J. Am. Chem. Soc. **1986**, *108*, 5847-5853

initially irreversibly decomposed to atomic C, O, and H at 300 K. Higher exposures result in formation of surface methoxy which undergoes several competing processes: methane formation, H_2CO production, decomposition to yield CO and H_2, and regeneration of methanol. As in this study, initial decomposition of methanol was proposed to result in "passivation" of the W(100) surface. On the -(5×1)-C surface, a larger fraction of the methanol reversibly desorbs below 400 K, reflecting a reduced amount of irreversible decomposition compared to the clean surface. Surface methoxy is formed via O-H bond scission which further reacts to yield CH_4, CH_3OH, H_2CO, $HCOOCH_3$, CO, H_2, CO_2, and H_2O. In the case of methanol, products resulting from both C-O and C-H bond scission are observed. The fact that H_2CO is observed from methanol reaction while HCN is not observed from reactions of $(CH_3)NH_2$ or $(CH_3)_3N$ is a rather surprising contrast. This may be the result of differences in adsorption structure of the two molecules or differences in the lability of C-H bonds. Alternatively, the fact that HCN formation requires scission of two N-H or C-N bonds and two C-H bonds whereas only one O-H and one C-H bond must be cleaved in order to form H_2CO from methanol may account for this discrepancy. It is interesting to note that the energetics of methoxy reaction are essentially the same on the -(5×1)-C vs. W(100) surfaces, analogous to the similar energetics observed for NH_3 and CH_4 formation from the amines. Further, the reactivity and selectivity for methanol were reported to be essentially the same on clean and modified Mo(100) as their W(100) analogues,[27] in contrast to the reported differences in amine reactivity on Mo(100)[6] vs. W(100).

Conclusions

The reactivity and selectivity associated with methyl- and trimethylamine on W(100), W(100-(5×1)-C, and W(100)-(2×1)-O surfaces are dependent on the presence of adlayers and the extent of amine substition. The stability of both amines and ammonia with respect to irreversible decomposition is greatly enhanced on the -(2×1)-O and -(5×1)-C compared to W(100). The generality of this trend suggests that the extent and energetics of both N-H and C-H bond activation are altered by the presence of the oxide and carbide layer and may result from the adsorption energetics and the ability to accommodate adatoms on modified surfaces.

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Stable Ylides H_2CClH, H_2CFH, H_2COH_2, and H_2CNH_3 Studied by Neutralization-Reionization Mass Spectrometry

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Abstract: Contrary to the predictions of ab initio theory, the neutral ylides H_2CClH (**1**), H_2CFH, and H_2COH_2, as well as H_2CNH_3, exist in local energy minima. These have been prepared for study from fast gaseous $H_2CYH^{\bullet+}$ ions by neutralization with Hg vapor. Reionization of the resulting fast neutrals produces abundant molecular ions, which could represent $H_2CYH^{\bullet+}$ or $H_3CY^{\bullet+}$ from partial or complete isomerization of H_2CYH to the more stable isomer H_3CY. However, increasing the pressure of the reionizing collision gas (O_2 or He) increases the relative abundance of YH dissociation products, such as HCl from **1**, which must originate from H_2CYH, not H_3CY. Thus an appreciable fraction of each of these neutral ylides must have survived for the microsecond lifetime of the experiment. For **1** this was confirmed by reionization to H_2CClH^{2+}, which shows a significantly different fragmentation pattern from that obtained from H_3CCl. More than half of **1** molecules formed by vertical neutralization are still undissociated after 10^{-6} s, and of these less than half have isomerized to H_3CCl. It appears that theory overestimates the heat-of-formation values for such hypervalent neutral species.

Ylides are widely utilized as intermediates in organic synthesis.[1] For these hypervalent species stable forms such as certain iodonium ylides (R_2C^{-}—$I^{+}R \leftrightarrow R_2C{=}IR$) are rare,[2] so that most characterizations of the structure and energetics of the simplest ylides H_2CYH have been based on molecular orbital theory.[3] In contrast, the ionized forms of many such simple ylides are actually more stable thermodynamically than their conventional isomers (e.g., $^{\bullet}CH_2O^{+}H_2$ vs. $H_3COH^{\bullet+}$); theoretical and experimental studies show that the ionic isomers are usually separated by high isomerization barriers.[4] Here we use neutralization[5,6] of the appropriate ylide ions to prepare several simple gaseous ylides (Y = Cl, **1**; F, **2**; OH, **3**; NH_2, **4**), studying these by collisionally activated dissociation (CAD) and reionization.[5]

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Previous theoretical studies have indicated H_2CNH_3 (**4**) to be stable, with a calculated energy barrier of 24[3b] or 13[3c] kcal/mol for isomerization to H_3CNH_2, whose energy is calculated to be 72[3c] or 66[3d] kcal/mol below that of **4**. Similar stabilities are predicted for the ylides H_2CSH_2 and H_2CPH_3 of the second-row elements, for which d orbital bonding is possible.[3d,g] Although Hartree–Fock calculations[3e] indicated that H_2COH_2 (**3**) (whose energy is 18 kcal/mol below that of $H_2C{:} + OH_2$) is separated from H_3COH by a ~3-kcal/mol isomerization barrier, this barrier vanishes after corrections for electron correlation and zero-point vibrations are made.[3c] H_2CFH (**2**) was similarly predicted to be unstable.[3c]

A preliminary communication of the present study[5b] showed that neutralization of fast gaseous $H_2CClH^{\bullet+}$ ions produced the ylide H_2CClH (**1**), and that its reionization gave a significant yield of $(CClH_3)^{\bullet+}$, isomeric composition unknown. Subsequent ab initio calculations[3g] suggest that these ions come from the stable isomer H_3CCl formed by rearrangement of **1**, with a predicted barrier of ≪1 kcal/mol for the dissociation $\mathbf{1} \rightarrow H_2C{:} + ClH$. Also experiments are reported[5e] to show that neutralization and reionization of $H_2CClH^{\bullet+}$ form only $H_3CCl^{\bullet+}$, as charge-stripping[7] (CS) yields no $(CClH_3)^{2+}$, which should be formed from **1**.[4c,d] In contrast, we present here evidence that ylides **1**, **2**, and **3**, as well as **4**, are stable, with significant energy barriers to both isomerization and dissociation.

