A Theoretical Study of Nitrososilane and Six Isomers of SiH_3NO

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Abstract

Geometries have been obtained for seven SiH_3NO molecules using HF/6-31G* and MP2/6-31G* theory: nitrososilane, isonitrososilane, silaformaldoxime, silaformaldonitrone, siloxaziridine, iminosilanol and silaformamide. Vibrational frequencies and some internal rotations have been characterized, and relative energies were obtained with MP4/6-31G* and MP4/6-311G** theory at the minimum energy geometries. A theoretical $\text{SiH}_3\text{-NO}$ bond strength of 124 kJ mol^{-1} in nitrososilane was obtained, that is in accord with an RRKM analysis of $\text{SiH}_3 + \text{NO}$ recombination kinetics which yielded $117 \pm 11 \text{ kJ mol}^{-1}$.

1. INTRODUCTION

Sugawara *et al.* have recently measured the rate constant k_1 for the elementary reaction

and demonstrated that third-order kinetics were obeyed [1]. An $\text{SiH}_3 \cdot \text{NO}$ adduct is therefore formed, although its nature is unknown. Reaction (1) has been employed in our laboratory to prevent interference by SiH_3 in measurements of $\text{O} + \text{SiH}_4$ kinetics [2], and was used to remove SiH_3 during silicon chemical vapor deposition by Longeway *et al.* in their investigations of the mechanism of CVD [3]. The main aim of the present work is to characterize the most likely product of reaction (1) by *ab initio* methods. Nitrososilane is found to be the probable adduct, and the results permit an RRKM analysis of the experimental k_1 to estimate the $\text{SiH}_3\text{-NO}$ bond dissociation energy, E_0 . This value is compared to theoretical estimates.

The results for SiH_3NO are discussed in the context of the carbon analogue, nitrosomethane. CH_3NO has been extensively studied, both experimentally and theoretically [4][5][6][7][8][9], partly because it is an example of a molecule where the lowest energy conformation of the hindered internal rotation about the C-N bond has the O and H atoms *eclipsed*. The attractive C-H...O interaction has been described as weak hydrogen bonding or van der Waals bonding [4],[7]. The first results for internal rotation in SiH_3NO are presented here for comparison. The geometries, vibrational frequencies and relative enthalpies of six other isomers of SiH_3NO have also been estimated, as an aid to the design of experiments for their synthesis and detection. These molecules include examples of π bonding between Si and O or N, an area of continuing interest [10][11][12][13], and are the simplest silicon analogues of several classes of compound including amides, oximes, nitrones and

oxaziridines. The silicon and carbon analogues are found to have many similarities, with some exceptions that are discussed.

2. COMPUTATIONAL METHOD

Quantitative molecular orbital calculations were carried out as described in detail elsewhere [14] using the GAUSSIAN 90 program [15] implemented on a Solbourne 5E/902 computer. The split-valence 6-31G* atomic basis set was employed, which includes polarization functions on C, N, O and Si atoms. Full geometry optimizations were first performed for each closed-shell molecule using the spin-restricted Hartree-Fock (RHF) method. Harmonic vibrational frequencies were calculated to verify each equilibrium structure as a true energy minimum, and were scaled by a standard factor of 0.89 [14] before zero-point vibrational energies (ZPE) were computed. Internal rotations were characterized by calculation of the HF/6-31G* energy as a function of the rotation angle, with all other geometry parameters held constant [16]. Single point energies at the optimized HF/6-31G* geometries were partially corrected for electron correlation effects by means of fourth-order Møller-Plesset perturbation theory (MP4) with single, double, triple and quadruple substitutions, using the frozen core approximation with the 6-31G* basis set. Next, the HF/6-31G* geometries were reoptimized using MP2/6-31G* theory, and final energies were obtained at these new geometries with MP4/6-311G** theory. The larger basis set employed in the final step includes polarization functions on all the atoms.

