^{1}H, ^{13}C, ^{15}N NMR and Ab Initio/IGLO/GIAO-MP2 Study of Mono-, Di-, Tri-, and Tetraprotonated Guanidine[1]

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Abstract: Mono- and diprotonated guanidines were prepared in superacid solutions and studied by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy. The structures, energies, and NMR chemical shifts were also calculated by ab initio/IGLO/GIAO-MP2 method. Excellent agreement were found between experimental and calculated ^{13}C and ^{15}N NMR chemical shifts. No persistent triprotonated guanidine was observed. Tri- and tetraprotonated guanidines were also studied by ab initio/IGLO/GIAO-MP2 method.

Introduction

Guanidine and its derivatives are biologically important. They are present as substructures in the amino acid arginine, the pyrimidine base of DNA, and many other biologically significant molecules. The structure and properties of guanidine and guanidinium ion has also attracted much attention by theoretical chemists.[2] Gabbi and Frenking reported[3] high level *ab initio* calculations on guanidine and guanidinium ion while focusing on the Y-aromaticity of the systems.

The propensity for protonation of guanidine in various acids has not yet fully been established. Based on early studies using cryoscopic methods, Hantzsch suggested tetraprotonation of guanidine in sulfuric acid.[4] Subsequent investigations, however, found only monoprotonated guanidine (i.e., guanidinium ion $(NH_3)_3C^+$) under these conditions.[5] The protonation of guanidine in superacid has been studied by ^{1}H NMR spectroscopy.[6] Guanidine was found to be diprotonated in Magic acid (FSO_3H-SbF_5-SO_2) at −80 °C. Methyl and 1,1-dimethylguanidine were also found to be diprotonated in Magic acid.[6]

Protosolvolytic activation of diprotonated guanidine in superacids (in the limiting case leading to triprotonated guanidine) could play an important role in strong acid catalyzed electrophilic reactions. In superelectrophilic[7] activation, nonbonded electron pairs on onium ions further interact with Brönsted or Lewis acids and in the limiting case can lead to *gitonic* dications (polycations), i.e., proximal as contrasted with conventional distonic (distant) dications. In their studies Berkessel and Thauer have suggested that such activation may also play an important role in some enzyme catalytic reactions.[8] For example, a recently discovered metal-free hydrogenase enzyme catalyzes the reversible dehydrogenation of methylenetetrahydromethaneopterin ($CH_2=H_4MPT$) to methenyltetrahydromethanopterin (CHH_4MPT^+) and H_2. It was suggested that the amidinium ion entity is further activated by N-protonation in the enzyme to bind a H_2 molecule via a two-electron, three-center (2e-3c) bond.[8] The present experimental and theoretical study of protonated guanidines is therefore also relevant to a better understanding of protolytic activation of guanidine containing biological systems. We have previously investigated the structures of protonated urea,[9] thiourea,[10] and carbonic acid.[11] Herein, we report the investigation of protonated guanidine by ^{1}H, ^{15}N, and ^{13}C NMR spectroscopy and by ab initio/IGLO/GIAO-MP2 calculations.

Results and Discussions

The experimental NMR data of mono- and diprotonated guanidines under various acid conditions are tabulated in Table 1. Ab initio calculations were performed with the GAUSSIAN-94[12] package of programs. Optimized geometries were obtained at the MP2/6-31G* level. Improved energies were obtained by single point energy calculations at the MP4(SDTQ)/6-31G*//MP2/6-31G* level. Vibrational frequencies at the MP2/6-31G*//MP2/6-31G* level were used to characterize stationary points as minima or transition state and to evaluate zero point vibrational energies (ZPE) which were scaled by a factor of 0.93.[13] Calculated energies and relative energies are listed in

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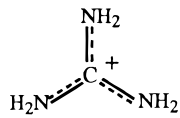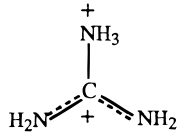
Table 1.   Measured NMR Chemical Shifts