Experimental Section

Measurements were made with a tandem mass spectrometer described previously,[5a,b,d,8] which contains a Hitachi RMH-2 double-focusing instrument as the first mass analyzer (MS-I) and an electrostatic sector as MS-II, using 70-eV electron ionization and 10-kV ion acceleration. For NR mass spectra the mass-selected precursor ions exiting MS-I undergo charge-exchange neutralization[5f,6] with mercury vapor produced by heating Hg in a special target chamber with cryogenic Hg trapping.[9] In this study the Hg pressure is adjusted to give ~30% precursor ion transmittance for maximum sensitivity.[5f] Unneutralized ions are deflected electrostatically, and the resulting fast neutrals are reionized[5g] by collision with a molecular beam of oxygen or helium of a pressure giving either 90 or 30% transmittance of precursor ions, corresponding to either single collision (on average, 1.06 per affected species) or multiple collision (2.1; maximum sensitivity) reionization conditions, respectively.[5g,6d,10] The distance between neutralization and reionization is 18 cm, so that neutrals formed from 10 keV $(C^{37}ClH_3)^{\bullet+}$ (m/z 52) will require 1.1×10^{-6} s to travel this distance. Along this flight path two stages of differential pumping give pressures of $\sim 10^{-6}$ torr for 14 cm, $\sim 10^{-3}$ torr for 3 cm, and ~1 torr at the reionization gas orifice.[8] For normal CAD spectra[11] ions exiting MS-I undergo collisions with a molecular beam of oxygen[5g] (the same beam location used for reionization with NRMS) whose pressure is adjusted to give 30% precursor ion transmittance (T). Neutral abundances were recorded at a retractable detector located 28 cm beyond the neutralization furnace, while the abundances of the reionized neutrals and their ionic fragments were detected after mass separation through MS-II.[5f,g] A "Hg/O_2 (30% T) NR" spectrum is one obtained with mercury neutralization and oxygen reionization using an O_2 pressure reducing the neutral abundance to 30% of its original value.

Results

Neutralization–Reionization (O_2) Spectra of H_3CY. NR mass spectra produced by neutralization with mercury and reionization with oxygen and with helium of $H_3C^{37}Cl^{\bullet+}$, $H_2C^{37}ClH^{\bullet+}$ (from $ClCH_2COOH$),[4c,d] $H_3CF^{\bullet+}$, $H_2CFH^{\bullet+}$ (from FCH_2COOH), $H_3COH^{\bullet+}$, $H_2COH_2^{\bullet+}$ (from $HOCH_2COOH$), $H_3CNH_2^{\bullet+}$, and $H_2CNH_3^{\bullet+}$ (from $HOCH_2CH_2NH_2$) are shown in Figures 1–8.

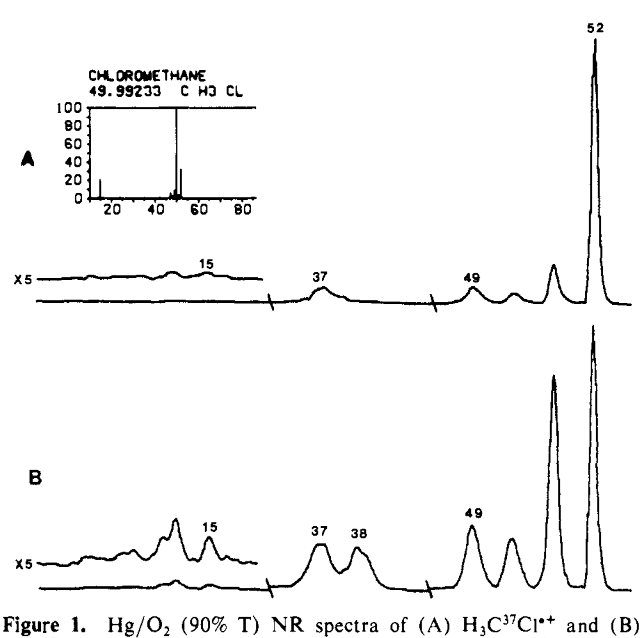

Figure 1. Hg/O_2 (90% T) NR spectra of (A) $H_3C^{37}Cl^{\bullet+}$ and (B) $H_2C^{37}ClH^{\bullet+}$. Insert is the EI spectrum of chloromethane.[12]

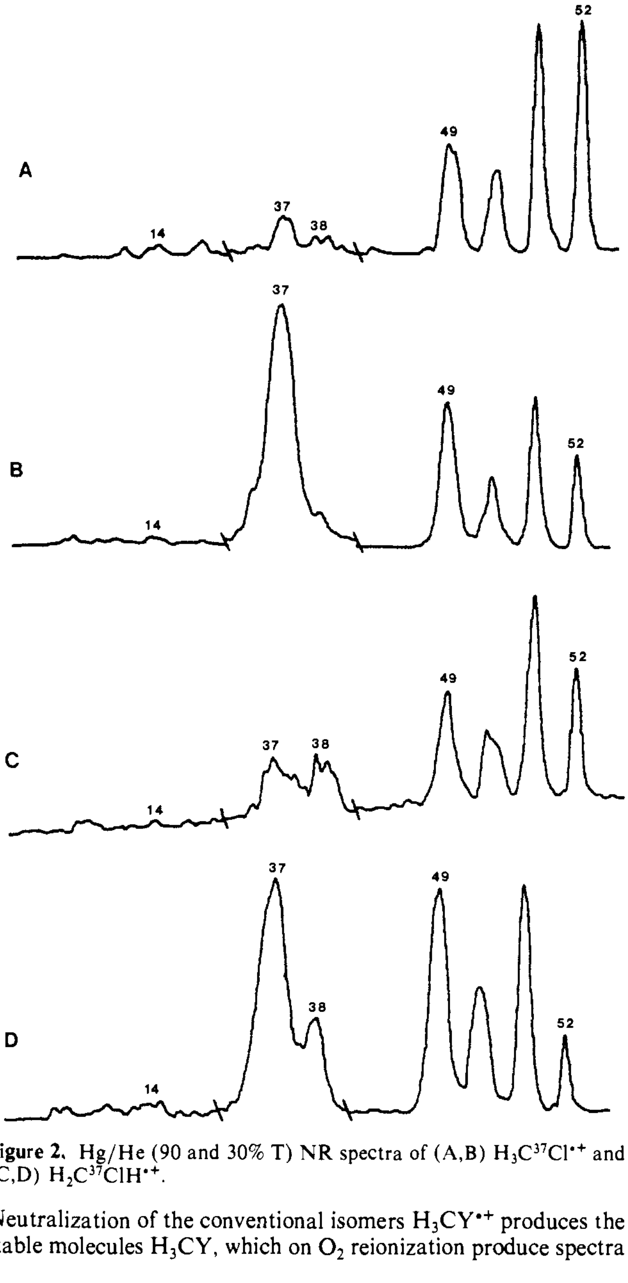

Figure 2. Hg/He (90 and 30% T) NR spectra of (A,B) $H_3C^{37}Cl^{\bullet+}$ and (C,D) $H_2C^{37}ClH^{\bullet+}$.

