hydrogen-bonded C=O group in uracils.[22] The bending mode of the NH_2 group is assigned to a shoulder on the main band in the spectrum of solid, at 1640 cm^{-1} or possibly at 1700 cm^{-1}. Frequencies of the other bands observed in the IR spectrum of cytosine as a crystalline solid, together with the assignment of these bands to the normal modes of vibration for the a–o tautomer, are summarized in Table III. As may be seen in this table and also in Figure 4, the frequencies of most of the lower frequency modes, with the exception of those related to the bending vibrations of the N1H and NH_2 groups, are not very strongly affected by the interactions that occur between cytosine molecules in the crystal.

Conclusions

The main conclusions from the present study are outlined as follows.

1. Ab initio molecular orbital calculations have been made with a 3-21G basis set at the SCF level for the infrared spectra (vibrational frequencies, intensities, and potential energy distributions (PEDs)) for two tautomers of cytosine (i.e., the amino–oxo and amino–hydroxy forms) and for their deuteriated analogues.

2. Comparison of the calculated and experimental matrix spectra confirms the existence of both the amino–oxo and the amino–hydroxy tautomeric forms of cytosine, and of its deuteriated analogue, when they are isolated in the matrices and allows us to determine the ratio of the concentrations of each form (the "equilibrium constant" for tautomerization) in Ar and N_2 matrices.

3. Furthermore, this comparison permits an initial assignment of the absorption bands in the spectrum of cytosine from each tautomer.

4. Our study has verified the effect of UV irradiation on the relative concentrations of tautomers in matrix-isolated samples of cytosine and N-deuteriated cytosine that has been observed earlier by Nowak.[37] We have been able to utilize this effect to change the ratio of tautomers in our sample and hence to use the subtraction routine of the Nicolet spectrometer to obtain experimentally separated spectra for each tautomer.

5. When frequencies *and intensities* from these separated spectra are compared with the calculated spectra, we have been able to assign with confidence most of the spectrum of each tautomer. The reasonable agreement between the calculated and experimental spectra leads to the conclusion that the calculated force constants and intensity parameters (APTs) for each tautomer form a reasonably good starting point for the experimental values of these parameters.

6. Finally, we have examined the drastic change of the tautomeric equilibrium toward the amino–oxo form and the change of the infrared spectrum for the strongly self-associated cytosine in the crystalline solid compared with cytosine isolated in the Ar matrix. The weaker interaction with an N_2 matrix does not change tautomeric equilibrium significantly, but it does affect the vibrational frequencies and intensities of the normal modes of each tautomer, particularly those of the N1H and OH stretching modes.

Acknowledgment. We thank Dr. M. J. Nowak (Warsaw) for his remarks concerning the UV irradiation procedure based on the yet unpublished results of matrix studies of pyrimidine bases including cytosine. This investigation was supported by NIH Research Grant No. 32988 with additional partial support provided by grants from the Polish Ministry of National Education Project No. CPBP 01.06 (J.S.K.) and No. CPBR 11.5 (M.S.).

Registry No. Cytosine (amino-oxo form), 71-30-7; cytosine (amino-hydroxy form), 66460-21-7.

Supplementary Material Available: Tables of optimized (3-21G) geometries (Table 4), symmetry coordinates for the description of vibrational modes (Table 5), diagonal elements of force constants matrix (Table 6), and atomic polar tensors and their invariants (Table 7) for cytosine tautomers and Figure 5 with definition of internal coordinates (6 pages). Ordering information is given on any current masthead page.

Experimental Evidence for the Existence of Ionized and Neutral Fluorohydroxymethylene (FCOH) in the Gas Phase[†]

Detlev Sülzle, Thomas Drewello, Ben L. M. van Baar,[‡] and Helmut Schwarz*

Contribution from the Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, West Germany. *Received March 25, 1988*

Abstract: The elusive ionic and neutral fluorohydroxymethylenes (FCOH) are accessible in the gas phase by dissociative ionization of methyl fluoroformate followed by neutralization of $FCOH^{\bullet+}$ with xenon. The experimental findings are supported by high-level ab initio MO calculations (MP2/6-31G**//MP2/6-31G** + ZPVE). Both FCOH and $FCOH^{\bullet+}$ are separated by significant barriers from their respective formyl fluoride isomers.