3. RESULTS AND DISCUSSION

3.1 Structures

Figure 1 summarizes the HF/6-31G* and MP2/6-31G* minimum-energy geometries derived for seven SiH_3NO isomers: nitrososilane **1**, isonitrososilane **2**, silaformaldoxime **3**, silaformaldonitrone **4**, siloxaziridine **5**, iminosilanol **6** and silaformamide **7**. HF vibrational frequencies are listed in Table 1. There are apparently no measurements available to test these theoretical results for any of the molecules considered. However, the predictions can be compared with results obtained for the carbon analogues [9][17][18] and other silicon compounds [13]. A general observation is that HF/6-31G* bond lengths are too small when compared to experiment while MP2/6-31G* values are too large [14], so that the data of Fig. 1 probably bracket the true values.

In nitrososilane **1** $r(\text{N-O})$ is similar to that measured for CH_3NO [19] and the $r(\text{Si-N})$ distance is about 0.14 Å greater than a typical Si-N single bond length of about 1.71 Å [13]. By contrast $r(\text{C-N})$ in CH_3NO of 1.49 Å is close to that in CH_3NH_2 . The barrier to internal rotation is about 4 kJ mol⁻¹ relative to the equilibrium eclipsed geometry, which suggests a slight attractive Si-H...O interaction, even though the H is 2.9 Å from O. This is similar to the C-H...O attraction in CH_3NO , where the rotational barrier is 5 kJ mol⁻¹ [4]. At the HF level isonitrososilane **2** has a long Si-O bond of 1.73 Å, which is 0.10 Å greater than a typical single bond distance of 1.63 Å [13]. Unlike **1** the lowest energy conformation is predicted to be staggered, with a repulsive Si-H...N interaction and a rotational barrier of 8 kJ mol⁻¹. However, there is no corresponding structure when electron correlation is included with MP2 theory, and the existence of this species as a true energy minimum is doubtful.

In silaformaldoxime **3** $r(\text{Si-N})$ is similar to a typical $\text{Si}=\text{N}$ length of 1.57 Å [13], and the $r(\text{N-O})$ is intermediate between values for N-O (1.46 Å in nitrous acid) and N=O (1.24 Å in HNO) [20], and is close to that measured for the carbon analogue [19]. Some multiple bond character in the N-O bond would be consistent with the 41 kJ mol^{-1} barrier to rotation about this bond, similar to the 37 kJ mol^{-1} derived for the carbon analogue [9]. The conformation of **3** with H *cis* to Si is about 39 kJ mol^{-1} less favorable at the HF/6-31G* level than the conformation shown in Fig. 1, an energy difference comparable to the 25 kJ mol^{-1} difference predicted between the carbon analogues [9].

Formaldonitrone is planar and substituted nitrones have a small $r(\text{C-N}) \approx 1.32$ Å consistent with a $\text{C}=\text{N}$ bond and $r(\text{N-O}) \approx 1.29$ Å [21], which is confirmed by new HF/6-31G* and MP2/6-31G* calculations. At the HF/6-31G* level silaformaldonitrone **4** is also predicted to be planar with an $\text{Si}=\text{N}$ bond, and a high barrier to rotation about this bond of about 248 kJ mol^{-1} is obtained, although this is an upper limit [16]. However, a pyramidal geometry around Si is favored at the MP2/6-31G* level (see Fig. 1). The $r(\text{N-O})$ is similar to that in the carbon analogue but here the $r(\text{Si-N})$ suggests a single Si-N bond length. The sp^3 hybridization around Si reflects poor overlap between the p orbitals on Si and N , which reduces the tendency towards π bonding by comparison to the carbon analogue. In formaldonitrone the HOMO-LUMO separation in the HF/6-31G* wavefunction is about 1260 kJ mol^{-1} , but the separation is reduced to 870 kJ mol^{-1} in the planar silicon analogue. The smaller the HOMO-LUMO gap, the more favorable pyramidalization about the trivalent atom becomes, since there is an opportunity for mixing the HOMO and LUMO to obtain a new MO of greater stability [22].

The $r(\text{Si-O})$ and $r(\text{Si-N})$ in siloxaziridine **5** are typical of single bonds, but $r(\text{N-O})$ shows a lengthening of around 0.1 Å relative to the usual single bond distance to accommodate ring formation.