Neutralization of the conventional isomers $H_3CY^{\bullet+}$ produces the stable molecules H_3CY, which on O_2 reionization produce spectra

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[7] (a) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973. (b) Bowen, R. D.; Barbalas, M. P.; Pagano, F. P.; Todd, P. J.; McLafferty, F. W. *Org. Mass Spectrom.* **1980**, *15*, 51. (c) Holmes, J. L.; Terlouw, J. K.; Burgers, P. C.; Rye, R. T. B. *Ibid.* **1980**, *15*, 149–151.

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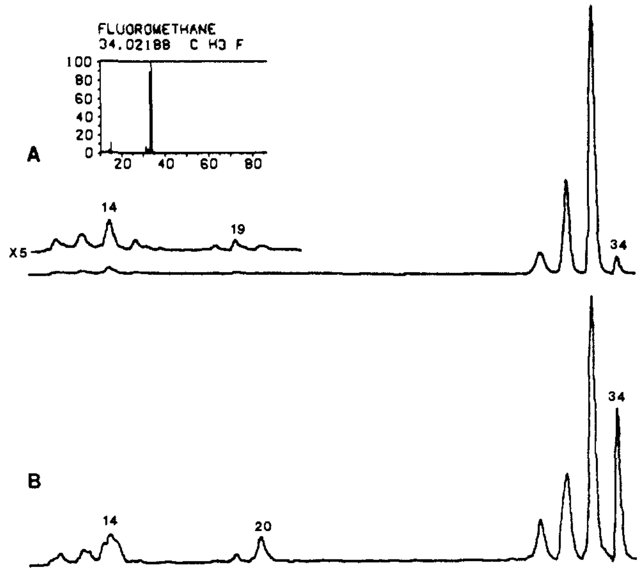

Figure 3. Hg/O_2 (90% T) NR spectra of (A) $H_3CF^{\bullet+}$ and (B) $H_2CFH^{\bullet+}$. Insert is the EI spectrum of fluoromethane.[12]

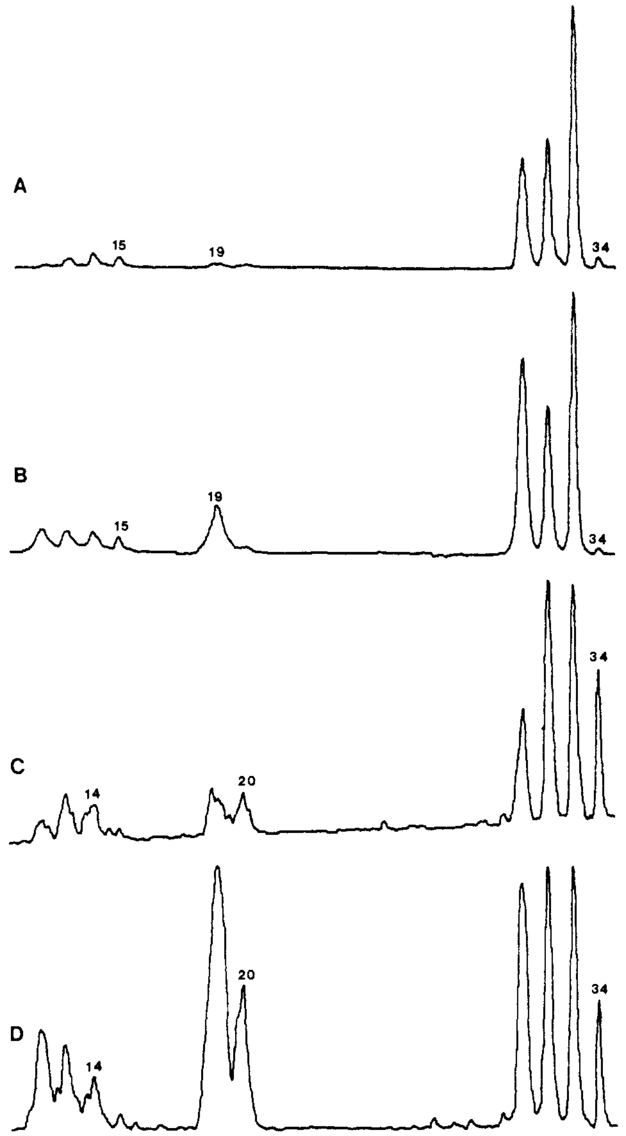

Figure 4. Hg/He (90 and 30% T) NR spectra of (A,B) $H_3CF^{\bullet+}$ and (C,D) $H_2CFH^{\bullet+}$.

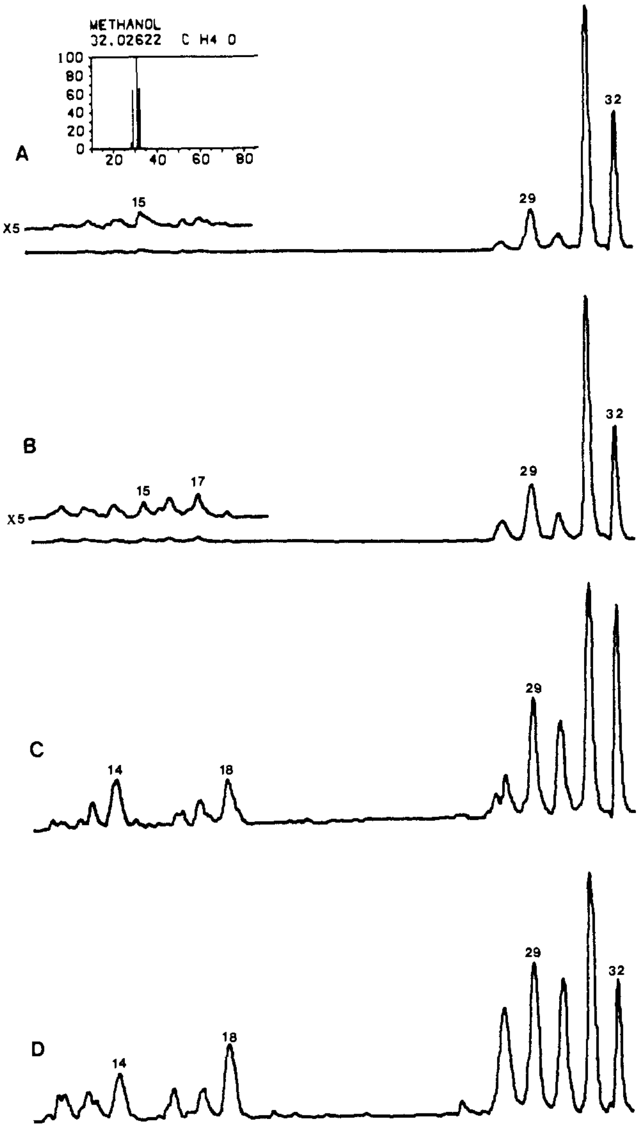

Figure 5. Hg/O_2 (90 and 30% T) NR spectra of (A,B) $H_3COH^{\bullet+}$ and (C,D) $H_2COH_2^{\bullet+}$. Insert is the EI spectrum of methanol.[12]

