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LETTERS

G2 Calculations of Weak Molecular Complexes: H_2O-NO

David W. Ball[†]

Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115

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A variety of complexes between NO and H_2O molecules were studied using *ab initio* G2 theory. Calculations showed that both H-bonded and O-bonded complexes with NO were slightly stable with respect to free H_2O and NO at 0 K, but at 298 K the free molecules were slightly stabler than all of the four possible complexes studied. Implications for atmospheric and biochemical systems will be introduced.

Introduction

The stable free radical NO is an important component in smog and direct corrosion.[1,2] The discovery of NO's role in physiological processes[3] has expanded nitric oxide interest into biology, making it the target of many studies. In the atmosphere, NO is constantly produced by high-energy reactions (i.e. lightning or combustion) and is oxidized to nitrogen dioxide, NO_2, by ozone or hydroperoxide. While NO concentrations in the troposphere are usually below 1 ppm, localized buildups of nitrogen oxides ("NO_x") are necessary for photochemical smog formation.[4]

NO is considered hydrophobic with respect to an aqueous phase. However, there should be some interaction between NO and H_2O molecules at least due to dipole−dipole interactions. The formation of even a weak complex would have implications in atmospheric chemistry, where gas-phase water can be considered a ubiquitous species, and in aqueous chemistry of nitric oxide. A weak complex was announced in a 1973 paper by Fredin,[5] who cocondensed NO and H_2O vapors in solid nitrogen matrices at 10 K. New infrared absorptions were noted in the H_2O asymmetric and symmetric stretching regions, as well as the H_2O bending and the NO stretching regions. No low-frequency (i.e. below 1597 cm^{-1}) vibrational absorptions were reported.

We have examined four possible interactions between individual NO and H_2O molecules using G2 calculations.[6] The reason for going to such high-level calculations is that the interactions between these molecules are expected to be weak, as suggested by the earlier experimental work.[5] While NO has a strong affinity for unpaired-electron species (like the Fe^{2+} ion in oxyhemoglobin or the unpaired electrons in molecular oxygen), it is relatively unreactive toward electron-paired compounds. We have been unable to find any previous work on H_2O-NO interactions except for the 1973 reference cited above. However, there has been some work on the isomeric aminoperoxy radical, $H_2NOO^{\bullet}$.[7] To compare the stabilities of H_2O-NO complexes to the aminoperoxy radical as well as the separated molecules, G2 calculations were also performed on two stereoisomers of $H_2NOO^{\bullet}$.

Calculational Details

GAUSSIAN 94[8] was used for this study. All calculations were performed on a Cray Y-MP8/864 supercomputer. The G2 level of *ab initio* calculations uses all-electron, second-order Møller−Plesset (MP) calculations to determine an optimized geometry, appends energy corrections using fourth-order MP calculations using various basis sets, and then includes energy corrections for residual correlation effects using a QCISD(T) calculation and a final empirical correction to the correlation energy. (Details can be found in refs 6 and 9.) Optimum structures were visualized using Hyperchem 4.5.

[†] E-mail: d.ball@popmail.csuohio.edu.

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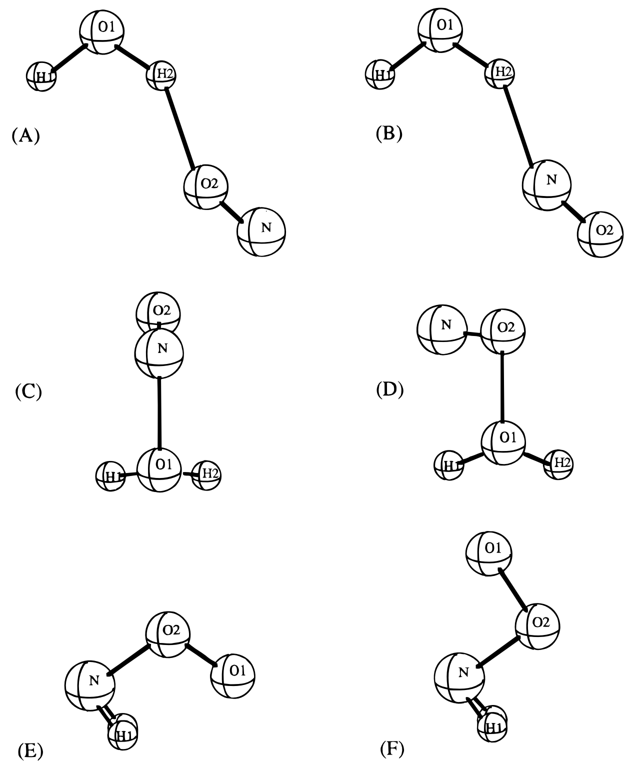