The Si-O bond in iminosilanol **6** is surprisingly rigid, with a predicted barrier to rotation of 32 kJ mol⁻¹, by contrast to a barrier of only 2 kJ mol⁻¹ in silanol even though both molecules have similar $r(\text{Si-O})$ [13]. The barrier demonstrates partial conjugation between the p orbitals in the O-Si-N moiety. The conformation with the two H atoms *cis* about the Si-O bond lies approximately 22 kJ mol⁻¹ above the conformation shown in Fig. 1, which reflects an unfavorable H...H steric interaction. The barrier to rotation about the Si-N bond is 39 kJ mol⁻¹, which suggests there is partial π bonding between Si and N, and is consistent with the $r(\text{Si-N})$ that corresponds to an Si=N bond. The alternative conformation arising from a 180° rotation lies about 14 kJ mol⁻¹ above the lowest energy configuration. Similar conformational behavior is seen in imino-ethers, and reflects a favorable interaction between a lone pair on O and the lobe of the antibonding σ^* orbital in the C-N bond [23].

Silaformamide **7** is predicted to be planar, and the barrier to rotation about the Si-N bond is estimated to be about 59 kJ mol⁻¹, which is similar to the barrier of 75 ± 13 kJ mol⁻¹ measured for planar formamide in solution [24]. The $r(\text{Si-N})$ is slightly smaller than for a typical single Si-N bond, so there is partial conjugation between the p orbitals on the O, Si and N atoms, as expected by analogy with formamide.

3.2 Thermochemistry

The calculated ZPEs and total electronic energies for **1-7** and $\text{SiH}_3 + \text{NO}$, together with

enthalpies at 0 K relative to **1**, are summarized in Table 1. The relative MP4/6-311G** enthalpies H_{rel} can be converted to absolute $\Delta H_{\text{f},0}$ for the gas-phase species by the addition of $\Delta H_{\text{f},0}(\text{SiH}_3 + \text{NO}) - 100 \text{ kJ mol}^{-1}$, i.e. 196 kJ mol^{-1} [20][25], to each value. The similarity between H_{rel} derived with MP4/6-31G* and MP4/6-311G** theory shows there is little basis set dependence.

The order of decreasing stability of the isomers is silaformamide **7** > iminosilanol **6** > siloxaziridine **5** > nitrososilane **1** > silaformaldonitrone **4** $\approx$ silaformaldoxime **3**, both at the simple HF/6-31G* and more expensive MP4/6-311G** levels of calculation. For comparison the order of stability for the carbon analogues derived by Robb and Csizmadia [17] is formamide > iminomethanol > formaldoxime > nitrosomethane $\approx$ formaldonitrone > oxaziridine. The same order, except for a reversal of the latter two species (by only 5 kJ mol^{-1}) is obtained at the HF/6-31G* level. The most significant difference between the two sets of compounds is the stability of the strained three-membered ring molecules relative to the other isomers: oxaziridine is the least stable carbon species and lies around 360 kJ mol^{-1} above formamide, while siloxaziridine is the third most stable silicon isomer and lies about 280 kJ mol^{-1} above silaformamide. Two effects contribute to this behavior. First, in **5** the lone electron pairs on N and O are further apart than in oxaziridine, and second, the electron densities in the Si-N and Si-O bonds are more separated than the densities in the C-N and C-O bonds. Not only is Si larger than C, but because Si is more electropositive there is a greater charge transfer towards the hetero atoms. This is exemplified by the Mulliken charges on the N and O atoms in oxaziridine of 0.0 and -0.45 in the HF/6-31G* wavefunction, which are significantly smaller than the charges of -0.15 and -0.60 in **5**.

The data in Table 1 imply an $\text{SiH}_3\text{-NO}$ bond energy E_0 of 100 kJ mol^{-1} , which is much less than the Si-N bond strength in SiH_3NH_2 of around 415 kJ mol^{-1} [13][26], and is smaller than the measured $E_0(\text{CH}_3\text{-NO})$ of $163 \pm 6 \text{ kJ mol}^{-1}$ [27]. Both the $\text{SiH}_3\text{-NO}$ and $\text{CH}_3\text{-NO}$ bonds are weaker than H-NO, for which E_0 is 203 kJ mol^{-1} [20]. All these R-NO bonds are weaker than the corresponding R-NH₂ bonds because the LUMO of NO is antibonding, and formation of RNO weakens the N-O interaction. For example $r(\text{N-O})$ increases from $1.15 \text{ \AA}$ in NO to $1.24 \text{ \AA}$ in HNO [20].