Although fluorohydroxymethylene (**1**) is predicted[1] by ab initio molecular orbital (MO) calculations to be prevented by a significant barrier from its isomerization to the global minimum of the [H,C,O,F] potential energy surface, i.e., formyl fluoride (**2**), all attempts failed to generate **1** as a stable species in solution. In view of the high reactivity[2,3] of most carbenes towards addition and insertion reactions, the prospects of ever generating stable fluorohydroxymethylene[4] in the condensed phase are indeed quite remote. In contrast, in the absence of any intermolecular reactions and because of the high barrier of the process **1** → **2** (E_0 = 40 kcal/mol[1]), elusive **1** should be accessible by performing appropriate experiments in the gas phase. We describe here the results of a mass spectrometric investigation using the powerful method

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[†] Dedicated to Professor J. H. Beynon FRS on the occasion of his 65th birthday.

[‡] Permanent address: Organic Chemistry Department, The Free University of Amsterdam, NL-1081HV Amsterdam, The Netherlands.

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(4) According to MO calculations using the minimal STO-3G basis set, **1** is predicted to be a singlet carbene being 23.7 kcal/mol more stable than its triplet form: Mueller, P. H.; Rondan, N. G.; Houk, K. N.; Harrison, J. F.; Hooper, D.; Willen, B. H.; Liebman, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 5049

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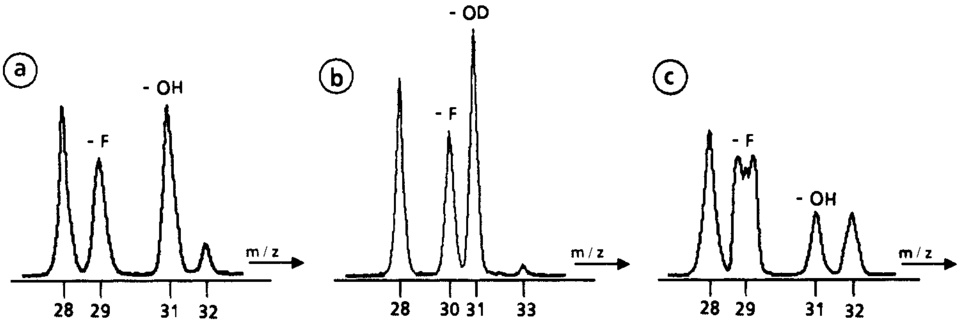

Figure 1. Partial CID Mass Spectra (*m*/*z* 28–33) of (a) $FCOH^{\bullet+}$ ($\mathbf{1}^{\bullet+}$), (b) $FCOD^{\bullet+}$ ($\mathbf{1a}^{\bullet+}$), and (c) $HCOF^{\bullet+}$ ($\mathbf{2}^{\bullet+}$).

of neutralization–reionization mass spectrometry (NRMS).[5] In this experiment a beam of solitary, structurally characterized ions m_1^+ is first neutralized to m_1; reionization of the beam of the neutral m_1 survivor, followed by dissociation, may then be used to characterize m_1. By applying this technique, many exciting neutral species could indeed be generated and characterized in the gas phase,[5] most of which are unknown to exist in the condensed phases. With regard to the detection of elusive carbenes using NRMS, McLafferty and co-workers recently described[6] the gas-phase synthesis of hydroxycarbene (HCOH) and its higher homologue, hydroxyethylidene (CH_3COH).

Our experimental findings on **1**, its cation radical $\mathbf{1}^{\bullet+}$, and the isomers **2** and $\mathbf{2}^{\bullet+}$ are supported by high-level ab initio MO calculations, executed at the MP2/6-31G**//MP2/6-31G** + ZPVE level of theory.