Table I. Dissociation Product Energies

precursor ($\Delta H_f°$)[a]	dissociation products	$\sum\Delta H_f°$(products)[a] neut, neut[b]	neut, ion[c]	ion, neut
H_3CCl (−19),	$H_3C + Cl$	64	362	290
H_2CClH	$H + H_2CCl$	80	281	394
	$H_2C + ClH$	72	366	312
	$H_2C + Cl + H$	175	474	415
H_3CF (−56),	$H_3C + F$	54	455	280
H_2CFH	$H + H_2CF$	44	252	358
	$H_2C + FH$	29	398	269
H_3COH (−48),	$H_3C + OH$	44	343	270
H_2COH_2	$H + H_2COH$	46	221	360
	$H_2C + OH_2$	36	327	276
H_3CNH_2 (−5),	$H_3C + NH_2$	79	335	305
H_2CNH_3	$H + H_2CNH_2$	88	230	402
	$H_2C + NH_3$	83	317	323

[a] Values in kcal/mol from ref 13. [b] Dissociation of the neutral to yield neutral products. [c] Dissociation of the ionized species to yield the second product (that containing the heteroatom) as an ion.

which are quite similar[5] to the corresponding electron-ionization mass spectra[12] shown as inserts (that for H_3CCl includes the $H_3C^{35}Cl$ isomer; the intensity of CH_3^+ in the NR spectrum is reduced by poor collection efficiency).[5f] The NR spectrum of $H_3CF^{\bullet+}$ (Figure 3A) is the least similar, exhibiting a much smaller molecular ion. The ionization energy (IE) of H_3CF is 48 kcal/mol

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(12) Stenhagen, E.; Abrahamson, S.; McLafferty, F. W. *Registry of Mass Spectral Data*; Wiley-Interscience: New York, 1974.

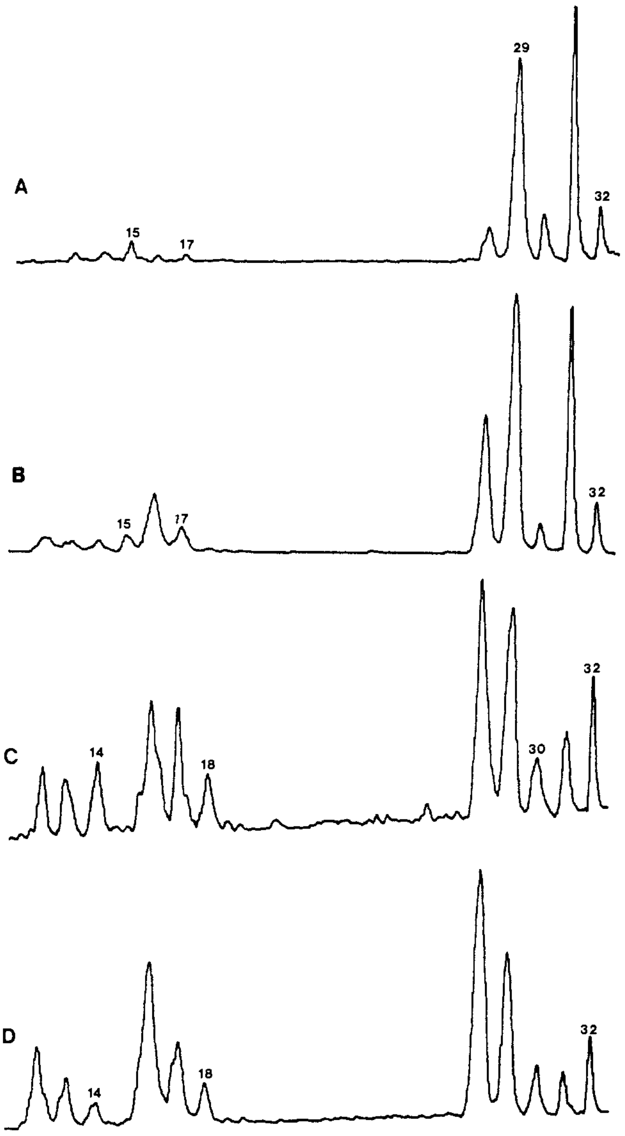

Figure 6. Hg/He (90 and 30% T) NR spectra of (A,B) $H_3COH^{\bullet+}$ and (C,D) $H_2COH_2^{\bullet+}$.

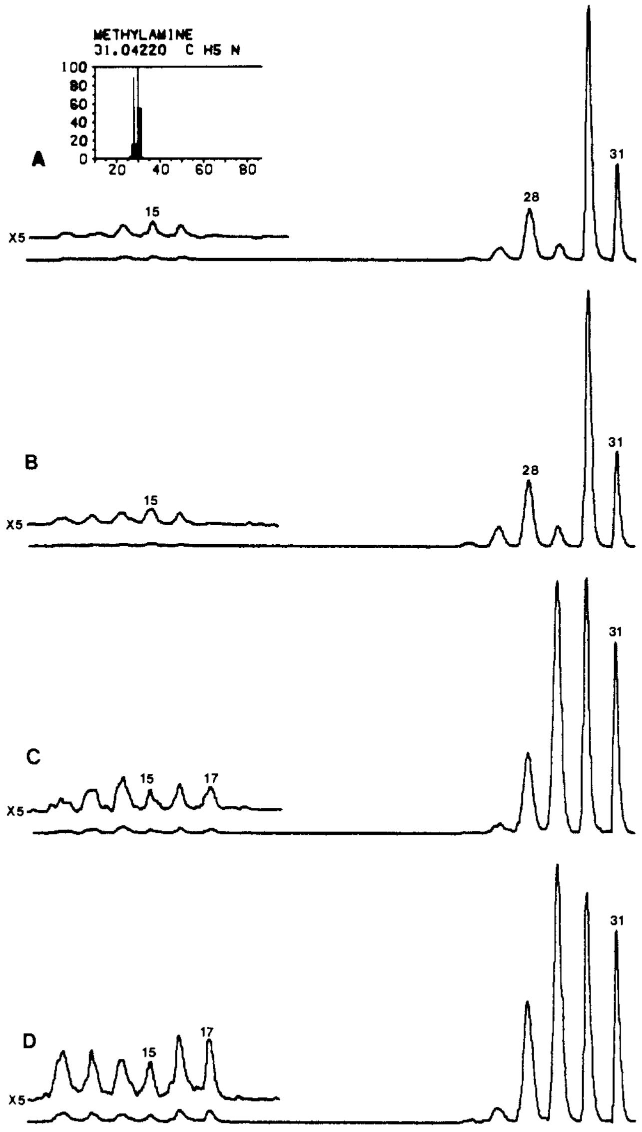

Figure 7. Hg/O_2 (90 and 30% T) of (A,B) $H_3CNH_2^{\bullet+}$ and (C,D) $H_2CNH_3^{\bullet+}$. Insert is the EI spectrum of methylamine.[12]