At the MP4/6-311G** level E_0 for H-NO is calculated to be 176 kJ mol^{-1} , rather smaller than the experimental value quoted above, so there is a possibility that E_0 for $\text{SiH}_3\text{-NO}$ has also been underestimated. A more reliable derivation is via the partial hydrogenation reaction

A combination of MP4/6-311G** energies and scaled HF/6-31G* ZPE yields $\Delta H_0 = -25 \text{ kJ mol}^{-1}$ for reaction 3, which corresponds [20] to $\Delta H_{f,0}(\text{SiH}_3\text{NO}) = 172 \text{ kJ mol}^{-1}$, and thus $E_0 = 124 \text{ kJ mol}^{-1}$ [28]. A minimum estimate of the uncertainty in the energies of Table 1 is $\geq 20 \text{ kJ mol}^{-1}$.

3.3 Kinetic implications

Table 1 indicates that species **2** is endothermic with respect to $\text{SiH}_3 + \text{NO}$ and therefore is an unlikely product of reaction 1, in accord with the discussion by Sugawara *et al.* [1], and as noted in Section 3.2 is probably not a bound species. Nitrososilane **1** is a reasonable candidate since it may be formed without breaking any existing bonds, but rearrangement of **1** formed by addition of SiH_3 to NO, initially excited by about 100 kJ mol^{-1} before stabilization by collisions

with the bath gas M, cannot be ruled out on thermodynamic grounds. However, gas-phase isomerizations of **1** to **3** and **4** by 1,2 and 1,3 hydrogen shifts are likely to have significant kinetic barriers, which in the case of nitrosomethane are around 250-300 kJ mol⁻¹ [9]. In solution such isomerizations may be acid or base-catalyzed and therefore fast. Formation of **5-7**, although thermodynamically favored, requires more extensive bond rearrangements and therefore is likely to be slow in the gas phase. As shown below, formation of **5-7** is inconsistent with the measured k_1 . Quantitative characterization of the transition states for isomerizations in the SiH₃NO system is a topic for future investigation.

The idea that SiH₃NO is the main product of reaction 1 can be tested by an RRKM analysis of k_1 . In terms of the Tre formalism

$$k_1 = \beta_c Z_{LJ} \frac{\rho(E_0) \cdot RT}{Q_{vib}(SiH_3NO)} F_E F_{anh} F_{rot} F_{introt} \frac{Q(SiH_3NO)}{Q(SiH_3) Q(NO)} \quad (2)$$

where the symbols have their usual meanings [29]. $\rho(E_0)$ is the vibrational density of states of SiH₃NO at the threshold energy for dissociation, E_0 . Q is the partition function, and for SiH₃NO the internal rotor is approximated with a free rotor. F_E , F_{anh} , F_{rot} and F_{introt} are correction factors to account for the energy dependence of $\rho(E_0)$, for the effects of vibrational anharmonicity, for centrifugal barriers and for the internal rotor [29]. These quantities are derived from the *ab initio* structure and scaled vibrational frequencies. $\beta_c Z_{LJ}$ is the weak-collision stabilization rate constant, which is set at a reasonable value for N₂ bath gas at 298 K of 2.5×10^{-10} cm³ s⁻¹. The ρ and F parameters in equation 2 depend either explicitly or implicitly on E_0 , which was varied until agreement was obtained with the measured k_1 of $(8.2 \pm 0.9) \times 10^{-30}$ cm⁶ s⁻¹ [1]. E_0 was found to be approximately proportional to $k_1^{0.14}$. Allowance of a factor of two

uncertainty in the RRKM parameters leads to a fitted E_0 of 117 ± 11 kJ mol⁻¹. This is in reasonable agreement with the MP4/6-311G** estimate of 100 kJ mol⁻¹ (Table 1) and the result of 124 kJ mol⁻¹ obtained via analysis of reaction 3. The assumption of SiH₃NO formation is therefore self-consistent. If part of the rate-determining process for loss of SiH₃ in reaction 1 involved formation of **5**, **6** or **7** then the k_1 predicted from equation 2 would be much larger, because of the larger E_0 , and could not be reconciled with the measured k_1 .