Experimental and Theoretical Section

The mass spectrometric experiments were performed using a VG Instruments ZAB-HF-3F mass spectrometer.[7] This is a triple-sector instrument of BEB configuration (B stands for magnetic and E for electric sector). Ions are generated by 70-eV electron impact ionization of the corresponding neutrals under the following conditions: ion trap current 100 μA; accelerating voltage, 8 kV; ion source temperature, 200 °C. Collision-induced dissociations, CID,[8] used to characterize the primary ions m_1^+ were brought about by mass-selecting a beam of m_1^+ by means of B(1)E and colliding it in the third field-free region with helium (80% transmittance, *T*; this transmittance corresponds on the average to 1.1–1.2 collisions[9]). Ionic dissociation products were recorded by scanning B(2). NRMS experiments were performed in the second field-free region. To this end a beam of m_1^+, mass-selected by B(1), was neutralized in the first cell of a differentially pumped tandem collision cell by colliding it with either oxygen or xenon ($T = 90\%$). Residual ions were deflected away from the beam of neutral m_1 by putting a charge on a deflector electrode; subsequent reionization of m_1 occurred in the second collision cell by collision with oxygen or helium ($T = 80\%$). The mass spectrum of the resulting m_1^+ and its fragments were recorded by scanning E. The minimal lifetime *t* (identical with the transit time from collision cell I to cell II) is in the present experiment ≈ 0.5 μs. In most experiments approximately 20 scans were accumulated using the VG 11/250 data system.

Formyl fluoride, methyl fluoroformate (FCO_2CH_3), and its D_3-labeled analogue (FCO_2CD_3) were synthesized according to ref 10.

All computations have been performed using the CRAY-XMP version of the GAUSSIAN 82 series of programs.[11] Open-shell species were treated in the unrestricted and closed-shell species in the restricted Hartree–Fock formalism. The geometries were fully optimized with the polarized 6-31G** basis set,[12] using analytical gradient techniques. The effects of electron correlation were taken into account by Møller–Plesset calculations (MP) terminated at the second order (MP2).[13] All stationary points have been characterized to correspond either to local minima or transition structures by having zero or one negative eigenvalue(s) in the numerical evaluated force constant matrix, respectively. Zero-point vibrational energies (ZPVE) have been calculated from the MP2/6-31G** harmonic normal frequencies. For their inclusion in the calculation of relative energies they were scaled by a factor of 0.93 in order to account for the errors due to the harmonic approximation.[14] Total (in hartrees) and relative energies (in kcal/mol) are listed in Table I (for the open shell) and Table II (for the closed-shell system). For the latter, in

Table I. Total Energies, Zero-Point Vibrational Energies (ZPVE), Relative Energies (in kcal/mol), and $\langle \hat{S}^2 \rangle$ Expectation Values for $[H,C,F,O]^{\bullet+}$ Species

species	MP2/6-31G**// MP26-31G**, hartrees	ZPVE, kcal/mol	E_{rel}, kcal/mol	$\langle \hat{S}^2 \rangle$
$\mathbf{2}^{\bullet+}$	−212.788 880	13.1	0	0.767
TS $\mathbf{1}^{\bullet+}/\mathbf{2}^{\bullet+}$	−212.727 670	9.6	35.2	0.793
Z-$\mathbf{1}^{\bullet+\,a}$	−212.804 058	13.0	−9.6	0.760
TS Z-$\mathbf{1}^{\bullet+}/E$-$\mathbf{1}^{\bullet+}$	−212.786 208	11.5	0.2	0.757
E-$\mathbf{1}^{\bullet+\,a}$	−212.810 844	13.2	−13.7	0.758
$HF + CO^{\bullet+}$	−212.713 119	10.1	44.8	0.941
$HF^{\bullet+} + CO$	−212.656 178	7.5	78.1	0.754
$HO^{\bullet} + CF^+$	−212.648 340	8.1	83.5	0.755
$HO^+ + CF^{\bullet}$	−212.387 735	6.6	245.7	0.759
$H^{\bullet} + FCO^+$	−212.752 565	6.8	16.9	0.750
$H^+ + FCO^{\bullet}$	−212.574 492	5.3	127.3	0.776
$F^{\bullet} + HCO^+$	−212.761 356	10.2	14.6	0.753
$F^+ + HCO^{\bullet}$	−212.278 450	8.5	316.0	0.765
$F^{\bullet} + COH^+$	−212.689 668	8.5	58.0	0.753
$F^+ + COH^{\bullet}$	−212.203 974	8.8	363.0	0.759