above that of mercury,[13a] so that charge-exchange neutralization of $H_3CF^{\bullet+}$ would produce H_3CF with internal energies 52 kcal/mol below its lowest dissociation threshold (Table I.)[13a] The corresponding values for H_3CCl, H_3COH, and H_3CNH_2 of 62, 83, and 84 kcal/mol, respectively, indicate that these neutralized products will be more stable. More importantly, IE(H_3CF) $\simeq$ IE(CH_4), indicating that $H_3CF^{\bullet+}$ is produced by removal of a C–H σ electron,[13d,e] which should give a much more unfavorable Franck-Condon factor on neutralization[5h] than formation of H_3CCl, H_3COH, and H_3CNH_2, whose lower IE values indicate ionization of a nonbonding electron. The most abundant product ions are H_2CY^+, corresponding to the lowest energy dissociation of the ionized molecules, and not reionized $H_3C^\bullet$ or $^\bullet Y$ (Table I). This indicates that most fragment ions in the Hg/O_2 NR spectra of these H_3CY (except H_3CF) arise from dissociation after reionization. In Figure 5A,B increasing the O_2 pressure causes a small increase in [OH^+], corresponding to the neutral dissociation $H_3C–OH \rightarrow H_3C^\bullet + {}^\bullet OH$. Such changes are less in the other Hg/O_2 NR spectra, consistent with the previously observed[5f] lower effectiveness of O_2 for CAD of neutrals or ions.

Helium Dissociation of Neutral H_3CY. The Hg/He (90% transmittance, single collisions) NR spectra of the H_3CY isomers show much more fragmentation of the reionized species than do the Hg/O_2 spectra. The substantial increase in $[(M - H)^+]/[M^{\bullet+}]$ is consistent with He reionization producing more excited $H_3CY^{\bullet+}$ than O_2 reionization.[5g] The similarity of the He/CAD and Hg/He NR spectra of $H_3CCl^{\bullet+}$ ions ($[51^+]/[37^+]$ = 8.2 and 6.3, and [38]/[37] = 0.37 and 0.37, respectively) indicates that the product ions of the NR spectra arise mainly from ionic, not neutral, dissociation. Increasing the helium pressure to 30% transmittance conditions (doubling the average number of collisions of species undergoing any collisions)[8] causes a much smaller further increase in $[(M - H)^+]/[M^{\bullet+}]$, but dramatic increases in Cl^+ (but not $HCl^{\bullet+}$) from NR of $H_3CCl^{\bullet+}$ and F^+ from $H_3CF^{\bullet+}$, and significant increases in OH^+ (and O^+) from $H_3COH^{\bullet+}$ and NH_2^+ from $H_3CNH_2^{\bullet+}$. These products must result largely from $H_3C–Y \rightarrow H_3C^\bullet + {}^\bullet Y$, a bond dissociation that, as noted above, is relatively more favorable in the neutral than in the ionized H_3CY species (Table I).[14] The much lower abundance increase in the counterpart product H_3C^+ in the Hg/He (30% transmittance)

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(14) Detailed kinetic studies reported separately (Feng, R.; Wesdemiotis, C.; McLafferty, F. W., to be submitted) using Hg neutralization, dissociation of the neutrals in a separate He collision region, and O_2 reionization confirm that most Cl^+ ions in Figure 2B and HCl^+ ions in Figure 2D result from dissociation of H_3CCl and H_2CClH, respectively.

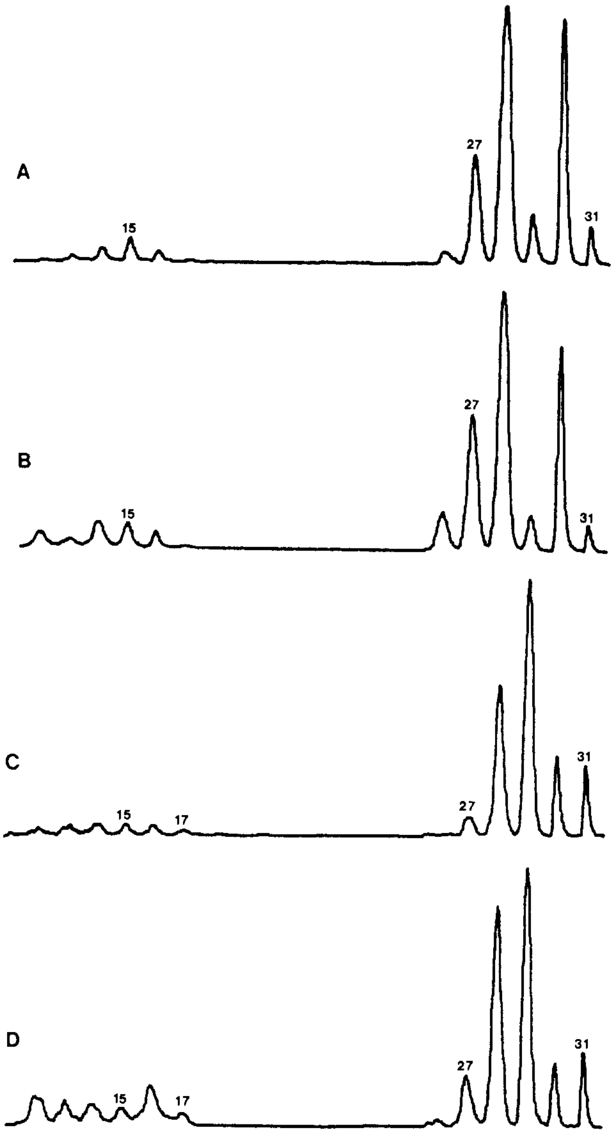

Figure 8. Hg/He (90 and 30% T) NR spectra of (A,B) $H_3CNH_2^{\bullet+}$ and (C,D) $H_2CNH_3^{\bullet+}$.