4. CONCLUSIONS

Nitrososilane is the most likely product of SiH₃ + NO recombination. Theoretical results for this molecule enable the SiH₃-NO bond strength to be estimated via an RRKM analysis to be 117 ± 11 kJ mol⁻¹, which is in accord with the *ab initio* value of 124 kJ mol⁻¹. Structures and relative stabilities for six other isomers of stoichiometry SiH₃NO are estimated. Areas for future work include more accurate analysis of internal rotations in these molecules, and characterization of transition states for possible isomerizations.

5. ACKNOWLEDGMENTS

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16. Because the molecular structure cannot relax in this procedure the barriers obtained are more accurately viewed as upper bounds. Furthermore, in the case of π bonds, the closed-shell RHF wavefunction excludes any contribution from low-lying triplet states and cannot describe the partially occupied p orbitals as the π bond is broken during

rotation, and yields erroneously large barriers [13]. Use of open-shell wavefunctions and correction for electron correlation effects leads to lower and more accurate barrier heights, as has been demonstrated e.g. for $\text{SiH}_2=\text{CH}_2$ by R. Ahlrichs and R. Heinzmann, J. Amer. Chem. Soc. 99 (1977) 7452 and references therein.

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Table 1.

Ab initio frequencies and energies for SiH₃NO species.

Species	HF/6-31G* vibrational frequencies, cm ⁻¹	HF/6-31G* energy ^a	MP4/6-31G* energy ^{a,b}	MP4/6-31G* H _{rel} ^{b,c}	MP4/6-311G** energy ^{a,d}	MP4/6-311G** H _{rel} ^{b,d}
nitrososilane 1	86, 306, 562, 583, 708, 905, 916, 919, 1700, 2151, 2157, 2164	-419.86497	-420.31574	0	-420.43884	0
isonitrososilane 2	149, 252, 643, 669, 724, 927, 927, 933, 1322, 2167, 2181, 2188	-419.83556	-420.27095	117	-	-
silafomaldoxime 3	232, 323, 448, 538, 651, 813, 926, 1147, 1407, 2164, 2211, 3660	-419.83698	-420.30579	34	-420.43047	30
silafomaldonitrone 4	121, 290, 445, 623, 814, 817, 886, 1067, 1428, 2205, 2248, 3237	-419.80921	-420.29793	53	-420.43079	27
siloxaziridine 5	498, 626, 647, 731, 777, 866, 943, 1007, 1226, 2179, 2203, 3340	-419.89071	-420.35105	-81	-420.46853	-67
iminosilanol 6	312, 433, 441, 555, 569, 805, 859, 900, 1171, 2193, 3498, 3651	-419.97038	-420.42674	-278	-420.53289	-234

silafornamide 7	302, 390, 466, 619, 731, 848, 919, 1229, 1555, 2182, 3390, 3483	-419.99922	-420.45757	-355	-420.57841	-349
silyl + nitric oxide	779, 903, 903, 2104, 2121; 1978	-419.85400	-420.27423	95	-420.39563	100

^aIn Hartrees ($\approx 2625 \text{ kJ mol}^{-1}$).

^bAt the HF/6-31G* geometry.

^cEnthalpy relative to 1 at 0 K in kJ mol^{-1} .

^dAt the MP2/6-31G* geometry.

FIGURE CAPTION

Fig. 1 MP2/6-31G* (upper) and HF/6-31G* (lower) geometries for C_s nitrososilane **1**, C_s isonitrososilane **2** (HF data only), C₁ silaformaldoxime **3**, C₁ silaformaldonitrone **4**, C₁ siloxaziridine **5**, C_s iminosilanol **6** and C_s silaformamide **7**. Bond lengths are in Å.

5

6

7