[a] The prefixes *Z* and *E* refer to the configuration of $\mathbf{1}^{\bullet+}$ around the C–O bond.

Table II. Total Energies, Zero-Point Vibrational Energies (ZPVE), Relative Energies, and $\langle \hat{S}^2 \rangle$ Expectation Values for $[H,C,\dot{F},O]$ Species

species	MP2/6-31G**// MP26-31G**, hartrees	ZPVE, kcal/mol	E_{rel}, kcal/mol	$\langle \hat{S}^2 \rangle$
2	−213.236 987	13.4	0	
TS **1**/**2**	−213.103 642	9.3	79.9	
Z-**1**	−213.158 071	12.7	48.9	
TS Z-**1**/E-**1**	−213.124 247	11.1	68.6	
E-$\mathbf{1}^a$	−213.158 291	13.0	49.0	
HF + CO	−213.224 873	9.0	3.5	
triplet **1**	−213.073 019	12.3	101.9	2.008
$HO^{\bullet} + CF^{\bullet}$	−212.965 269	7.4	164.9	0.755/0.759
$H^{\bullet} + FCO^{\bullet}$	−213.072 725	5.3	95.5	0.750/0.776
$F^{\bullet} + HCO^{\bullet}$	−213.037 106	8.5	120.9	0.753/0.765
$F^{\bullet} + COH^{\bullet}$	−212.962 630	8.8	167.9	0.753/0.759

[a] See footnote in Table I.

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(12) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

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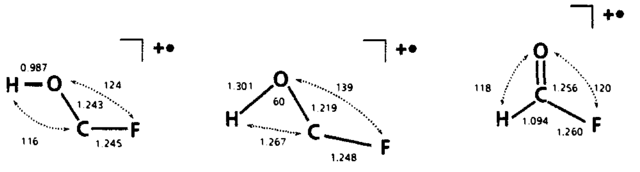
Chart I. Bond Lengths (in Å) and Bond Angles (in Degrees) of **1**$^{\bullet+}$, **2**$^{\bullet+}$, and TS **1**$^{\bullet+}$/**2**$^{\bullet+}$ [a]



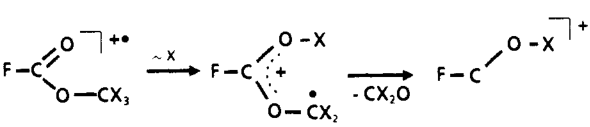
1$^{+\cdot}$ TS **1**$^{+\cdot}$/ **2**$^{+\cdot}$ **2**$^{+\cdot}$

[a] All species have C_s symmetry.

particular, for species **1** and **2**, there exists excellent agreement with the data reported in ref 1.[15] We also note the very good agreement between our theoretically calculated and the experimentally determined[17] geometry (given in parentheses in Chart II) of neutral HCOF (**2**). In order to estimate the problem of spin contamination, which might be due to the deficiencies of the UMP2 procedure, we have calculated the $\langle \hat{S}^2 \rangle$ values. The data given in Tables I and II are excellent, except for CO$^{\bullet+}$ which, however, is known as a notorious case.[16] Optimized geometries (bond length in Å, bond angles in degrees) of the species of interest are given in Chart I.