NR spectra is consistent with the lower reionization efficiency of $H_3C^{\bullet}$ to produce collectible CH_3^{+}.[5g]

Discussion

Methylenechloronium Ylide. In the Hg/O_2 NR spectrum of $H_2C^{37}ClH^{\bullet+}$ (Figure 1B), the reionized molecules (m/z 52) represent 36% of the total ions, nearly half of that found for $H_3CCl^{\bullet+}$ in Figure 1A.[15] The proportion of neutrals that are undissociated at ionization must be substantially higher than this, as product ions are also formed after reionization. These molecular ions could be H_3CCl formed by the isomerization of H_2CClH (**1**).[3g,5b] The Franck–Condon factor for formation of **1** by neutralization should not be particularly favorable. Further, the ab initio calculations of Radom and co-workers[3g] indicate that the energy of **1** is nearly identical with the sum of energies of its dissociation products H_2C: + ClH. However, this is 8 kcal/mol *above* that of $H_3C^{\bullet}$ + $^{\bullet}Cl$ (Table I); this predicts that any H_3CCl^{*} formed by isomerization of **1** would rapidly dissociate to $H_3C^{\bullet}$ + $^{\bullet}Cl$, inconsistent with $(CClH_3)^{\bullet+}$ as the most abundant peak in Figure 1B. If some of this peak arises from H_3CCl molecules that survive undissociated until reionization, then the energy of the $H_2CClH \rightarrow H_3CCl$ isomerization barrier must be *below* that for $H_3C–Cl \rightarrow H_3C^{\bullet} + {}^{\bullet}Cl$, and the energy of **1** would be at least 8 kcal/mol below the dissociation energy for $H_2CClH \rightarrow H_2C$: + ClH.

The Hg/O_2 NR spectrum of **1** also shows a significant $HCl^{\bullet+}$ peak. The predominant formation of DCl^{+} in the NR spectrum of $H_2CClD^{\bullet+}$ demonstrates[5b] that this loss occurs mainly before isomerization (although the loss could occur immediately after formation of **1**). Formation of HCl from H_2CClH is energetically the most favorable dissociation by 8 kcal/mol (Table I), while both the Hg/O_2 and Hg/He spectra of $H_3CCl^{\bullet+}$ (Figures 1A and 2A,B) show that HCl formation from H_3CCl is unfavorable (as is that from $H_2CCl^{\bullet}$; in the Hg/He NR spectrum of H_2CCl^{+}, $[Cl^{+}]/[HCl^{\bullet+}] = 8$). The Hg/He NR spectrum of $H_2CClH^{\bullet+}$ under single collision conditions of helium pressure (Figure 2C) shows abundances of $HCl^{\bullet+}$ and Cl^{+} comparable to those of the Hg/O_2 spectrum (Figure 1B), but with substantially increased H loss from the expected[5g] (Figure 2A vs. 1A, and the CAD spectrum of $H_2CClH^{\bullet+}$) increase in fragmentation of reionized $(CClH_3)^{\bullet+}$. Increasing the helium pressure (Figure 2D) increases the abundance of $HCl^{\bullet+}$, relative to that of $(CClH_3)^{\bullet+}$, by a factor of 3. This HCl must have come mainly from ylide **1** molecules[14] which have survived for $\sim 10^{-6}$ s, as the double differential pumping system causes most collisions to occur close to the helium collision beam.

The amounts of the neutral products 10^{-6} s after $H_2CClH^{\bullet+}$ neutralization can be estimated from the increase in [HCl] with increasing He pressure. First, [HCl] due to fast unimolecular dissociation of newly formed **1** is estimated: the Hg/He (90% T) NR spectrum of $H_2C^{37}ClH^{\bullet+}$ (Figure 2C) shows abundance (vs. total ions) values of [m/z 38] = 8.7% and [m/z 37] = 8.9%; based on [m/z 38]/[m/z 37] = 1.33 for the Hg/He (90% T) NR spectrum of $HCl^{\bullet+}$, [HCl] = 8.7% + 8.7%/1.33 = 15.2% and [$Cl^{\bullet}$] = 8.9% − 8.7%/1.33 = 2.4%, assuming equal reionization efficiencies for HCl and Cl.[5g] Based on the absolute values of [m/z 38] from the Hg/He (90% T and 30% T) spectra of $HCl^{\bullet+}$, the contribution of the HCl formed by unimolecular dissociation of **1** to m/z 38 in the 30% transmittance Hg/He NR spectrum of $H_2CClH^{\bullet+}$ is 5.0% (vs. total ions) of the observed 9.5% m/z 38. Similarly, based on [m/z 38]/[m/z 37] = 0.83 for the Hg/He (30% T) spectrum of $HCl^{\bullet+}$, the unimolecular HCl and $Cl^{\bullet}$ products represent 8.2% of the 23% m/z 37. Thus the remaining 4.5% m/z 38 and 15% m/z 37 should represent 4.5% + 4.5%/1.33 = 8% HCl and 15% − 4.5%/1.33 = 11% $Cl^{\bullet}$ produced by the dissociation of the $CClH_3$ isomers in the one extra collision (1.06 → 2.1 collisions, on average) from increasing the helium pressure. The increased helium pressure also causes the abundance changes [H_2CCl^{+}], 31% → 22%; [$HCCl^{\bullet+}$], 11% → 12%; and [CCl^{+}], 17% → 22%, which should arise mainly from dissociation after reionization (Table I). These values are comparable to those from the Hg/He (90 and 30% T) NR spectra of $H_3CCl^{\bullet+}$. The CS data (vide infra) indicate ~15% $H_2CCl^{\bullet}$ formation, which would contribute mainly to the [Cl^{+}] value. We conclude that the major products from neutral dissociation caused by the increased helium pressure are HCl and $Cl^{\bullet}$ formed in nearly equal amounts. This indicates that **1** is the more abundant $CClH_3$ isomer present 10^{-6} s after formation, as substantially less energy is required for the CAD formation of $Cl^{\bullet}$ from the isomerized H_3CCl molecules than of HCl from **1**, and CAD of **1** could also produce $Cl^{\bullet}$ through further isomerization.

This evidence for the stability of **1** also conflicts directly with the charge-stripping (CS)[7] data of Holmes and co-workers,[5e] who found the CS/NR (Xe/He) spectrum of m/z 52 ions from $ClCH_2COOH^{\bullet+}$ to be closely similar to both the CS/CAD and CS/NR spectra of $H_3C^{37}Cl^{\bullet+}$, with $(C^{37}ClH_3)^{2+}$ absent. The latter is characteristic of the ylide ion $H_2C{=}ClH^{2+}$, as the isomeric H_3CCl^{2+} is unstable.[4c,d] Our similar experiments using $(C^{35}ClH_3)^{\bullet+}$ (m/z 50, containing <1% $CH^{37}Cl^{\bullet+}$)[16] and O_2 reionization for increased sensitivity gave the Hg/O_2 (30% T) CS/NR spectra of Figure 9 and O_2 (30% T) CS/CAD spectra of Figure 10. For stable species NR and CAD spectra are usually

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[15] The yield of neutral products from $H_2CClH^{\bullet+}$ using Hg is 50% of that from $H_3CCl^{\bullet+}$, consistent with IE(**1**) ≪ IE(Hg). The absolute yield of m/z 52 from NR of $H_2CClH^{\bullet+}$ is ~6% of that from $H_3CCl^{\bullet+}$.

