Formaldehyde Oxime ⇌ Nitrosomethane Tautomerism

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Formaldehyde oxime ⇌ nitrosomethane tautomerism, isomeric nitrone, and their common cations and anions are studied with Gaussian-2 theory using MP2(full)/6-31G* geometries and with density functional theory using B3LYP/6-311+G**. Geometrical parameters, harmonic vibrational frequencies, relative stabilities, conformational stabilities, and ionization energies are compared with experimental gas-phase data when available. The formaldehyde oxime ⇌ nitrosomethane tautomerism is compared with the amide ⇌ imidol, imine ⇌ enamine, keto ⇌ enol, and nitro ⇌ *aci*-nitro tautomeric processes. Solvent effects are estimated by the self-consistent isodensity polarizable continuum model (SCIPCM). The influence of hydrogen bonding interactions with the solvent is addressed by including two water molecules. In the final evaluation, formaldehyde oxime is 15.8 kcal/mol more stable than nitrosomethane when the aqueous solvation correction of 3.8 kcal/mol is applied to the G2 energies. Unsolvated formaldehyde oxime is estimated to be 11.1 kcal/mol more stable than nitrone. The estimated gas-phase ionization energies (G2) are 362.5 kcal/mol for formaldehyde oxime, 350.6 kcal/mol for nitrosomethane, and 351.4 kcal/mol for nitrone.

Investigations into tautomerism have led to greater understanding of such concepts as acid−base relationships, structure−reactivity correlations, and hydrogen bonding and have provided valuable insights into the nature of chemical processes.[1] The properties of tautomeric nucleic acids and their relation to genetic errors are illustrative.[2] The wealth of experimental data on tautomers is complemented by an abundance of theoretical calculations that give detailed insights. This is evident for such elementary processes as the amide ⇌ iminol,[3] keto ⇌ enol,[4] imine ⇌ enamine,[5] and nitro ⇌ acinitro[6] tautomerisms.[7] Here we address the oxime ⇌ nitroso system with emphasis on the effect of solvation.

Nitroso compounds are of broad interest with applications ranging from synthetic reagents to spin trapping agents and high energy materials.[8,9] The monomers are usually blue in color in solvents of low dielectric constant. They are often characterized as white solid dimers that result from an NN connection to give diazene dioxides. Even the cis and trans dimers of nitrosomethane are known.[10] Heating nitroso dimers gives the gaseous or liquid monomers.[11] Aqueous solutions of nitroso compounds are invariably colorless. Tautomerization to the more stable oxime occurs readily in aqueous solution and in the presence of hydroxylic groups, suggesting effective acid/base catalysis by protic solvents.[8] Oximes are, of course, important synthons in many organic reactions of which the Beckmann rearrangement is illustrative.[12]

Nitrones are isomeric with the oxime−nitroso tautomers and can be formed as byproducts in the alkylation of oximes.[8] Nitrones are established reagents for 1,3-dipolar cycloadditions and are used as radical spin traps, such as C-phenyl-N-*tert*-butylnitrone (PBN) and 5,5-dimethyl-1-pyrroline-1-oxide (DMPO).[13] A recent theoretical study focused on the trapping of hydrogen, methyl, hydroxyl, and peroxyl radicals.[14] The parent formaldonitrone remains experimentally elusive.

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Despite the abundance of literature data on formaldehyde oxime, nitrosomethane, the nitrone isomer, their various protonated forms, but not the common anion, the potential energy profiles are not complete, especially with respect to the effect of solvation.[12b,15] In the present study we report on all these species, using the accurate Gaussian-2 method[16] and the more economical Becke3-Lee−Yang−Parr hybrid density functional method,[17] and investigate the effect of solvation on the oxime ⇌ nitroso tautomerism explicitly.