Results and Discussion

The cation radical **1**$^{\bullet+}$ is easily accessible by dissociative ionization of methyl fluoroformate[10] presumably via an intermediate distonic ion,[18] its deuterium analogue **1a**$^{\bullet+}$ by loss of CD_2O from ionized FCO_2CD_3; the cation radical **2**$^{\bullet+}$ was generated by 70-eV ionization of formyl fluoride (**2**)[10] (eq 1). That **1**$^{\bullet+}$ and **2**$^{\bullet+}$ do not interconvert is clearly indicated by their distinct collision-induced dissociations (Figure 1). While loss of H$^\bullet$ (and D$^\bullet$ from **1a**$^{\bullet+}$) corresponds to the base peak for **1**$^{\bullet+}$, **1a**$^{\bullet+}$, and **2**$^{\bullet+}$, the region m/z 28–33 exhibits a structure-specific CID pattern which leaves no doubt about the structural integrity of **1**$^{\bullet+}$ and **2**$^{\bullet+}$. We note in particular the following.

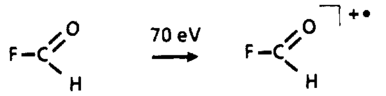


(1)

(X = H, D)

1$^{+\cdot}$ (X = H)

1a$^{+\cdot}$ (X = D)



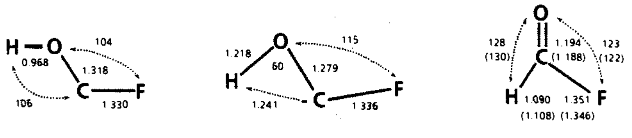
(2)

2$^{+\cdot}$

(1) In line with structures **1**$^{\bullet+}$ and **2**$^{\bullet+}$ the ratio for losses of OH$^\bullet$ versus O (m/z 31 versus m/z 32) is significantly larger for **1**$^{\bullet+}$ than for **2**$^{\bullet+}$. It is even more pronounced in the CID spectrum of **1a**$^{\bullet+}$; this is presumably due to the operation of a kinetic isotope effect as loss of an oxygen atom from **1a**$^{+}$ requires the migration of a deuterium atom.

(2) The shapes of the signals due to the processes **1**$^{\bullet+}$ (**1a**$^{\bullet+}$) → m/z 29 (m/z 30) + F$^\bullet$ are very different from that of the analogous process **2**$^{\bullet+}$ → m/z 29 + F$^\bullet$. While the former is of Gaussian-type, the latter corresponds to a dish-topped signal.[19]

Chart II. Geometries of **1**, **2**, and TS **1**/**2** [a]



1 TS **1**/**2** **2**

[a] See Figure caption of Chart I. Data given for **2** in parentheses refer to the experimentally determined geometry.[17]

(3) Weak signals (not shown in Figure 1) at m/z 17 (OH$^+$) and m/z 18 (OD$^+$) in the CID spectrum of **1**$^{\bullet+}$ and **1a**$^{\bullet+}$ are not present in the spectrum of **2**$^{+}$.

(4) The base peak (not shown) corresponds to loss of H$^\bullet$ for both **1**$^{\bullet+}$ and **2**$^{\bullet+}$.

The conclusion that **1**$^{\bullet+}$ and **2**$^{\bullet+}$ are indeed distinct species on the [H,C,O,F]$^{\bullet+}$ potential energy surface is substantiated by our MO calculations. At the MP2/6-31G**//MP2/6-31G** + ZPVE level of theory, **1**$^{\bullet+}$ is calculated to be 13.7 kcal/mol *more* stable than **2**$^{\bullet+}$. The spontaneous rearrangement **2**$^{\bullet+}$ → **1**$^{\bullet+}$ via TS **1**$^{\bullet+}$/**2**$^{\bullet+}$ is prevented by a significant barrier of E_0 = 35.2 kcal/mol.