[16] The NR mass spectra of ^{37}Cl and ^{35}Cl isotopomers are identical within experimental error.

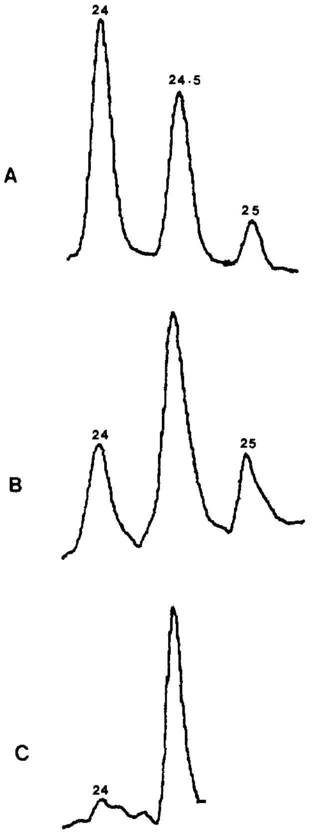

Figure 9. Charge-stripping region of Hg/O_2 (30% T) NR spectra of (A) $H_3CCl^{•+}$, (B) $H_2CClH^{•+}$, and (C) H_2CCl^+. Peak heights of *m/z* 24.5 relative to those of the reionized precursor are (A) 0.025%, (B) 0.11%, and (C) 0.29%.

quite similar,[5] as shown by those of H_2CCl^+ (Figures 9C and 10C). The Figure 10 CAD spectra show the characteristic differences noted earlier,[4c,d] with the dominant formation of $HCCl^{2+}$ (*m/z* 24) from $H_3CCl^{•+}$ and $(CClH_3)^{2+}$ from $H_2CClH^{•+}$. The CS/NR data from reionization of H_3CCl (Figure 9A) are explicable as a combination of the CS/CAD spectra of $H_3CCl^{•+}$ and H_2CCl^+ (Figure 10A,C), consistent with formation from neutral H_3CCl of ~10% $H_2CCl^•$ (corrected for relative ionization cross sections).[17] However, in the CS/NR spectrum of $H_2CClH^{•+}$ (Figure 9B), the abundance of $(CClH_3)^{2+}$, *m/z* 25, relative to that of *m/z* 24, has clearly increased, confirming that a significant proportion of **1** ions have not isomerized in the ~10^{-6} s between formation and reionization. Presumably the previous report[5e] that the "*m/z* 26 ... is absent" resulted from lower sensitivity. Calculations using the Figure 10 CAD spectra as references, including relative ionization efficiencies,[17] indicate that H_2CClH, H_3CCl, and $H_2CCl^•$ present at reionization have relative concentrations of ~3:2:1, supporting the $[H_2CClH]/[H_3CCl]$ value derived above.

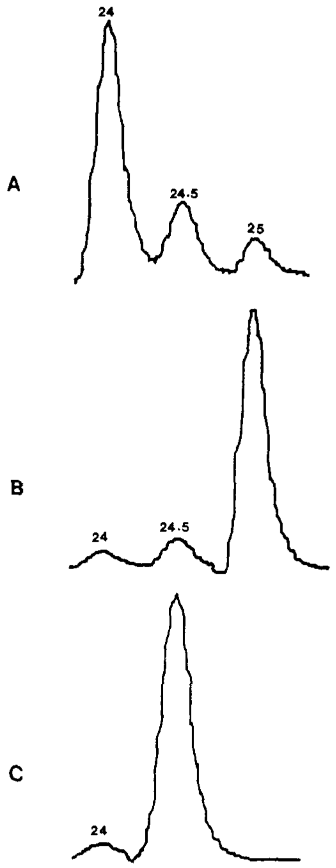

Figure 10. Charge-stripping region of CAD spectra (O_2, 30% T) of (A) $H_3CCl^{•+}$, (B) $H_2CClH^{•+}$, and (C) H_2CCl^+. Base peak heights relative to those of the precursor ions are (A) 0.011%, (B) 0.071%, and (C) 0.054%.

The proportion of H_2CClH molecules which are still undissociated after 10^{-6} s can also be estimated. Increasing the helium pressure (90% T → 30% T) increases the dissociation products HCl and Cl• from 5.0% + 8.2% = 13.2% to 9.5% + 23% = 32.5%. Because this yield has more than doubled, and because 7.4% molecular ions are still undissociated at 30% T, before the pressure increase much less than half the $CClH_3$ molecules must be undissociated. Of these (vide supra) somewhat less than half have isomerized to H_3CCl ($\Delta H_f = -19$ kcal/mol).[13] The lowest energy dissociation of the latter yields products whose sum of energies is 64 kcal/mol, so that energies of **1** molecules formed by neutralization should be well below this value. Also the energies of the observed stable **1** molecules could be substantially above that of ground state **1**; the H_2C–ClH bond is predicted[3g] to be much longer in the neutral than in the ion, so that vertical neutralization would have a high probability of producing energetically excited **1**. Ab initio calculations[3g] predict $\Delta H_f(\mathbf{1}) = 83$ kcal/mol and an insignificant barrier for **1** dissociation. For these predictions to be correct, both the H_2CClH and H_3CCl observed after 10^{-6}s must represent unusually long-lived metastable states, suggesting that these calculations overestimate ΔH_f values for such hypervalent species.

Methylenefluoronium Ylide. No energy surface minimum is predicted[3c] for H_2CFH (**2**), for which the d-orbital stabilization of **1** is not possible. However, the NR mass spectra (Figures 3 and 4) again give convincing evidence of substantial energy barriers to the isomerization and dissociation of **2**. The Hg/O_2 NR spectrum of $H_2CFH^{•+}$, in contrast to that of $H_3CF^{•+}$, gives $(CFH_3)^{•+}$ as the second most abundant peak. The energy of $H_2CFH^{•+}$ is 11 kcal/mol less than that of $H_3CF^{•+}$,[4] so that Hg neutralization followed by isomerization would give a much higher proportion of H_3CF neutrals below their lowest dissociation barrier (vide supra). For the Hg/He NR spectra (Figure 4) from $H_3CF^{•+}$ (or from H_2CF^+, not shown), increasing the helium pressure to 30% transmittance gives a barely measurable HF^+ (*m/z* 20) peak, but for $H_2CFH^{•+}$ this gives a dramatic increase in HF^+ abundance. Formation of F• from H_3CF is competitively less favorable than that of Cl• from H_3CCl (Table I and Figure 2B), so that the base *m/z* 19 peak representing F atoms probably arises largely by the dissociation of **2**, either directly or through HF. Increasing the He pressure also increases $[CH_2^{•+}]$ (which is greater than $[CH_3^+]$) for Figure 4D, but not 4B, consistent with the presence of H_2CFH. Theory[3c] did find an energy minimum for the isomer H_2C–H–F, but vertical neutralization to its ground state from $H_2CFH^{•+}$ should be relatively unfavorable.