Computational Methods

Ab initio molecular orbital calculations[18] were carried out with the GAUSSIAN 94 suite of programs.[19] Geometries and harmonic frequencies were computed with a heavy atom d-polarized split valence basis set using all electron second-order Møller−Plesset perturbation theory, i.e. MP2(full)/6-31G*. Transition structures were identified by their one imaginary frequency. Energies are reported at the G2 level of theory[16a] for which we use instead the 0.95 scaled[20] MP2/6-31G* ZPE correction. Geometries and energies were also computed with the B3LYP method[17] using the 6-311+G** basis set, hereafter referred to as B3LYP. Unless noted otherwise MP2(full)/6-31G* geometrical parameters and G2 energies will be used throughout the text with B3LYP values in parentheses. Optimized MP2(full)6-31G* structures are displayed in the text with B3LYP geometrical parameters in italics and underlined experimental[21,22] values; units are in Å and deg. Energies and vibrational frequencies are given in Tables S1 and S2, respectively, in the Supporting Information. Relative G2 energies are graphically displayed in Figures 1 and 2. Table 1 summarizes G2 energy differences for a series of prototypic tautomeric systems. Bonding properties, such the electron density $\rho(\mathbf{r})$, Laplacian $\nabla^2\rho(\mathbf{r})$, ellipticity ϵ, and energy density $H(\mathbf{r})$ at bond critical points, were determined with Bader's topological one-electron density analysis[23] using optimized MP2(full)/6-31G* wave functions and are sum-

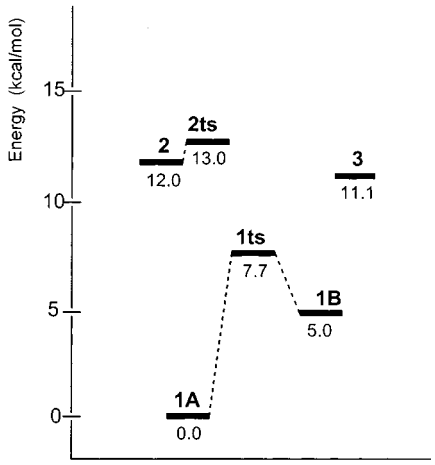

Figure 1. Relative energies (in kcal/mol) of formaldehyde oxime, nitrosomethane, and nitrone and their associated transition structures.

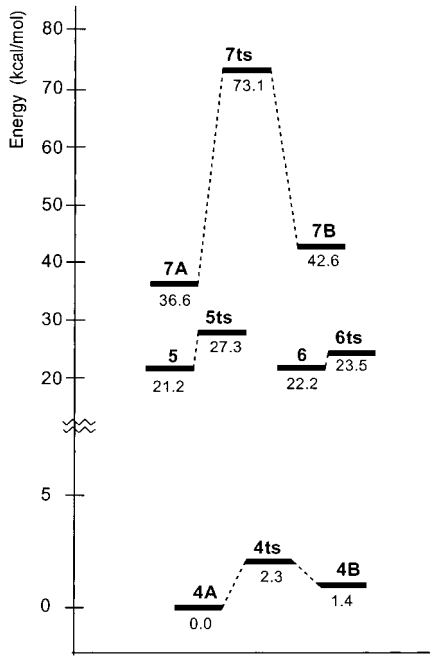

Figure 2. Relative energies (in kcal/mol) of the protonated forms **4**−**7** and their associated transition structures.

Table 1. Summary of G2 Energies (in kcal/mol) for Prototypic Tautomeric Systems[a]

tautomeric pairs	compounds	ΔE	PA
oxime ⇌ nitroso[b]	CH_2=N−OH ⇌ CH_3−N=O	12.0	362.5
nitro ⇌ aci-nitro[c]	CH_3−NO_2 ⇌ CH_2=NO−OH	14.1	355.9
imine ⇌ enamine[d]	CH_3−CH=NH ⇌ CH_2=CH−NH_2	3.9	377.1
keto ⇌ enol[e,f]	CH_3−CH=O ⇌ CH_2=CH−OH	10.8	365.9
amide ⇌ imidic[e,g]	H_2N−CH=O ⇌ HN=CH−OH	11.5	359.5
nitramide ⇌ aci-nitramide[e]	NH_2−NO_2 ⇌ HN=NO−OH	8.8	339.7

[a] All G2 energies include ZPE corrections at MP2/6-31G*. ΔE is the tautomeric energy difference. PA is the proton affinity of the most stable anion. [b] This work. [c] Reference 6. [d] Reference 5. [e] Unpublished work. [f] Reference 4a. [g] Reference 3.

