lower energies the fragments from high-energy dissociations have lower abundances.

Reaction of OH^- with allene or dissociative electron capture yields propargyl anions.[13] Such ions, generated with 8-kV translational energy, produce on charge reversal a CA mass spectrum identical with that of propargyl cations produced by electron impact but having only 5-kV translational energy (Table I). This apparent difference in translational energy could arise from the charge-reversed C_3H_3 cations having an internal energy distribution lower than that for collisionally activated cations by the amount required to strip two electrons from the anion. For the reaction [CH_2=C=CH]$^-$ → [CH_2=C=CH^+] + 2e the energy required, ca. 11 ± 1 eV, was estimated from the displacement of the *m/z* $[39]^+$ peak from its calculated position[14,15] and is in fair agreement with that derived from the ionization energy of the radical, 8.7 eV,[16] and its electron affinity, 0.9 eV.[17]

The Cyclopropenium Cation. Although a CA mass spectrum of this ion has been reported,[9] it was deemed necessary to perform a series of experiments similar to those described above for the propargyl cation. Although in some systems appearance energy measurements have clearly shown the threshold ion to be [cyclopropenium]$^+$, there is evidence that the propargyl cation may be cogenerated at energies above threshold. For example, Tsai et al. in a photoion–photoelectron coincidence study[18] argued that although [cyclopropenium]$^+$ is generated from $[HC{\equiv}CCH_2Cl]^{+\cdot}$ at threshold, [CH_2=C=CH^+] ions are produced at slightly higher internal energies. The composite nature of the metastable peak for the reaction $[C_3H_5]^+ \rightarrow [C_3H_3]^+ + H_2$ and its change of shape upon lowering the ionizing electrons' energy[19] also has been ascribed to the formation of both [cyclopropenium]$^+$ and propargyl cations. Accordingly, the CA mass spectra of $[C_3H_3]^+$ ions derived from a variety of precursor molecules, all of which yield [cyclopropenium]$^+$ at threshold, were recorded over a range of ion acceleration voltages from ion source generated and first field free region generated $[C_3H_3]^+$ ions. The results are presented in Table II. Observations of masses *m/z* 36, 37, and 38 are not listed because they are relatively structure insensitive.

The large difference between the metastable peak observations and those for daughter ions of comparable translational energy

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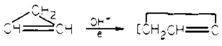
Table II. Partial Collisional Activation Mass Spectra[a] of $[C_3H_3]^+$ Ions Derived from a Variety of Precursor Molecules, All Known To Produce [Cyclopropenium]$^+$ at Threshold

precursor molecule	translational energy kV	*m/z* 27	26	25	24	14	13	12
					(4.6)[a]			(1)[a]
$CH_3C{\equiv}CCH_3$	8	1	41	43	15	17	46	37
$CH_3C{\equiv}CCH_3$	6	1	43	42	14	18	47	35
$CH_3C{\equiv}CCH_3$	4	1	47	40	11	20	50	30
$CH_3C{\equiv}CCH_3$	2	1	50	40	9	26	47	27
metastable (m*) $[CH_3C{\equiv}CCH_3]^{+\cdot}$ [b]	5.8	5	46	39	10	10	54	36
$HC{\equiv}CCH_2CH_3$	8	1	40	43	15	21	44	35
					(4.2)[a]			(1)[a]
metastable (m*) $[HC{\equiv}CCH_2CH_3]^{+\cdot}$ [b]	5.8	4	50	37	9	11	55	34
$HC{\equiv}CCH_2Br$	8	1	39	43	16	26	41	33
					(4.4)[a]			(1)[a]
$HC{\equiv}CCH_2Br$	6	1	42	43	14	29	41	30
$HC{\equiv}CCH_2Br$	4	1	45	42	12	33	41	26
$HC{\equiv}CCH_2Br$	2	1	46	43	10	38	40	22
m* $HC{\equiv}CCH_2Br$[b]	2.6	4	49	38	9	20	53	27
m* $HC{\equiv}CCH_2Br$[c]	2.6	5	48	38	10	14	55	31
$HC{\equiv}CCH_2Cl$	8	1	40	43	16	20	44	35
					(4.6)[a]			(1)[a]
$HC{\equiv}CCH_2Cl$	6	1	43	42	13	23	44	32
$HC{\equiv}CCH_2Cl$	4	2	46	41	11	26	44	29
m* $HC{\equiv}CCH_2Cl$[b]	4.2	3	50	37	9	13	53	34
m* $HC{\equiv}CCH_2Cl$[c]	4.2	2	50	38	10	11	56	33
cyclopropenium (estimated)	8	4	48	38	9	10	55	35
m* $[C_3H_5]^+$ [b,d]	7.6	1	43	42	13	24	44	32
m* $[C_3H_5]^+$ [c,d]	7.6	1	48	40	11	14	51	35
m* $[C_5H_5]^+$ [b,e]	4.8	2	43	43	12	34	40	26
m* $[C_5H_5]^+$ [e,f]	4.8	1	48	40	11	19	51	30
$CH_3C{\equiv}CH$	8	1	39	44	16	19	44	36