According to the ab initio calculations **1**$^{\bullet+}$ as well as its neutral counterpart **1** exists in two conformations i.e., the *E* and the *Z* isomer; the former is more stable by 4.1 kcal/mol, and both are separated by a barrier of 9.8 kcal/mol (relative to *Z*-**1**$^{\bullet+}$). Although we have not aimed at calculating all the transition structures for the various dissociation channels given in Table I, it is obvious from the data that all chemically feasible processes are endothermic. We note that in line with the experimental findings the eliminations of H$^\bullet$, OH$^\bullet$, F$^\bullet$, and HF are favored thermochemically.

If **1**$^{\bullet+}$, **1a**$^{\bullet+}$, and **2**$^{\bullet+}$ are subjected to a NRMS experiment, one does obtain in both the Xe/O_2 and O_2/He spectra not only recovery signals at m/z 48 (**1**$^{\bullet+}$ and **2**$^{\bullet+}$) and m/z 49 (**1a**$^{\bullet+}$); moreover, the characteristic intensity pattern in the m/z 28–33 mass range is also observed. This is clear evidence that both **1**$^{\bullet+}$ and **2**$^{\bullet+}$ survive the neutralization/reionization steps as intact species. This finding is also corroborated by the ab initio MO data (Table II) according to which, and in line with previous data,[1] **1** and **2** are separated by a significant barrier. We note that **1** is *less* stable than **2**, in contrast to the corresponding cation radicals **1**$^{\bullet+}$/**2**$^{\bullet+}$. This is another example for the reversal in energy ordering when comparing neutral isomers with their corresponding radical cations.[20,21] We further note that while electron attachments in the reactions **1**$^{\bullet+}$ → **1** and **2**$^{\bullet+}$ → **2** are accompanied by changes in the relative stabilities of the isomers, the changes in geometries of the respective pairs **1**$^{\bullet+}$/I and **2**$^{\bullet+}$/**2** are quite minor (compare Charts I and II). This result together with the fact that **1** and **2** reside in deep potential wells (Table II) explain that in the neutralization steps (vertical process) abundant fluxes of survivor species are observed.

In conclusion, the present combined experimental/theoretical study of fluorohydroxymethylene (FCOH) and formyl fluoride (HCOF) clearly demonstrates that under isolated conditions, i.e.,

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(15) We are fully aware of the problem, also raised by a referee, that for a very accurate description of the (C,H,F,O) potential energy surface (but not of the geometries, see ref 16 and also Discussion) a multiconfiguration wave function is required. The size of the system does not permit us to perform such calculations for the time being. In view of the size inconsistency of a partial CI treatment (ref 16), we rather prefer the MP perturbation approach.

(16) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(17) Huisman, P. A. G.; Klebe, K. J.; Miglhoff, F. C.; Renes, G. H. *J. Mol. Struct.* **1979**, *57*, 71.

(18) For a review and exhaustive references on this class of remarkable ions, see: Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123.

(19) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973.

(20) For many examples and further references, see: Heinrich, N.; Koch, W.; Frenking, G.; Schwarz, H. *J. Am. Chem. Soc.* **1986**, *108*, 593.

(21) Another example is that of hydroxymethylene versus formaldehyde. Here, again, for the cation radical it is HCOH$^{\bullet+}$ which is more stable than $H_2CO^{\bullet+}$. For the neutral isomers, there exists experimental evidence, based on ion cyclotron resonance mass spectrometry, that HCOH is 54 kcal/mol less stable than H_2CO, in good agreement between theory and experiment.[22] We suppose that the smaller energy difference noted in the FCOH/HFCO case is consistent with the ability of fluorine to preferentially stabilize the singlet carbene. In fact, as borne out by the data shown in Table II, the triplet of FCOH is substantially higher in energy than its singlet electromer (101.9 versus 48.9 kcal/mol).

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J. Am. Chem. Soc. 1988, 110, 8333-8336

in the gas phase, both the neutral and cation radicals can be generated and characterized as distinct species.