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Table 2. Absolute (in au) and Relative Energies (in kcal/mol) for the 1 − 2 Tautomeric Pair under the Influence of the SCIPCM Model and of H_2O−Complexation

theor level	**1**	**2**	ΔE(**1**−**2**)	$\Delta\Delta E^a$
HF/6-31+G*	168.84811	168.83553	7.89	
+ SCIPCM	168.85685	168.84108	9.89	2.00
+ $2H_2O$	320.90152	320.88176	12.40	3.78
+ $2H_2O$ + SCIPCM	320.92003	320.89962	12.81	4.19
MP2/6-311+G**	169.42005	169.40092	12.00	
+ SCIPCM	169.42647	169.40506	13.44	1.44
+ $2H_2O$	321.99118	321.96383	17.16	3.58
+ $2H_2O$ + SCIPCM	322.00436	321.97656	17.44	3.86
B3LYP/6-311+G**	169.87171	169.85030	13.44	
+ SCIPCM	169.87842	169.85549	14.39	0.95
+ $2H_2O$	322.80907	322.78085	17.71	3.87
+ $2H_2O$ + SCIPCM	322.82145	322.79493	16.65	2.81

[a] Relative energies for the influence of the solvent model on the tautomeric energy difference for each theoretical level. Those for the biswater complexes include a correction for the basis set superposition error.

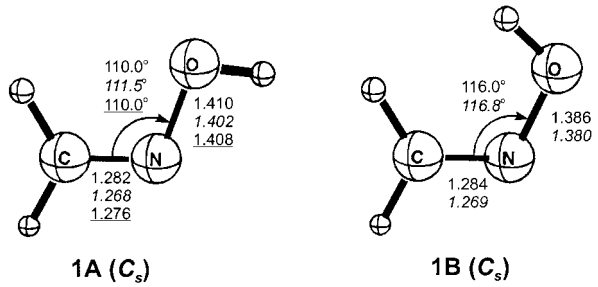
marized in Table 3S together with their NBO natural charges.[24]

The aqueous solvent effect on the geometries of the tautomers was calculated with the self-consistent isodensity surface polarizable continuum model (SCIPCM)[25] using HF/6-31G* and a dielectric constant of $\epsilon = 78.5$. Solvation energies were computed with the 6-311+G** basis set at MP2(fc), using the MP2/6-31G* gas-phase geometry, and at B3LYP using the "solvent geometry" obtained with the same basis set. Because continuum models generally represent the effects of hydrogen bonding inadequately,[26] explicit water−oxime and water−nitrosomethane complexes were studied with and without the SCIPCM model.[27] The effect of solvation (SCIPCM) and H_2O-complexation on the energies of the tautomeric pair are summarized in Table 2.

Results and Discussion

The discussion on geometrical features and energetics of the tautomeric structures, the nitrone isomer, and their cations and anions will be followed by an evaluation of the solvent effect.

Formaldehyde Oxime, CH_2═N−OH (1), prefers an s-trans (**A**) over s-cis (**B**) conformation by 5.0 (5.8) kcal/mol, which may reflect the lone-pair−lone-pair repulsion between the oxygen and nitrogen atoms.[15e] The geometry of s-trans **1A** compares very well with a reported microwave structure,[21] as do the vibrational frequencies (rms = 35 (77) cm^{-1}).[28] Rotating the OH group by 70° out of the molecular plane results in a transition structure with a 0.031 Å elongated N−O bond, which is reduced again by 0.024 Å on rotating the OH group further to s-cis **1B**. The barrier for this rotation of 7.7 (9.7) kcal/mol is similar to an earlier theoretical estimate of 8.5 kcal/mol.[12b] It disagrees strongly with the reported experimental value of 1.16 kcal/mol[28] and suggests that a reexamination of the experimental rotation barrier is warranted.