[a] Relative abundances normalized to $\Sigma = 100$ within each group of ions. At 8 kV group relative abundances are shown in parentheses where appropriate. Relative abundances for metastable $[C_3H_3]^+$ ions were obtained by signal averaging; the estimated error was ±5%. [b] Centroid of metastable peak. [c] High mass "horn" of metastable peak. [d] $[C_3H_5]^+$ generated from ionized propene. [e] $[C_5H_5]^+$ generated from ionized cyclopentadiene. [f] Low mass "horn" of metastable peak.

Table III. Partial Collisional Activation Mass Spectra[a] of $[C_3H_3]^+$ Ions Generated by Charge Reversal of the Corresponding Anions, Single and Double Collisions (See Text) (All Ions Have 8-kV Translational Energy)

structure of $[C_3H_3]^-$ ion	*m/z* 27	26	25	24	15	14	13	12
		Single-Collision Spectra						
$CH_3C{\equiv}CD \xrightarrow[e]{OH} [CH_3C{\equiv}C]^-$ [b]	22	32 (5.0)[a]	14	32	41	13 (1)[a]	9	37
	20	35 (7.0)[a]	33	11	1	32 (1)[a]	32	35
$CH_3C{\equiv}CH \xrightarrow[e]{OH^-} \left\{\begin{matrix}[CH_3C{\equiv}C]^- \\ [CH_2{=}C{=}CH]^-\end{matrix}\right\}$	6	38 (5.5)[a]	36	19	13	29 (1)[a]	29	29
		Double-Collision Spectra						
$[\overline{CH_2CH{=}C}]^-$	1	32 (2.7)[a]	48	19		19 (1)[a]	41	40
$[CH_2{=}C{=}CH]^-$	1	33 (3.9)[a]	46	20	1	22 (1)[a]	40	37
$\left.\begin{matrix}[CH_3C{\equiv}C]^- \\ [CH_2{=}C{=}CH]^-\end{matrix}\right\}$ mixture from propyne	0.5	34 (2.9)[a]	46	20	0.5	21 (1)[a]	40	38

[a] Relative abundances normalized to $\Sigma = 100$ within the C_2 and C_1 groups of ions. Relative abundances of the groups shown in parentheses. [b] Results corrected for incomplete labeling; sample contained ca. 9% $CH_3C{\equiv}CH$. Relatively few $[CH_3C{\equiv}^+C]$ ions survived, making a double-collision experiment impractical.