Acknowledgment. The continuing support of our work by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and the Gesellschaft von Freuden der Technischen Universität Berlin is appreciated. We are grateful to Drs. D. Lentz and K. H. Moock for their assistance in the synthesis and purification of formyl fluoride, and to Dr. T. Weiske for his support in the operation of the ZAB-HF-3F mass spectrometer. The generous supply of computer time by the Technische Universität Berlin (ZRZ) is particularly acknowledged.

Registry No. 1, 71946-82-2; $1^{\bullet+}$, 117270-08-3; $2^{\bullet+}$, 99766-68-4.

Quantitative Measure of α-Silyl Carbanion Stabilization. The Electron Affinity of (Trimethylsilyl)methyl Radical

Donna M. Wetzel and John I. Brauman*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305-5080. *Received April 11, 1988*

Abstract: We have generated (trimethylsilyl)methyl anion, $(CH_3)_3SiCH_2^-$, in the gas phase and measured cross sections for electron photodetachment using ion cyclotron resonance spectrometry. From the electron photodetachment spectrum we obtain the electron affinity of (trimethylsilyl)methyl radical, EA = 21.9 ± 0.3 kcal/mol, and derive the proton affinity of the anion, PA = 390.9 ± 1.5 kcal/mol. These thermochemical parameters provide a quantitative measure of α-silyl carbanion stabilization of about 20 kcal/mol.

The phenomenon of carbanion stabilization by α-silyl groups has received considerable attention from theoretical and experimental chemists over the past few years. Synthetic chemists, taking advantage of the enhanced α-CH acidity in organosilicon compounds, have developed a powerful class of reagents, α-silyl organometallics.[1] These reagents have been used in the conversion of carbonyl compounds to alkenes,[2] as Grignard reagents,[3] and in nucleophilic displacement reactions.[3] Dramatic kinetic effects upon substitution of an α-silyl moiety have been observed (rates increased by factors of[4] 5 to orders of magnitude[5]) in reactions proceeding through carbanionic intermediates or transition states. Results of dynamic NMR studies (measuring rotational barriers in π-conjugated carbanions)[6] have suggested significant delocalization of electron density into *p*-silyl-substituted phenyl rings. Prompted by experimental evidence, theoreticians have worked to both quantify and explain the stabilization which appears to dictate observed organosilane chemistry.[7-9]

Although the α-CH reactivity in organosilicon compounds indicates enhanced stability, it does not provide direct evidence that α-silyl carbanions exist as isolated, stable species. Such direct evidence is provided, however, by the results of recently reported gas-phase experiments. α-Silyl carbanions were observed in the reaction of amide ion with alkylsilanes[10,11] and in the reactions of trimethylsilane with methoxide ion.[12]

Gas-phase experiments have proven to be useful in obtaining quantitative measures of intrinsic molecular properties[13] and are thus appropriate for obtaining a measure of α-silyl carbanion stabilization. One attractive approach for evaluating the relative stability of anionic species is through comparisons of experimental gas-phase proton affinities (acidities of the conjugate acids). The usual method for obtaining proton affinities (proton-transfer equilibria studies) is difficult in the case of α-silyl carbanions, since organosilanes are very weak acids. Reference acids (whose ΔH°_{acid}'s have been precisely measured) are scarce in this regime. Water, which does have an acidity in the correct range, cannot be used as a reference acid in proton-transfer reactions involving organosilanes due to competing nucleophilic displacement reactions.[14]

Experiments bracketing organosilane acidities have been reported. The acidities of isobutylene ($Me_2C{=}CH_2$) and α-silicon analogue, dimethylsilene ($Me_2Si{=}CH_2$), have been estimated.[15] Proton-transfer reactions indicated that dimethylsilene, whose acidity falls between that of *tert*-butyl alcohol[16] and water,[16] is

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[14] We observed the reaction $Me_3SiCH_2 + H_2O \rightarrow Me_3SiO^- + CH_4$. Damrauer et al. have also observed this reaction.[11]

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