1A (C_s) **1B (C_s)**

The modest structural difference between the two conformers is reflected in the 0.106 $eÅ^{-3}$ higher electron density ρ at the NO bond critical point of **1B**, indicating a tighter bond. The natural charges show a more polarized character for **1A**, as expected for an s-trans conformation, but this does not appear to influence the properties of the C═N double bonds. Still, the dipole moment for **1A** is small (i.e., 0.71 D at MP2/6-311+G(3df,2p), 0.44 D experimentally)[21b] because of the s-trans relationship between the CH_2 group (+0.285*e*) and the hydroxyl hydrogen (+0.501*e*).

Nitrosomethane, CH_3−N═O (2) has an eclipsed conformation and a barrier for rotation of the methyl group of 0.99 (1.44) kcal/mol that is in excellent agreement with the 1.137 ± 0.005 kcal/mol determined by microwave spectroscopy.[22,29] The agreement with the experimental geometries[22] is also very good with as largest difference the 0.024 Å longer N═O bond; the C−N bond lengthens by 0.011 Å in the staggered transition structure. The calculated frequencies of **2** compare well with the experimental ones (rms = 68 (99) cm^{-1}),[29,30] although the 160 cm^{-1} difference from the observed CH_3 rock frequency of 967 cm^{-1} is rather large. The bond critical point data suggest double bond character for the NO bond despite its small ellipticity. The natural charges show nitrosomethane to be less polarized than its formaldehyde oxime tautomer **1A**. Still, its dipole moment is much larger because of the terminal NO group. The computed dipole moment of 2.81 D at MP2/6-311+G(3df,-2p) agrees well with the observed value of 2.32 D.[22]

The energy difference between tautomers **1** and **2** amounts to 12.0 (13.4) kcal/mol in favor of the formaldehyde oxime isomer. We are unaware of an experimentally determined value for this parent system. For comparison, the G2 energy differences between the parent keto ⇌ enol, amide ⇌ imidol acid, and nitro ⇌ aci-nitro tautomers are similar in magnitude and amount to 10.8, 11.5, and 14.1 kcal/mol (see Table 1).

Nitrone, CH_2═NHO (3) has a long C═N bond of 1.321 Å and a 1.256 Å short dative $^{\oplus}N-O^{\ominus}$ bond. The bond critical point data indicate significant double bonding for both, but this is less pronounced than in its isomers as the bond length differences of 0.039 Å for C═N (**1A**) and

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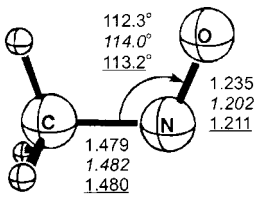
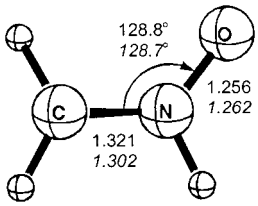


2 (C_s)

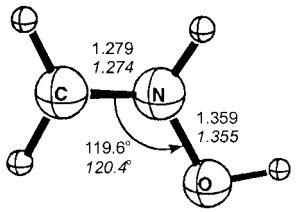


3 (C_s)

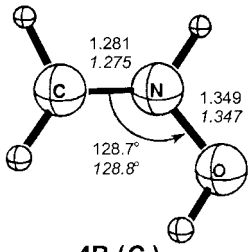
0.021 Å for N=O (**2**) illustrate. The calculated frequencies of 1256 and 1640 cm^{-1} for the respective C=N and N−O (coupled) stretches are in line with a weakened C=N double bond; this CN bond in oxime **1A** has a stretch frequency of 1617 cm^{-1}. The 0.976e difference in charges between the oxygen atom and the NH group underscores the dative nature of the N−O bond. Rotation of the formal C=N double bond by 90° requires a hefty 73.6 kcal/mol. The associated transition structure has an essentially C−N single bond of 1.414 Å and a pyramidalized carbon due to the transfer of charge from the oxygen.

Nitrone **3** is 11.1 kcal/mol less stable than formaldehyde oxime **1A** and is thereby nearly isoenergetic with nitrosomethane while even 4.0 kcal/mol more stable at B3LYP.