Methyleneoxonium Ylide. Higher level theory[3c] predicts no minimum in the energy surface of H_2COH_2 (**3**), but again the

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[17] Equal intensities of the neutral beams produced from $H_2CClH^{•+}$, $H_3CCl^{•+}$, and H_2CCl^+ (which include neutral products from the spontaneous dissociation of H_2CClH, H_3CCl, and H_2CCl) give a total yield of 0.0011, 0.0030, and 0.0073%, respectively, of the doubly charged ions *m/z* 24, 24.5, and 25 after reionization. The total yields based on the precursor *ions* are 0.000023, 0.00012, and 0.00033%, respectively.

NR mass spectra (Figures 5 and 6) indicate otherwise. With $H_2COH_2^{\bullet+}$, increasing the O_2 pressure increases $[H_2C^{\bullet+}]$ and $[OH_2^{\bullet+}]$, relative to $[(COH_4)^{\bullet+}]$, without increasing $[H_3C^+]$. This strongly supports a nearly 10^{-6} s lifetime for a significant portion of the **3** neutrals. Increasing the He pressure (Figure 6) also causes dissociation of the primary neutral products H_2C:, $^{\bullet}OH$, OH_2, and CH_nO, but the Figure 6D data are still also consistent with the stability of **3**. The losses of H_2 and $2H_2$ (*m/z* 30, 28) appear favored in the ylide spectra, possibly because they can occur in the reionized $H_2COH_2^{\bullet+}$ (and/or **3**) via symmetry-allowed[18] 1,1-H_2 losses.

Methyleneammonium Ylide. Theory[3c] finds the energies of H_2CNH_3 (**4**) to be 11 and 13 kcal/mol, respectively, below the energies of the products H_2C: + NH_3 and of the barrier for rearrangement to H_3CNH_2. This indicated stability is supported by the NR mass spectra of Figures 7 and 8. Only $H_2CNH_3^{\bullet+}$ gives an appreciable $NH_3^{\bullet+}$ (*m/z* 17) peak, and this triples in height with the increased O_2 pressure. Increased He pressure increases $NH_3^{\bullet+}$, but also appears to cause dissociation to NH_2^+. Multiple O_2 collisions also increase *m/z* 29, which could arise by a symmetry-allowed[18] 1,1-H_2 loss from **4**. The H_2 loss from $H_2CNH^{\bullet+}$ must be associated with a significant isotope effect. In the Hg/O_2 (30% T) spectrum of $H_2CND_3^{\bullet+}$ (from $DOCH_2CH_2ND_2$) the reionized precursor (*m/z* 34) becomes the base peak, and *m/z* 33 ($H^{\bullet}$ loss) the most intense fragment (99%); the abundances of the ions at *m/z* 32 ($H_2/D^{\bullet}$ losses), 31 (HD loss), 30 (D_2 loss), and 20 ($ND_3^{\bullet+}$) are 67, 28, 40, and 53% of the base peak abundance, respectively. Very similar isotope effects and peak shifts are observed in the CAD spectrum of $H_2CND_3^{\bullet+}$ vs. that of $H_2CNH_3^{\bullet+}$.[19]

Conclusions

The unique capability of NRMS for preparation and study of unusual neutral species has been utilized to demonstrate the surprising stability of the simple ylides H_2CYH, **1**–**4**. Unless these represent metastable states of unusually long lifetimes, this indicates that ab initio calculations overestimate ΔH_f values for such hypervalent species. A better understanding of the (H_2C)–(YH) bonding underlying this stability could be valuable in optimizing syntheses involving ylide intermediates.

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(19) Although CAD (O_2) charge stripping of $H_2CNH_3^{\bullet+}$ produces $H_2CNH_3^{2+}$ (*m/z* 15.5) in significant abundance (1% of the $H_2CNH^{\bullet+}$ base peak),[20] it cannot be observed in the Hg/O_2 NR mass spectrum because of the concomitant presence of intense ions at *m/z* 15 and 16 from the neutral dissociation of H_2CNH_3 to H_2C + NH_3; the abundance of *m/z* 15 and 16 under maximum sensitivity conditions (Figure 7D) are 4 and 7% of the reionized precursor abundance, respectively, obscuring any CS ions present whose intensities are substantially smaller. Similar circumstances prevent the detection of CS ions in the NR spectra of $H_2COH_2^{\bullet+}$. In the Hg/O_2 NR mass spectrum of $H_2CND_3^{\bullet+}$, [*m/z* 17] is 2.5% of the reionized precursor abundance (*m/z* 34) and flanked by [*m/z* 16] and [*m/z* 18] of 33 and 45%, respectively; $H_2CND_3^{2+}$ *m/z* 17 might also be NHD^+ and/or CHD_2^+.

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Two-Step Laser Excitation Fluorescence Study of the Ground- and Excited-State Proton Transfer in Alcohol Solutions of 7-Hydroxyisoflavone

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Abstract: The intermolecular excited-state proton transfer and relaxation processes to the parent molecule were investigated for the alcohol solutions of 7-hydroxyisoflavone (7-HIF) by means of nanosecond and two-step laser excitation (TSLE) fluorescence spectroscopies. The large Stokes shifted fluorescence spectra (λ_{max} 470–480 nm) were observed in methanol, ethanol, and propanol solutions of 7-HIF at room temperature to ~180 K. The fluorescence spectra consist of two component decays which were ascribed to two types of excited-state tautomers generated by the excited-state proton transfer in the intermolecularly hydrogen bonded 7-HIF with two alcohol molecules (1:2 H-bonding). The TSLE fluorescence including a variable delay technique demonstrates that the short- and long-lived ground-state tautomers are involved in the relaxation processes of the above excited-state tautomers. From the determination of lifetimes of the ground-state tautomers at various temperatures, the reaction rate and apparent activation energies of the reverse proton transfer from these two types of tautomers to the parent molecule were obtained for 7-HIF in comparison with those for 7-hydroxyflavone (7-HF), which exhibits the similar excited-state proton transfer and relaxation processes as reported in the previous paper.

In the inter- and intramolecular hydrogen bonding systems, the excited-state proton transfer to afford a so called excited-state tautomer takes place exhibiting characteristic large Stokes shifted fluorescence spectra.[1-7] Various nano- and picosecond fluorescence studies on the dynamic processes of the excited-state proton transfer and relaxation have been reported.[3-8] However, no concrete evidence of the existence of the ground-state transient, "the ground-state tautomer", was reported in the relaxation of the excited-state tautomer to the recovery of the parent molecule

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