Figure 1. Four H_2O-NO complexes and two aminoperoxy radicals. The labeling of the atoms in the complexes are consistent with Tables 1 and 2. (A) The H−O bonded complex; (B) the H−N bonded complex; (C) the O−N bonded complex; (D) the O−O bonded complex; (E) the *cis*-aminoperoxy radical; (F) the *trans*-aminoperoxy radical.

Results and Discussion

Figure 1 shows the optimized structures of the four H_2O-NO complexes and the two aminoperoxy radical species. Structures of the two isolated molecules will not be discussed except for comparative purposes. The four H_2O-NO complexes were not constrained to planar structures, but Figure 1 shows clearly that a near-planar geometry is adopted for the two H-bonded complexes. Conversely, for the O-bonded complexes the NO moiety is angled with respect to the H−O−H plane. In the O−N complex (Figure 1C), the NO molecule adopts a position whose projection almost perfectly bisects the H−O−H angle, while in the O−O complex (Figure 1D) the NO molecule almost eclipses one of the O−H bonds of H_2O. Both of the aminoperoxy radicals have minimum-energy geometries (Figure 1E,F) possessing a plane of symmetry (coincident with the plane of the figure).

TABLE 1: Structural Parameters for Four H_2O-NO Complexes (Refer to Figure 1)[a]

	1A	1B	1C	1D
r(H1−O1)	0.946	0.946	0.971	0.946
r(H2−O1)	0.947	0.947	0.961	0.947
r(N−O2)	1.125	1.125	1.145	1.128
r(H2−O2)	2.656			
r(H2−N)		2.655		
r(O1−N)			2.741	
r(O1−O2)				3.091
α(H1−O−H2)	105.4	105.5	103.9	105.7
α(H2−O2−N)	147.5			
α(O1−H2−O2)	158.1			
α(H2−N−O2)		147.4		
α(O1−H2−N)		158.0		
α(H1−O1−N)			85.7	
α(O1−N−O2)			109.6	
α(H1−O1−O2)				114.9
α(O1−O2−N)				92.8
$\delta 1$	4.5	4.6	84.5	126.1
$\delta 2$	4.2	4.4	128.8	137.3

[a] All distances in Å, all angles in deg.

Table 1 lists the specific structural parameters for the four G2-optimized H_2O-NO complexes. The atoms labeled in Figure 1 are used to describe bond distances, bond angles, and molecular dihedral angles. The dihedral angle $\delta 1$ is defined as the angle of the fourth atom out of the O1−H1−X or H1−O1−X plane, where X is the N or O2 atom (depending on the particular complex). The dihedral angle $\delta 2$ is defined as the angle of the final atom out of the plane of the previous three atoms along the same bond path. Bond angles and distance can be compared with the G2 results for free H_2O and NO of $r(O-H) = 0.947$ Å, $\alpha(H-O-H) = 105.5°$, and $r(N-O) = 1.127$ Å.