(De)protonation. C-, N-, and O-(de)protonations underlie the acid−base relationship of the two tautomers and its nitrone isomer.

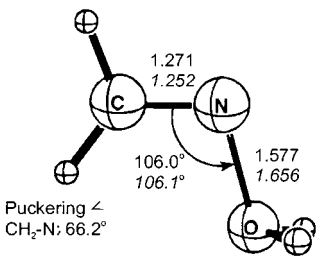


4A (C_s)

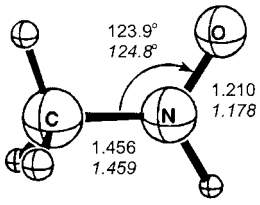


4B (C_s)

N-Protonation of formaldehyde oxime or O-protonation of the nitrone results in **4**. The corresponding proton affinities are 191.6 and 202.8 kcal/mol. Structure **4A** is favored over **4B** by 1.5 (1.2) kcal/mol and a OH rotation barrier of 2.3 (2.7) kcal/mol. The hydroxy group is "floppy" in **4A**, which has, in fact, an imaginary frequency at MP2-(full)/6-311G** and a nearly isoenergetic minimum (**4A′**) in which the OH group is rotated out of the molecular plane by 43°. Its C=N bond length is similar to that of the oxime and 0.042 Å shorter than in the nitrone. However, the N−O bond is elongated from that of the nitrone by a significant 0.103 Å and reflects the disappearance of the dative character on O-protonation; the N−O bond of **4A** is 0.051 Å shorter than that of **1A**.



5 (C_s)

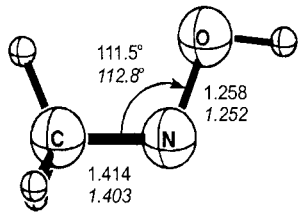


6 (C_s)

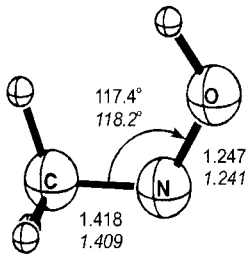
O-Protonation of formaldehyde oxime to give **5** is less favored than N-protonation by 21.2 kcal/mol. Structure **5** is a tight complex between H_2O and the CH_2=N⊕ nitrenium ion as is evident from the 1.577 Å long N−O and 1.271 Å short C=N bond distances. Its pyramidal "trans oxonium" group, with a puckering angle of 66.2°, planarizes on rotation around the N−O bond, which requires 6.1 kcal/mol.

N-Protonation of nitrosomethane and C-protonation of the nitrone gives **6** with proton affinities of 181.4 and 187.5 kcal/mol, respectively. Structure **6**, which is 22.1 kcal/mol less stable than **4A**, has a CH_3-rotation barrier of 1.31 kcal/mol. This cation is more contracted than nitrosomethane with 0.023 and 0.025 Å shorter C−N and N=O bonds, respectively.

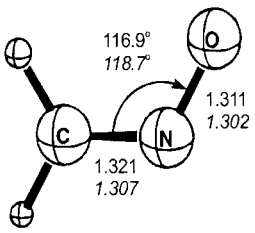
O-Protonation of nitrosomethane and C-protonation of formaldehyde oxime both give **7A**, which is a large 36.5 kcal/mol less stable than **4A**. The 6.0 (7.7) kcal/mol preference of s-trans conformer over the s-cis form **7B** is marginally more than that of neutral **1A** over **1B**. The much larger OH rotation barrier of 36.2 kcal/mol reflects its N=O double bond nature, which is only 0.023 Å longer than in nitrosomethane, while the C−N bond is 0.065 Å shorter.



7A (C_s)



7B (C_s)



8 (C_s)

Evidently, both formaldehyde oxime and nitrosomethane prefer the thermodynamically driven N-protonation. For nitrone this is not an option and expectantly O-protonation is favored. The energetic preference of **4A** over the other cations is largely due to a better dissipation of positive charge over the N-substituent.