Molecule	Solv.	Temp. (^{0}C)	^{1}H-NMR		^{13}C-NMR	^{15}N-NMR	
			-NH$_2$	-NH$_3$	C	-NH$_2$	-NH$_3$
Monoprotonated guanidine							
	DMSO-d$_6$	r.t.	7.07 (*br*) $J_{H,N}$ = 90		157.9 (*tr*) $J_{C,N}$ = 10.8	78.0 (*tr*) $J_{N,H}$ = 88.1	
	H$_2$SO$_4$	r.t.	6.68 (*br*)		156.7 (*tr*) $J_{C,N}$ = 10.7	73.5 (*br*)	
	CF$_3$SO$_3$H	r.t.	6.63 (*br*)		156.8 (*tr*) $J_{C,N}$ = 10.3	74.0 (*br*)	
	FSO$_3$H in SO$_2$ClF	-40	6.66 (*br*)		156.7 (*tr*) $J_{C,N}$ = 10.9	74.1 (*br*)	
Diprotonated guanidine							
	FSO$_3$H:SbF$_5$ in SO$_2$ClF	-40	6.32 6.09	6.76	148.9 (*br*)	107.0 (*tr*) $J_{N,H}$ = 99.7	57.0 (*qt*) $J_{N,H}$ = 79.5
	FSO$_3$H:2SbF$_5$ in SO$_2$ClF	-40	6.33 6.09	6.74	149.1 (*br*)	105.2 (*tr*) $J_{N,H}$ = 98.4	55.6 (*qt*) $J_{N,H}$ = 81.1

Table 2.   Total Energies (−au), ZPE (kcal/mol) and Relative Energies (kcal/mol) of Protonated Guanidines

no.	MP2/6-31G*//MP2/6-31G* (ZPE)^a	NIMAG^b	MP4(SDTQ)//6-31G*//MP2/6-31G*	rel energy^c (kcal/mol)
	Monoprotonated Guanidine, CH$_6$N$_2^{(+)}$			
1	205.120 65 (52.1)	0	205.170 08	0.0
2	205.070 33 (52.8)	0	205.121 48	31.2
	Diprotonated Guanidine, CH$_7$N$_2^{(2+)}$			
3	205.237 11 (60.2)	0	205.289 37	−66.7
4 (TS)	205.025 83 (52.9)	1	205.076 46	59.6
	Triprotonated Guanidine, CH$_8$N$_2^{(3+)}$			
5	205.132 20 (66.5)	0	205.187 70	3.4
6 (TS)	205.003 70 (61.0)	1	205.056 49	80.2
	Tetraprotonated Guanidine, CH$_9$N$_2^{(4+)}$			
7	204.719 78 (67.1)	0	204.776 37	262.1
8 (TS)	204.688 35 (65.1)	1	204.742 88	281.1

^{a} ZPE at the MP2/6-31G*//MP2/6-31G* level scaled by a factor of 0.93. ^{b} Number of imaginary frequencies. ^{c} Based on MP4(SDTQ)/6-31G*//MP2/6-31G* + ZPE.

Table 2. IGLO calculations were performed according to the reported method[14] at IGLO II levels using MP2/6-31G* geometries. Huzinaga[15] Gaussian lobes were used as follows; Basis II: C or N: 9s 5p 1d contracted to [51111, 2111, 1], d exponent: 1.0, H: 5s 1p contracted to [311, 1], p exponent: 0.70. GIAO-MP2[16] method, which includes dynamic electron correlation in chemical shift calculations, using the tzp/dz basis set have been performed with the ACES II[17] program. The calculated ^{13}C and ^{15}N NMR chemical shifts (δ values) are referenced to TMS and NH$_3$, respectively. Calculated NMR chemical shifts are listed in Table 3. For simplicity MP2/6-31G* geometries and MP4(SDTQ)/6-31G*//MP2/6-31G* + ZPE energies will be discussed throughout.