cannot be ascribed to an internal energy effect, e.g., the lower abundance of *m/z* 24, an energy demanding reaction, is accompanied by a lower abundance of *m/z* 14, a less endothermic process. We propose that ions produced in the ion source, which have a *wide* range of internal energies, are a mixture of [propargyl]$^+$ and [cyclopropenium]$^+$. In contrast, pure [cyclopropenium]$^+$ ions are obtained from the *metastable* $[C_4H_6]^{+\cdot}$ ions; daughter ions produced via metastable dissociations have narrow ranges of internal energy extending from the minimum (threshold) energy for the fragmentation. The metastable peaks for loss of halogen from $CH{\equiv}CCH_2Cl$ and $CH{\equiv}CCH_2Br$ are both broad, deeply dished signals.[2] The extrema or "horns" of these peaks represent $[C_3H_3]^+$ ions having *low* internal energy; these too, when selectively transmitted to the collision cell, gave a CA mass spectrum identical with the above. The metastable peak from $CH{\equiv}CCH_2Cl$ shows a slight discontinuity at its center, possibly indicative of a second component, while that from $CH{\equiv}CCH_2Br$ shows a weak but clear Gaussian-type second component at its center (see Table II). These observations are in keeping with the energetics of the fragmentations,[2] the bromide's AE for m/z 39 being closer to the threshold for $[\text{propargyl}]^+$ production than that for the chloride. Note that in earlier work,[2] a mass spectrometer of conventional geometry was used [AEI-Kratos MS902S, electric sector preceding magnet) and so the metastable peaks consisted of overlapping signals resulting from the natural isotopic abundances of $^{35/37}Cl$ and $^{79/81}Br$, thus making second components undiscernable. In the ZAB-2F instrument used in this work, the reversed geometry permits separation of the isotopically labeled precursor ions and second components may therefore readily be identified. The results in Table II indicate that the CA mass spectrum for pure $[\text{cyclopropenium}]^+$ (from metastable fragmentations of C_4H_6, C_3H_3Cl and C_3H_3Br) varies little with translational energy and the estimated 8-kV translational-energy values are included in the table. All the 8-kV CA mass spectra of ion source generated ions and center components of the composite metastable peaks can adequately be reproduced by proportionate summation of results for $[CH_2{=}C{=}CH^+]$ and $[\text{cyclopropenium}]^+$. Thus the conclusions[19] concerning the composite metastable peak for the fragmentation $[C_3H_5]^+ \rightarrow [C_3H_3]^+ + H_2$, namely that the broad, dished component corresponded to the formation of the cyclic ion and that the narrow, dished peak resulted from $[CH_2{=}C{=}CH^+]$, are clearly supported by the present observations (Table II). Similarly, the fragmentation $[C_5H_5]^+ \rightarrow [C_3H_3]^+ + C_2H_2$ also generates a composite metastable peak, consisting of a Gaussian peak superimposed upon a broader, dished signal.[20,21] Sen Sharma et al.[20] proposed that the components respectively arose for the cogeneration of $[CH_2{=}C{=}CH^+]$ and $[\text{cyclopropenium}]^+$ ions. The results, presented in Table II, show that the above proposal was correct. Note that the Gaussian peak contributes partially to the low mass "horn" of the metastable peak, hence the impure $[\text{cyclopropenium}]^+$ CA mass spectrum measured thereat.

The 1-Propynyl and Prop-2-en-1-yl-3-ylidene Cations. As described in the introduction,[13] reaction of OH^- with $CH_3C{\equiv}CD$ yields the 1-propynyl anion by abstraction of D. The charge inversion mass spectrum of this species is shown in Table III. Unlike all other $[C_3H_3]^+$ ions, m/z 15 and m/z 24 are prominent, in keeping with the structure of the anion precursor. It was noteworthy that the abundance of m/z $[39]^+$ in the charge-reversal experiment was very low, in agreement with the estimated thermochemistry, in that the fragmentation to $[C_3H]^+ + H_2$ may be only slightly above $\Delta H_f{}^\circ[CH_3C{\equiv}C^+]$.

Also shown in Table III is the partial CA mass spectrum of the m/z 39 ion resulting from charge reversal of the anion generated by abstraction of H (by OH^-) from and dissociative electron capture of cyclopropene. We propose that the ion has the structure $[CH_2{=}CH{-}C{:}^+]$ which is the simplest interpretation of the observations and in keeping with theoretical predictions pertaining to the anions.[22] Note that the cyclic form of this cation is predicted to be unstable.[4] The CA mass spectrum is significantly different from those of the other three isomers having an abundant m/z 27 but no m/z 15, indicating a vinyl group rather than $[CH_3{-}C]$. m/z 12, 13, and 14, having similar abundances, indicate a structure not unlike the propargyl cation. The obseration that m/z $[39]^+$ is observable as a charge-reversal signal indicates that the ion exists in a potential well, in keeping with the structure being that of the fourth stable $[C_3H_3]^+$ isomer. This conclusion also requires that the reaction of cyclopropene with OH^- and its dissociative electron capture result in the loss of an olefinic H yielding an ion which may then ring open before, or after, charge reversal to produce the prop-2-en-1-yl-3-ylidene cation. Abstraction of H· from the methylene group cannot entirely be ruled out, but the observed CA mass spectrum cannot accommodate much contribution from $[\text{cyclopropenium}]^+$.