Deprotonation of either **1**, **2**, or **3** results in the common anion **8**. The G2 ionization (deprotonation) energy is for formaldehyde oxime 362.5 kcal/mol, for nitrosomethane 350.6 kcal/mol, and for nitrone 351.4 kcal/mol. For comparison, the G2 energies are 377 kcal/mol for acetaldimine,[5] 366 kcal/mol for acetaldehyde,[5] and 356 kcal/mol for nitromethane.[6] Protonation of anion **8** at its most negatively charged center, oxygen, results in the most stable isomer, formaldehyde oxime. The anion is delocalized with nearly equal C−N (1.321 Å) and N−O (1.311 Å) bond lengths and correspondingly similar $\rho(\mathbf{r})$ at their bond critical points. When considered as deprotonated

nitrone, the natural charges of the anion show an increase of 0.234e for carbon and 0.175e for oxygen. The delocalization in this allylic-type anion has been discussed in detail for the related $CH_2-NO_2^{\ominus}$, $CH_2-OH^{\ominus}$, and $CH_2-NH_2^{\ominus}$ anions.[5,6,31] Rotation of the CH_2 group by 90° eliminates the π-resonance, results in lone-pair induced C-pyramidalization and requires 47.0 (50.6) kcal/mol.

Solvent Effects. To this point we have analyzed the structures and energies, but tautomeric equilibria and even structural parameters are known to be medium-dependent. We therefore decided to investigate the solvent effect on the oxime ⇌ nitroso tautomers by the SCIPC model and in addition by the use of explicit water molecules. Because of the significant difference in dipole moments between nitrosomethane and formaldehyde oxime, a strong influence on the tautomeric equilibrium might be expected from a polar medium such as water.

The electrostatic interaction between the solute (nitrosomethane and formaldehyde oxime) and a solvent (water) can be computed with Tomasi's polarizable continuum model (PCM),[25,32] which is derived from earlier self-consistent reaction field (SCRF) models.[33] The PCM model treats the solvent as a structureless, continuous medium characterized by a dielectric constant, ϵ. The charge distribution of the solute induces polarization of the solvent which is represented by a distribution of charge on the surface of the solute cavity. The polarization of the solvent in turn induces polarization of the solute electron density. The Coulombic interaction results in energetic stabilization of the solute. Wiberg and co-workers modified this model by redefining the size and shape of the solute cavity by using an isoelectron density contour.[34] This self-consistent isodensity polarizable continuum model (SCIPCM) has only two adjustable parameters, the dielectric constant ϵ of the solvent and the electron density ρ_o on the solute cavity surface. Wiberg and Rablen[35] have recommended using $\rho_o = 0.0004$ e.Bohr^{-3} for reproducing experimental values of the molar volume of small organic solutes.

The SCIPCM model computes the electrostatic solvation energy, but the solvation energy also includes nonelectrostatic terms for cavity formation and dispersion interactions.[25a] For charged or zwitterionic solutes, the electrostatic term is dominant,[36] but for small neutral solutes all three terms make important contributions. In recent studies on the solvent effects on amide rotational barriers and haloethane conformational equilibria, Wiberg and co-workers considered only the electrostatic term.[25a,34] The neglect of nonelectrostatic terms is justified in these cases since energetic comparisons are made between species having very similar sizes and shapes. In the present case it seems reasonable to neglect the nonelectrostatic terms for the same reason.

Nitrosomethane and formaldehyde oxime were studied with the SCIPCM model using $\epsilon = 78.5$, to mimic an aqueous solution. Geometries and energies were obtained at HF/6-31+G*, at MP2(fc)/6-311+G** (using the "gas phase" MP2(full)/6-31G* geometry), and at B3LYP/6-311+G**. Aqueous bulk solvation stabilizes the oxime relative to nitrosomethane by an additional 2.00 kcal/mol at HF/6-31+G*, 1.44 kcal/mol at MP2(fc)/6-311+G**, and 0.95 kcal/mol at B3LYP/6-311+G**.