Mono- and Diprotonated Guanidine. The ^{15}N labeled guanidinium sulfate [(H$_2$^{15}N)$_2$CNH$_2$]$^+$ $^1/_2$SO$_4$$^{2-}$ was prepared from ^{15}N labeled urea ((^{15}NH$_2$)$_2$CO) based on the procedure

Table 3.   Experimental and Calculated NMR Chemical Shifts^a

no.	atom	IGLO II	GIAO-MP2	expt
1	^{13}C	160.4	158.9	156.7
	^{15}N	64.3	83.5	74.1
2	^{13}C	145.7	140.9	
	^{15}N (NH)	236.3	218.4	
	^{15}N (NH$_2$)	58.6	78.2	
	^{15}N (NH$_3$)	53.8	82.3	
3	^{13}C	155.7	149.0	148.9
	^{15}N (NH$_3$)	41.3	66.2	57.0
	^{15}N (NH$_2$)	99.9	119.5	107.0
5	^{13}C	162.4	155.3	
	^{15}N (NH$_2$)	214.8	223.2	
	^{15}N (NH$_3$)	47.9	73.2	
7	^{13}C	268.2	278.9	
	^{15}N	94.7	126.1	

^{a} Calculated ^{13}C and ^{15}N NMR chemical shifts were referenced to TMS and NH$_3$; absolute shift, i.e., (GIAO-MP2) σ(C) = 198.7 and σ(N) = 279.6, and (IGLO II) σ(C) = 197.4 and σ(N) = 251.9, respectively.

reported by Boivin.[18] The ^{1}H, ^{13}C, and ^{15}N NMR chemical shifts of ^{15}N labeled guanidinium sulfate were measured in H$_2$SO$_4$ and CF$_3$SO$_3$H at room temperature as well as in FSO$_3$H/ SO$_2$ClF at −40 °C. Each of the solutions showed a broad peak at around δ^1H 6.6 in its ^{1}H NMR spectrum, a peak at around

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$\delta^{13}C$ 157 (t, J_{C-N} = 11 Hz) in its ^{13}C NMR spectrum and a peak at around $\delta^{15}N$ 74 in its ^{15}N NMR spectrum (Table 1). The equivalence of the ^{15}N NMR peaks indicate no further protonation of guanidinium ion to a persistent diprotonated guanidinium dication at these acidities. However, the magnetic equivalence of nitrogen atoms could also be attributed to rapid proton exchange between the acids and the guanidinium ion. To confirm this we also measured ^{13}C and ^{15}N NMR spectra of ^{15}N labeled guanidinium sulfate in DMSO at room temperature which show patterns similar to those obtained in other acid solutions (Table 1).

The optimized structures of the guanidinium ion are in agreement with previous calculations at the MP2/6-31G* level.[3] The propeller-shaped C_3 symmetrical structure **1** is the global minimum structure. The planar amino groups of structure are rotated out of plane around the C–NH_2 bonds by about 15.9°. The planar D_{3h} structure, however, is not a minimum on the potential energy surface. We have also considered the structure **2** which can be formed by protonation of –NH_2 group of guanidine. However, structure **2** is significantly (31.2 kcal/mol) less stable than isomer **1**.

The ^{13}C and ^{15}N NMR chemical shifts of **1** and **2** were calculated at the IGLO II and correlated GIAO-MP2/tzp/dz levels using MP2/6-31G* optimized geometries (Table 3). The GIAO-MP2 calculated $\delta^{13}C$ of 158.9 matches very closely to the experimental value of 156.7 (in FSO_3H/SO_2ClF). However, the GIAO-MP2 calculated $\delta^{15}N$ of 83.5 is slightly deviated from the experimental value of 74.1 (by about 9 ppm). Similarly, although, the IGLO calculated $\delta^{13}C$ of 160.4 is close to the experimental value, the $\delta^{15}N$ value of 64.3 is again deviated from the experimental value by about 10 ppm.