Also shown in Table III are the partial CA mass spectra of m/z 39 cations subjected to two collisional processes. The anions are charge reversed by collision in the first field free region and the chosen cation product is transmitted through the magnet and subjected to a second collisional activation in the second field free region. Fragment cations from the second collision are analyzed by the elec. sector in the usual way. The primary cations are ca. 8 μs old by the time they reach the second collision cell and thus may well have undergone some structural rearrangement in flight. Table III shows such results for ions initially formed as $[CH_2{=}CH{-}C{:}^+]$, $[CH_3C{\equiv}C^+]$, and $[CH_2{=}C{=}CH^+]$. Their second CA mass spectra are remarkably similar and satisfactorily can be reproduced by simple summations of $[CH_2{=}C{=}CH^+]$ and $[\text{cyclopropenium}]^+$. We conclude therefore that $[C_3H_3]^+$ ions generated by charge reversal, which can survive the flight time of ca. 8 μs to the second field free region, undergo rearrangement during this period to the two isomers of lowest enthalpy.

Experimental

All measurements were performed on a V.G. Micromass ZAB-2F mass spectrometer. Collisional activation mass spectra were recorded with all slits fully open to obtain maximum sensitivity and to minimize energy-resolution effects.[23] The ionizing electron energy was 70 eV, unless stated otherwise, the trap current was 100 μA, and ion source temp. was ca. 200 °C. The collision gas was He; the pressure in the first field free region was adjusted for maximum signal strength and the pressure in the second field free region was ca. $4\text{–}5 \times 10^{-7}$ torr, as measured by an ion gauge situated near the diffusion pump located between the electric sector and the collision-gas cell. Selected sections of metastable peaks were obtained with use of a variable Y-slit situated in the second field free region in front of the collision cell.

The negative ions were generated by proton abstraction by OH^- (or $H^- + O^-{\cdot}$) reagent ions.[24,25] The reagent negative ions were produced by 50-eV electrons on H_2O, producing secondary electrons.[26,27] The indicated source ion gauge pressure was ca. 2×10^{-5} torr; the EI slit was in position and the filament emission current was 1 mA. The secondary electrons react with the H_2O by dissociative electron capture[28] generating $H^- + O^-{\cdot}$ ions, which react by ion–molecule reactions[28] to give OH^-. In this work the OH^- ion current yield was found to be approximately third order in $[H_2O]$ whereas the O^- yield was of second order. The pressure of the substrate was typically in the range $2\text{–}6 \times 10^{-6}$ torr. The estimated total pressure within the ion source chamber is ca. 2×10^{-2} torr, a rather low pressure for chemical ionization. Use of the CI source slit generated a lower ion current yield than use of the EI source slit. Water was used rather than N_2O–hydrocarbon mixtures because N_2O shortens filament lifetimes considerably,[25,29] whereas H_2O has no apparent effect. The optimum yield of $[C_3H_3]^-$ ions as measured by a Faraday cup in the third field free region is typically $2\text{–}5 \times 10^{-8}$ A and that of OH^- about the same at the optimum source pressure of ca 2×10^{-5} torr.[29-31] The $H^-{:}O^-{\cdot}{:}OH^-$ relative intensities are approximately 1:5:25. (Some $[H_3O_2]^-$ (m/z 35) is also produced.)

Cyclopropene was prepared as described by Wiberg and Bartley.[32] $CH_3C{\equiv}CD$ was prepared by reacting $CH_3C{\equiv}CH$ with C_2H_5Li followed by decomposition of $CH_3C{\equiv}CLi$ with D_2O. $CH{\equiv}CCH_2I$ was prepared from the corresponding chloride.[33] All other compounds were commercially available.

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Registry No. $CH_2{=}C{=}CH^+$, 12542-67-5; $CH_3C{\equiv}C^+$, 24858-94-4; $CH_2{=}CH{-}C{:}^+$, 88000-25-3; $CH{\equiv}C{-}CH_2{-}I$, 659-86-9; $CH_3C{\equiv}CCH_3$, 503-17-3; $HC{\equiv}CCH_2CH_3$, 107-00-6; $HC{\equiv}CCH_2Br$, 106-96-7; $HC{\equiv}CCH_2Cl$, 624-65-7; $CH_3C{\equiv}CD$, 7299-37-8; $\overline{CH_2CH{=}CH}$, 2781-85-3; $CH_3C{\equiv}CH$, 74-99-7; $\overline{CH_2CH{=}C^-}$, 80251-77-0; $CH_2{=}C{=}CH^-$, 64066-06-4; $CH_3C{\equiv}C^-$, 36147-87-2; $CH_2{=}C{=}CH_2$, 463-49-0; cyclopropenium, 26810-74-2.