These results may seem surprising, because nitrosomethane has the larger dipole moment (exp. μ = 2.32 D,[22] comp. μ = 2.81 D) and might therefore be expected to benefit most by solvation in polar medium. However, many of the vibration−rotation bands of s-trans formaldehyde oxime **1A** exhibit large infrared transition moments, indicating that its small permanent moment (exp. $\mu = 0.44$ D,[21a] comp. $\mu = 0.71$ D) is due to cancelation of intramolecular bond dipoles.[28b] Hence, total permanent molecular dipole moments are poor indicators of expected trends in stabilization due to solvation. In agreement with this analysis, s-cis oxime **1B** has a larger dipole moment (exp. μ = 3,[21a] comp. μ = 3.54 D) than nitrosomethane. Aqueous solvation does decrease the energy difference between the s-cis and s-trans forms of formaldehyde oxime at MP2(fc)/6-311+G** (B3LYP) by 2.25 (2.55) kcal/mol to only 3.55 (3.24) kcal/mol with a corresponding reduction in the OH-rotation barrier. Similar effects have been reported for formamide,[37] sulfamic acid,[38] methyl formate,[39] methyl acetate,[39] and substituted vinylamines.[40]

Continuum models do not describe specific interactions, such as hydrogen bonding, that play a role in aqueous solvation. To account for such interactions mixed discreet-continuum models are used. In such models the solvent−solute hydrogen bonding is explicitly accounted for by including one or more water molecules complexed with the solute, while the continuum model is used to account for the effect of the bulk solvent on the complexed solute.[2,25a,41,42] Discrete water complexes will be described first, followed by the additional effect of the SCIPCM model.

One bis-solvated water complex of formaldehyde oxime and nitrosomethane each was investigated. While the potential energy surface is likely to contain many isomeric complexes, the two optimized structures shown in Figure 3 are representative for the hydrogen bonding between solvent and solute. They were composed from mono-solvated water complexes of which two equilibrium structures were identified for the oxime and three for nitrosomethane. Oxime−biswater complex **9** has C_1 symmetry with one water molecule bridging the N−OH group and the other hydrogen bonding to the oxime oxygen. In the nitrosomethane−biswater complex **10** (C_s symmetry) both water molecules lie in the CNO plane, one hydrogen bonded to oxygen and the other hydrogen bonded to nitrogen. For evaluation of the binding energies of these two biswater complexes a correction for basis set superposition errors (BSSE) was made using the counterpoise method of Boys and Bernardi.[43,44] Table 2 contains the

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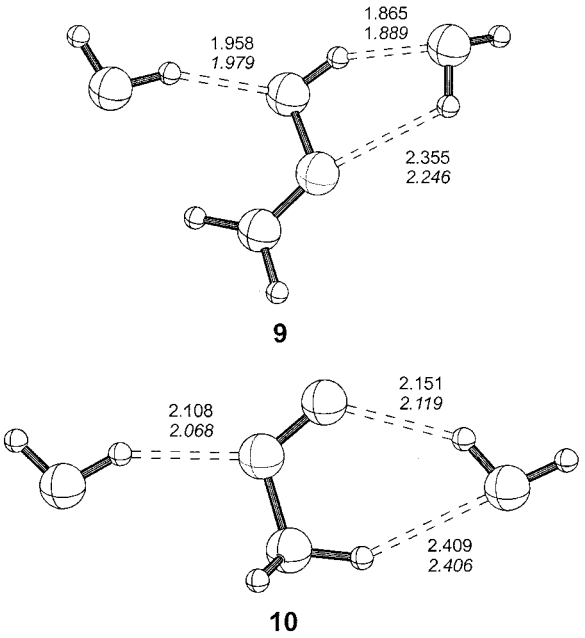

Figure 3. Geometries of the biswater complexes of formaldehyde oxime (**9**) and nitrosomethane (**10**). Upper parameters are at MP2/6-31+G and those in italics at B3LYP/6-311+G*.

resulting **1** ⇌ **2** tautomer energy difference ΔE. The additional stabilization of oxime **1** relative to nitrosomethane due to the explicit solvation of two water molecules is 3.78, 3.58, and 3.87 kcal/mol at HF/6-31+G*, MP2/6-311+G*, and B3LYP/6-311+G*, respectively. The importance of hydrogen bonding with the solvent is hereby illustrated as the corresponding stabilization is only 2.00, 1.44, 0.95 kcal/mol with the SCIPCM model. It is not surprising that the oxime has stronger hydrogen bonds, considering that its N- and O-proton affinities are larger than those of nitrosomethane. Moreover, the oxime can also contribute to hydrogen bonding through its hydroxyl group, whereas nitrosomethane can only act as an acceptor.