When substantially more acidic Magic Acid ($FSO_3H:SbF_5$, $H_0 = -22$) is used in the place of FSO_3H ($H_0 = -15$) at –78 °C with SO_2ClF as solvent, ^{15}N labeled guanidinium ion is readily further protonated (eq 1), and the resulting dication could be observed by ^1H, ^{13}C, and ^{15}N NMR spectroscopy at –40 °C. The ^1H NMR of diprotonated guanidine consists of an NH_3^+ peak at δ^1H 6.76 and two peaks at δ^1H 6.32 and 6.09. This is in agreement with the previously reported ^1H NMR spectrum of diprotonated guanidine in Magic Acid by Olah et al.[6]

(1)
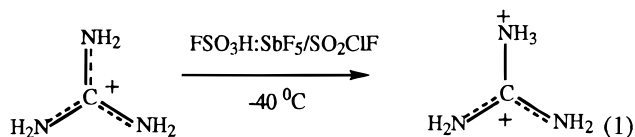
We measured the ^{13}C and ^{15}N NMR spectra of the guanidinium dication in $FSO_3H/SbF_5/SO_2ClF$ at –40 °C. ^{13}C NMR spectrum consists of a peak centered at $\delta^{13}C$ of 148.9. The $\delta^{13}C$ shift of guanidinium dication is shielded by about 8 ppm from that of the guanidinium ion. The ^{15}N NMR spectrum of the same solution shows a quartet centered at $\delta^{15}N$ 57.0 (J_{N-H} = 79.5 Hz) and a triplet centered at $\delta^{15}N$ 107.0 (J_{N-H} = 99.7 Hz) representing –NH_3^+ and –NH_2 nitrogens, respectively.

Calculated structure of diprotonated guanidine **3** shows (Figure 1) a longer C–N (NH_3) bond of 1.483 Å and a shorter C–N(NH_2) bond 1.309 Å compared to C–N bond of guanidinium ion **1**, which indicates that one of the positive charges is located on NH_3 group, and the second positive charge is delocalized among (NH_2) N–C–N (NH_2) as indicated. Previous calculations on diprotonated urea[9] and thiourea[10] have shown a similar pattern of charge distribution. This is also consistent with the ^1H NMR spectrum of protonated guanidine. The two absorptions at δ^1H 6.32 and at δ^1H 6.09 were assigned for H_a
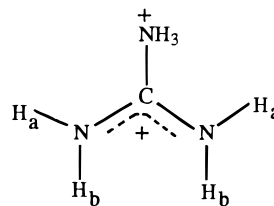
and H_b, respectively (by comparing the chemical shifts obtained by GIAO-MP2 calculations), and can be interpreted as showing restricted rotation about the C–N bond causing the nonequivalence of protons.

Protonation of **1** to form **3** is calculated to be exothermic by 66.7 kcal/mol. We have also identified the transition state **4** for protodissociation of **3** into **1**, which lies 126.3 kcal/mol above minimum structure **3**. Thus, dication **3** has a very high kinetic barrier to decomposition.

The GIAO-MP2 calculated ^{13}C and ^{15}N NMR chemical shifts of **3** also agree very well with the observed experimental data (see Tables 1 and 3). The GIAO-MP2 calculated $\delta^{13}C$ of 149.0 is almost identical with the experimental value of 148.9. Similarly, the two GIAO-MP2 calculated ^{15}N NMR chemical shifts of **3** at $\delta^{15}N$ of 66.2 (–NH_3) and 119.5 (–NH_2) compare well with the experimental values of 57.0 and 107.0, respectively. The IGLO calculated ^{13}C and ^{15}N NMR chemical shifts, however, differ somewhat from the experimental values (see Tables 1 and 3).