The minimum-energy distance between the H_2O and NO complexes ranges between 2.65 and 3.09 Å. This is a rather long bond distance and is consistent with the idea of a fairly weak molecular complex. There is support for this by noting that the O−H and N−O bond distances in the complexes are close to those values for the free molecules. The largest variance is in the N−O bond distance for the O1−N bonded complex, which has increased *ca.* 0.02 Å over free nitric oxide. A similar "extreme" is found for the H−O−H bond angles of the complexes, which vary very little from the calculated value for free H_2O (which is itself too high by about 1.0° from the experimental value). The O1−N bonded complex showed a slightly constricted H−O−H bond angle of 103.9°, while the rest of the complexes were calculated to have H−O−H bond angles very close to those of free water. (Structural parameters are not reported for the two aminoperoxy radicals.)

Vibrational frequencies were calculated for all complexes as a matter of course. For the high-frequency H_2O and NO vibrations (three for H_2O and one for NO), there is very little difference in the calculated harmonic frequencies for the four complexes. On this basis, it would therefore be difficult to determine which structure(s) were observed experimentally by Fredin,[5] especially in the absence of isotope substitution information. There were some variations in the values and descriptions of the low-frequency vibrations, as might be expected from the structures of the complexes. Far-IR vibrational absorption or microwave rotational spectra—with the appropriate isotopic substitution—would be useful in determining the preferred complex geometry. Listings of the vibrational frequencies, their descriptions, and rotational constants are not included here; interested persons can contact the author for the information.

Table 2 lists the calculated G2 energies of the six species

TABLE 2: Energy Differences between Species 1A−F and Free $H_2O + NO$[a]

	1A	1B	1C	1D	1E	1F
E_{el}	−206.072 76	−206.073 75	−206.072 82	−206.072 86	−205.951 98	−205.949 22
Δ*E*, 0 K	−1.96	−4.55	−2.11	−2.21	+315.2	+322.4
Δ*E*, 298 K	+2.02	+0.32	+2.21	+2.21	+311.0	+318.6

[a] Compare to $E_{el}(H_2O+NO) = -206.072\,02$ hartree and $E_{th}(H_2O+NO) = 0.030\,233$ hartree. All absolute energies in hartrees; all Δ*E*'s in kJ/mol.

studied here, as well as the differences in G2 energies with respect to free $H_2O + NO$. The table lists two energy differences: an energy difference at 0 K and an energy difference at 298 K. One immediate conclusion is that the two aminoperoxy radicals are much higher in energy than any of the four H_2O-NO complexes. It is doubtful that such radicals will have any significant impact on $H_2O + NO$ chemistry except where high-energy sources (i.e. hard UV photons) are present. The *cis* radical is slightly more stable than the *trans* radical owing, most likely, to a hyperconjugation effect from the amino hydrogens.

Table 2 also shows that the **1B** complex is most stable, in which the water interacts through a hydrogen atom and the NO through the N atom. This is surprising from dipole-moment arguments, since both of these atoms would be expected to carry the partial positive charge in the respective polar molecules. However, it might be justified on the basis of hyperconjugation or resonance effects. Complexation through the oxygen atom of water gives a slight energy stabilization which is largely indifferent to NO orientation.

All four H_2O-NO complexes are lower in energy with respect to free $H_2O + NO$ at low temperatures. However, at 298 K all four complexes are *higher* in energy with respect to the isolated molecules. The **1B** complex is only slightly higher in energy at 298 K, suggesting that it is the relatively stable species at only somewhat lower temperatures. The inversion of relative energies caused by an increase in temperature has two contributions. First, there is a contribution due to the higher vibrational temperatures of the complexes. The H_2O-NO complexes have five new low-frequency vibrations that are easily populated by thermal energy. This increases their thermal energy content faster than that of free $H_2O + NO$, thereby raising their relative energies. Second, there is a $T\Delta S$ term that should counteract the vibrational energy contribution. However, even in the formation of $(NO)_2$—in which the lone electrons of two NO molecules become paired—the $T\Delta S$ terms is considered negligible due, in part, to the weakness of the new N−N bond and the concomitant weakening of the two N−O bonds. It is therefore not surprising that entropic factors have a minor effect in the formation of these weak complexes.

These results do suggest that H_2O and NO would form weak but stable complexes at (not very) reduced temperatures.

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