Finally, to evaluate the combined influence of the nonspecific electrostatic interaction with the bulk solvent and the explicit complexation with two water molecules, we performed single point calculations for **9** and **10** with the SCIPCM model ($\epsilon = 78.5$ and $\rho_o = 0.0005$ e.Bohr^{-3})[45] using the same levels of theory as before. This combined solvent effect stabilizes oxime **1** over nitrosomethane by 4.19, 3.86, and 2.81 kcal/mol at HF/6-31+G* and MP2 and B3LYP/6-311+G**, respectively, when the BSSE correction is included. Thus, including the SCIPCM model for the biswater complexes increases the HF and MP2 energy difference between oxime **1** and nitrosomethane marginally (0.3−0.4 kcal/mol), as might be expected, while it is reduced at B3LYP by 1.1 kcal/mol.

(45) A slightly larger ρ_o value was used because of the ionic interactions. See, Harris, N. J.; Ohwada, T.; Lammertsma, K. *J. Comput. Chem.* **1998**, *19*, 250.

Thus, in the final evaluation the energy difference between the formaldehyde oxime and nitrosomethane increases significantly upon solvation in an aqueous medium. Using the MP2/6-311+G** solvation effect and their G2 energies gives a final energy difference between **1** and **2** of 15.8 kcal/mol.

Conclusions

Of the parent tautomeric system, formaldehyde oxime **1** is 12.0 kcal/mol more stable than nitrosomethane **2** at G2. Solvation enhances this stability by 3.8 kcal/mol (BSSE corrected) as determined by the self-consistent isodensity polarizable continuum model (SCIPCM) of the biswater complexes. Both the dielectric continuum and the complexation with two water molecules contribute to this relative stabilization of formaldehyde oxime. Nitrone **3** was only investigated as an isolated molecule and is isoenergetic with nitrosomethane at G2.

The MP2(full)/6-31G* geometries of formaldehyde oxime and nitrosomethane compare well with those reported from microwave studies. The computed 7.7 kcal/mol OH bond rotation of the preferred s-trans conformation of the oxime, however, suggests that the reported experimental value of 1.16 kcal/mol significantly underestimates this barrier. Rotation of the methyl group in eclipsed nitrosomethane requires 1.0 kcal/mol at G2 and is virtually identical to the experimental value. Natural charges and bond critical point data confirm the importance of the dative character of nitrone's NO bond.

Tautomerism is an acid/base-catalyzed process, and therefore the related cations and anions were considered. The gas-phase proton affinities of formaldehyde oxime, nitrosomethane, and nitrone are 191.6, 181.4, and 202.8 kcal/mol, respectively, and the corresponding deprotonation energies are 362.5, 350.6, and 351.4 kcal/mol, respectively. Cation **4**, which results from both N-protonation of formaldehyde oxime and an O-protonation of the nitrone, is by far the most stable of all the protonated isomers. Anion **8**, which results in deprotonation of any of the isomers, is highly delocalized.

Acknowledgment. This work was supported by the U.S. Air Force Office of Scientific Research under F49620-94-1-0451.

Note Added After ASAP: Formaldehyde oxime and nitrosomethane were mislabeled in Figure 3 and the TOC graphic in the version posted ASAP September 13, 2001. The corrected version was posted September 28, 2001.

Supporting Information Available: All geometries including those of transition structures. Tables of absolute and relative energies of all equilibrium and transition structures, and vibrational frequencies and bond critical data for **1**, **2**, **3**, **4A**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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