Tri- and Tetraprotonated Guanidine. Increasing the acidity of the $FSO_3H:SbF_5$ solution further by the addition of SbF_5 (i.e., $FSO_3H:2SbF_5$) at –78 °C did not lead to observable protonation of diprotonated guanidine into persistent static triprotonated guanidine (eq 2). In the ^{13}C NMR spectrum the

(2)
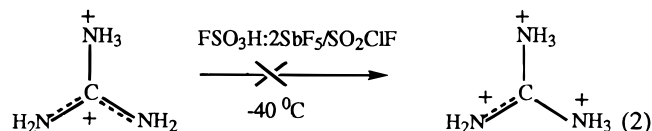
carbon peak is slightly deshielded by about 0.2 ppm. Similarly the $\delta^{15}N$ of –NH_3 and –NH_2 are shielded by about 1.8 and 1.4 ppm, respectively. This indicates either a proton exchange process occurring at the NMR time scale between the diprotonated guanidinium dication and the acid or probably an exchange involving a small equilibrium concentration of triprotonated guanidine (or protosolvated dication) with the dication.

Triprotonated guanidine **5** was calculated at the MP2/6-31G* level. The relatively long C–N (H_3) bond length of 1.473 Å (Figure 1) and short C–N (H_2) bond length of 1.280 Å in ion **5** compared to C–N bond length of monoprotonated guanidine **1** indicate that the two of its positive charges are localized on the two –NH_3 groups and the third one is delocalized over the aminocarbenium entity resembling in the ammonium–iminium structure.
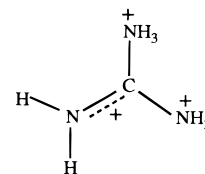
The protonation of diprotonated guanidine **3** to triprotonated guanidine **5** was found to be endothermic by 70.1 kcal/mol. We have also located the transition structure **6** for the deprotonation of **5**. Transition state **6** lies 76.8 kcal/mol above
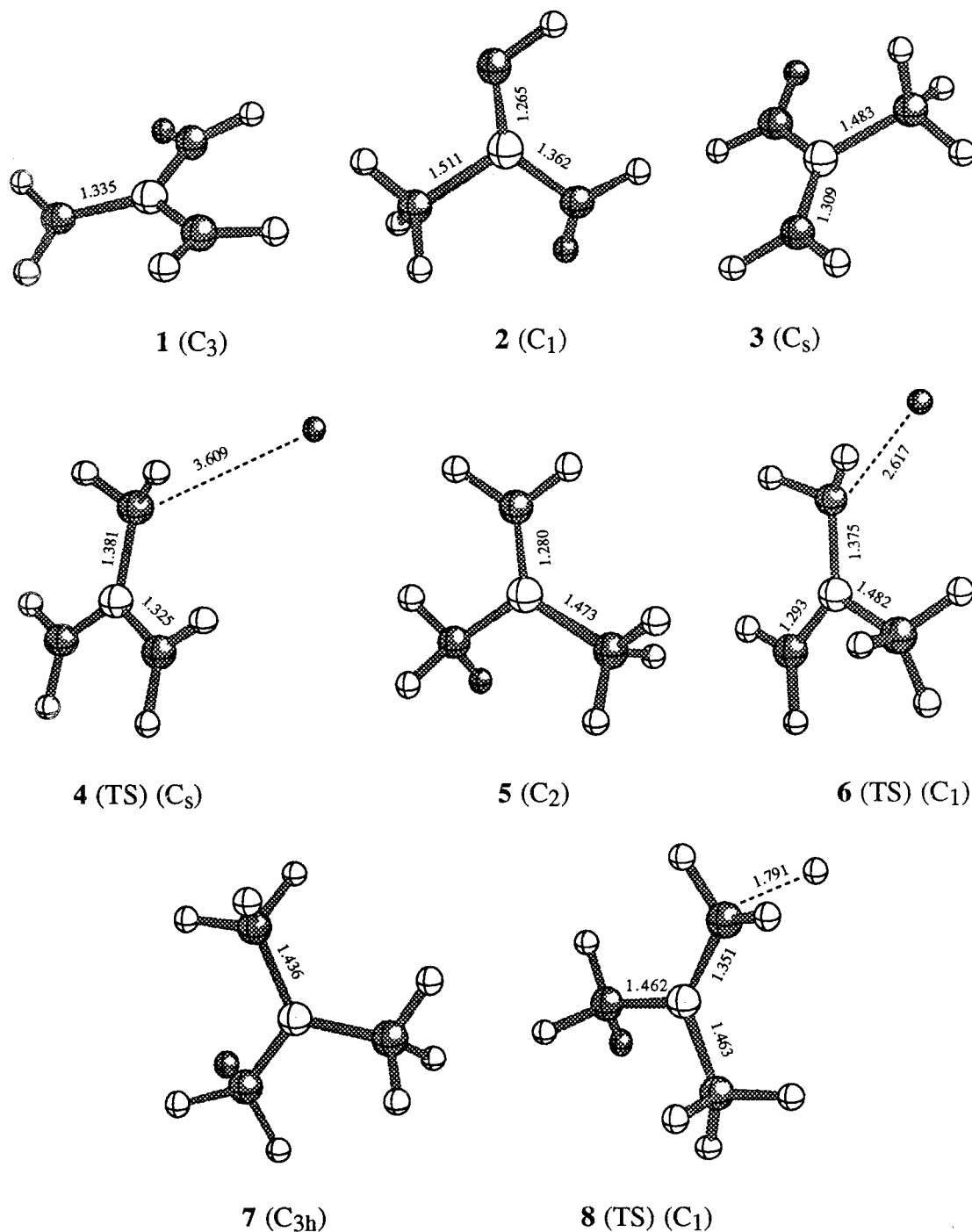
Figure 1. Selected MP2/6-31G* optimized parameters of **1**−**8**.