Polarized Infrared Spectroscopy of Matrix-Isolated Dimethylsilylene and 1-Methylsilene

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Abstract: Dimethylsilylene (**1**) was generated in an argon matrix by irradiation of dodecamethylcyclohexasilane and photolyzed at 450 nm to produce 1-methylsilene (**2**). Irradiation with linearly polarized light yielded matrices with both **2** and residual **1** partially oriented by photoselection. From the polarized infrared spectra of such samples, many of the absorption bands were classified as in-plane or out-of-plane polarized. Detailed assignments of the infrared spectra of **1** and **2** were made, based on comparison with spectra calculated with an MNDO program and with spectra of related molecules. The Si=C stretch in **2** falls at 988 cm^{-1}.

The reactive organosilicon species, dimethylsilylene (**1**) and 1-methylsilene (**2**), have been produced photochemically and characterized spectroscopically in both 3-methylpentane (3-MP) glass and argon matrix.[2,3] In these experiments **1** was obtained by 254-nm irradiation of dodecamethylcyclohexasilane (**3**):[2]

$$\underset{\mathbf{3}}{[(CH_3)_2Si]_6} \xrightarrow[254\ \text{nm}]{h\nu} \underset{\mathbf{4}}{[(CH_3)_2Si]_5} + \underset{\mathbf{1}}{(CH_3)_2Si}$$

It is stable for hours in an argon matrix at temperatures as high as 35 K. In 3-MP glass at 77 K, the same species was obtained[4] by irradiation of bis(trimethylstannyl)dimethylsilane, as judged by UV-vis spectrum, but in an argon matrix at 10–20 K this precursor fails to undergo significant photolysis. Bleaching of the yellow **1** by irradiation with 450-nm light induces its photoconversion to the colorless **2**:[3]

$$\underset{\mathbf{1}}{(CH_3)_2Si} \xrightarrow[450\ \text{nm}]{h\nu} \underset{\mathbf{2}}{CH_3SiH{=}CH_2}$$

This species is also stable for hours in an argon matrix at 35 K and below, but warming of the bleached argon matrix to 50 K leads to its dimerization and formation of a mixture of dimethyl-1,3-disilacyclobutanes,[3] identified by mass spectrometry and by comparison of several infrared absorption bands with those in the room-temperature spectra of an authentic sample.[5] In contrast, warming of a 3-MP glass containing **2** to ~100 K in the presence of trapping agents gave products expected for the trapping of **1** rather than those expected from the trapping of **2**.[3] The simplest interpretation of this result is to postulate that **2** undergoes fast thermal rearrangement to **1** at 100 K, and this was proposed as likely in ref 3. However, more recent work from several laboratories suggests that a more complex mechanism needs to be postulated: pyrolytic production of silenes appears to produce evidence for silylene formation either not at all[6] or only when very high temperatures are used,[7,8] state-of-art calculations suggest that the **2** → **1** conversion is thermoneutral but has an activation barrier of about 40 kcal/mol,[9] and the authors of an ion cyclotron resonance study suggest that the conversion is actually endothermic by 28 kcal/mol.[10] The considerable discussion which this subject has generated, and the questions which have been raised[11] concerning the correctness of the structural assignment of **2**, make it particularly important to examine the spectra of **1** and **2** in argon matrices in more detail. In the present paper, we report a number of new bands in the infrared spectra of **1** and **2** and show that both spectra are perfectly compatible with the proposed structures. In a separate communication,[12] we reported the reactions of **1** and **2** with N_2O in argon matrix at 35 K, which suggest a possible resolution of the above described dilemma. We now consider it likely that the "thermal rearrangement" of **2** to **1** is in fact a complex process brought about by reaction with the trapping agent.

Several inorganic silylenes have previously been characterized by infrared spectroscopy. The parent compound, SiH_2, was first produced in an argon matrix by Milligan and Jacox.[13] Margrave and co-workers have studied a series of halogenated and hydroxy-substituted silylenes and have provided complete vibrational analyses of these species.[14] While organosilylenes have been implicated in a number of reactions,[15] to our knowledge only a few direct observations have been reported,[2,3,16] and no detailed

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