structure **5**. Thus, the trication **5** has a high kinetic barrier for deprotonation.

GIAO-MP2 chemical shift calculations indicate a deshielding effect in the ^{13}C NMR chemical shift of triprotonated guanidinium trication **5** (δ^{13}C 155.3) of 6.3 compared to the diprotonated species **3** (δ^{13}C 149.0). The ^{15}N NMR chemical shifts of **5** are also indicated to be deshielded compared to **3**. GIAO-MP2 calculated a deshielding of 103.7 and 7.0 ppm for the NH$_2$ and NH$_3^+$ groups in **5**, respectively, as compared to **3**.

We have also calculated tetraprotonated guanidine at the MP2/6-31G* level. The C_{3h} symmetrical structure **7**, with C−N length of 1.436 Å, is the global minimum for the tetraprotonated guanidine (Figure 1). Structure **7** is isoelectronic and isostructural with the *tert*-butyl cation (CH$_3$)$_3$C$^+$.[19] In structure **7** three

of the positive charges are localized on the three −NH$_3$ groups, and the fourth one on the carbon, is clearly a highly unfavorable situation.
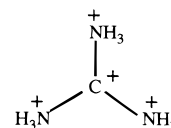
The tetracation **7** lies 258.7 kcal/mol above **5**. Ion **7** has also a low kinetic barrier of 19.0 kcal/mol toward dissociation into **5** and H$^+$ through transition state **8**. Therefore, the tetracation

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7 is both thermodynamically and kinetically unstable toward protodissociation. GIAO-MP2 predict a $\delta^{13}C$ of 278.9 and a $\delta^{15}N$ of 126.1 for the tetracation **7**.

Conclusions

^{15}N labeled mono- and diprotonated guanidine were prepared and studied under superacidic conditions by ^1H, ^{13}C, and ^{15}N NMR spectroscopy and by ab initio calculations. In H_2SO_4, CF_3SO_3H, and FSO_3H/SO_2ClF only monoprotonated guanidinium ion $[(NH_2)_3C]^+$ was observed. Addition of SbF_5 to the FSO_3H/SO_2ClF solution increases its acidity and results in the observation of persistent diprotonated guanidine $[(NH_2)_2\text{-}CNH_3]^{2+}$. No NMR evidence was found for the static triprotonated guanidine under these conditions although in highly acidic media the exchanging system may involve the trication in some limited equilibrium. NMR chemical shifts were evaluated using the IGLO and GIAO-MP2 methods and are compared to the experimental values. GIAO-MP2 calculated ^{13}C and ^{15}N NMR chemical shifts of the preferred structures are in excellent agreement with the experimental data. Structures, energies, and ^{13}C and ^{15}N NMR chemical shifts of tri- and tetraprotonated guanidines were also calculated.

Experimental Section

98% ^{15}N enriched urea ($^{15}NH_2)_2CO$ (Cambridge Isotope Laboratories), anhydrous NH_3 (Aldrich), sulfur dioxide (Matheson), and anhydrous HF (Matheson) are commercially available and were used as received. SbF_5 (Allied Chemical) and FSO_3H (3M) were doubly distilled prior to use.

^1H, ^{13}C, and ^{15}N NMR spectra were obtained on Varian Associates Model Unity 300 spectrometer equipped with a 5 mm variable temperature broad band probe at 300, 75.4, and 30.4 MHz, respectively. ^1H and ^{13}C NMR spectra were obtained with respect to TMS by using an acetone-d_6 capillary as external standard. ^{15}N NMR chemical shifts were referenced to anhydrous NH_3.

Preparation of ^{15}N Labeled Guanidinium Salt. $[(H_2{}^{15}N)_2CNH_2]^+$ $^1/_2SO_4{}^{2-}$ was prepared from ^{15}N labeled urea (($^{15}NH_2)_2CO$), anhydrous ammonia, and sulfur dioxide similar to a procedure previously reported by Boivin.[18] In an autoclave (30 mL volume) was placed 0.89 g of urea-^{15}N and added 3.78 g of SO_2 (condensed at -20 °C) and 2.75 g of anhydrous NH_3 (condensed at -80 °C). The bomb was closed and heated to 300 °C (sand bath) at a rate of approximately 3 °C/min (pressure at this temperature: approximately 300 psi). After 5 min at 300 °C, the bomb was placed into boiling water (10 min) and subsequently allowed to cool to room temperature. The reaction mixture was dissolved in water (23 °C), and remaining elemental sulfur was separated by filtration. Removal of water in vacuo yielded a yellowish solid, which was treated with 30 mL of liquid NH_3 in order to dissolve guanidinium sulfamide formed as byproduct. After filtration, the remaining solid was recrystallized twice from ethanol. ^{15}N NMR (in DMSO): $\delta^{15}N$ 76.4 (tr, $J_{N,H} = 89.1$ Hz); ^{13}C NMR (in DMSO): $\delta^{13}C$ 157.9 (tr, $J_{C,N} = 10.96$ Hz); ^1H NMR (in DMSO): δ^1H 5.39 (br).

Study of Protonation of Guanidinium Salt. ^{15}N labeled Guanidinium sulfate ($\sim$30 mg) was dissolved in approximately 0.5 mL of SO_2ClF in a 5 mm NMR tube and cooled to -78 °C in a dry ice/acetone bath. Approximately 1.5 mL of 50% v/v solution of FSO_3H:SbF_5 (1:1 molar solution), HF:SbF_5 (1:1 molar solution), FSO_3H in SO_2ClF was added to the solution at -78 °C. The ensuing mixture was vigorously stirred (Vortex stirrer) under periodic cooling prior to transfer to a precooled NMR probe (-40 °C). Experiments with concentrated H_2SO_4 and CF_3SO_3H were done neat at 0 °C and the spectra obtained at room temperature.