Hydroxylamine as an oxygen nucleophile. Structure and reactivity of ammonia oxide

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Electronic Supporting Information

1. Details of the crystallography.

2. Calculations. Tables S1 – S4.

Calculated geometries and energies for hydroxylamine, ammonia oxide and hydroxylamine hydrochloride, in the gas phase and with solvation by water molecules.

1. Details of the crystallography.

The crystals were first obtained from the decomposition of 2-chloroacetohydroxamic acid in solution in alcohol at pH 6. They are best prepared by mixing equal volumes of 1 M $NH_2OH.HCl$ and 0.5 M KOH in hot methanol, giving a solution containing equal quantities of NH_2OH and its hydrochloride. After filtering off the KCl which immediately precipitates, slow evaporation of the solvent at room temperature gives colorless crystals, mp 86-87°C. These show two well-resolved ^{15}N (natural abundance) signals, at -312.7 and -314.6 ppm (relative to NO_3^-) in the solid state NMR.

Crystal data: $ClH_7N_2O_2$, Mw=102.53, colourless prism 0.35x0.18x0.07mm^3, monoclinic P21/c (No. 14), a=7.2167(1), b=8.1338(2), c=7.0381(2)Å, β=92.35(1)°, Z=4, V=412.79(2)Å3, T = 120(2)K, DX = 1.650 g cm-3, λ = 0.71073 Å, μ = 0.762 mm-1, Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems Cryostream cooling apparatus, 3.78° < θ < 45.27°, 12868 measured reflections, 3441 independent (Rint=0.025), 3071 with I > 2σ(I). The structure was solved by direct methods (SHELXS-97) and refined by least squares (SHELXL-97) using Chebyshev weights on Fo2 to R1 = 0.023, wR2 = 0.056 (I > 2σ(I)), 53 parameters, goodness-of-fit on F2 1.083, residual electron density 0.39 e Å-3. All hydrogen atoms were located unambiguously in the final difference map. For the refinement, the –NH$_3$ groups were treated as rigid groups with idealized tetrahedral geometry and the hydrogen atoms of these groups were assigned a common isotropic displacement parameter (there are no significant differences if the structure is refined without these restraints). The coordinates of the –OH hydrogen atom were refined successfully without any restraints.

Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax (+49) 7247-808-666; e-mail crysdata@fiz-karlsruhe.de) on quoting the deposition number CSD-415541.

2. Calculations

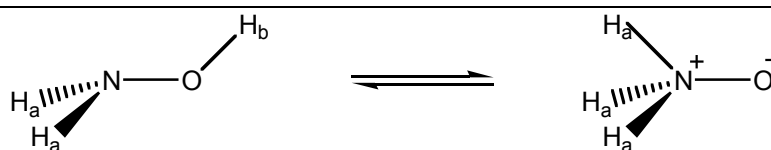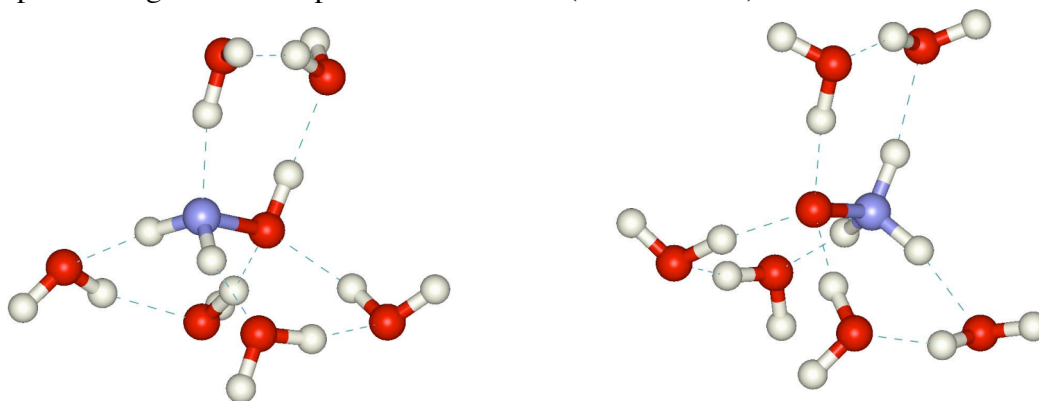### Geometries of 1 and 1z in the gas phase and in the presence of solvating H_2O

Table S1. B3LYP/6-311++G(d,p) geometries for hydroxylamine and ammonia oxide in the gas phase,[a] and PCM/B3LYP/6-311++G(d,p) single-point energies for the optimized structures.

	H_2NOH	H_3NO[b]
R (N-O)	1.444	1.367
R (O-H)	0.963	
R (N-H)	1.018	1.034
θ (N-O-H)	102.8	
θ (H-N-O)	104.2	113.1
θ (H-N-H)	106.2	
q (H_a)	0.250	0.281
q (H_b)	0.278	
q (N)	-0.496	-0.365
q (O)	-0.281	-0.478
E_{elec}[b]	-131.766887	-131.728118
G[b]	-131.749030	-131.710051
$E_{elec}^{PCM, b}$	-131.781612	-131.764816
$G_{nuclear}^{corr}$	-82.67	-82.00
$\Delta G_{sol} = E_{elec}^{sol} - E_{elec}^{gas}$	-9.24	-23.03
ΔE_{elec}	24.3	
$\Delta G_{nuclear}$	0.67	
$\Delta G^{o} = \Delta G_{nuclear} + \Delta E_{elec}$	25.0	
$\Delta\Delta G_{solv}$	-13.8	
$\Delta G^{o}_{sol} = \Delta G^{o} + \Delta\Delta G_{solv}$	11.2	

[a] Bond lengths in Å, angles in deg. [b] C_{3v} symmetry.
These values are comparable with literature values.[1, 3]

Table S2. B3LYP/6-31+G(d) geometries for hydroxylamine and ammonia oxide with six water molecules included explicitly as the first solvation shell, [a]and PCM/B3LYP/6-31+G(d) single-point energies for the optimized structures (shown below).

	H$_2$NOH	H$_3$NO
R (N-O)	1.460	1.419 [b]
R (O-H)	0.995	
R (N-H)	1.028	1.041
θ (N-O-H)	104.1	
θ (H-N-O)	103.8	109.4
	104.5	109.5, 109.7
θ (H-N-H)	107.7	110.0, 108.9, 109.4
q (H$_a$)	0.484	0.524
q (H$_b$)	0.603	
q (N)	-0.876	-0.892
q (O)	-0.713	-0.680
E_{elec} [b]	-590.3485852	-590.3552879
$E_{elec}^{PCM, b}$	-590.3828816	-590.3899498
ΔE_{elec}	-4.21	K(calc) = 1.73 e-3
$\Delta E_{PCM/B3LYP}$	-4.44	K(calc) = 1.22 e-3

[a] Bond lengths in Å, angles in deg. [b] *Cf.* the value of 1.417(1) in the crystal.

Table S3. B3LYP/6-31+G(d) geometry of hydroxylammonium in the gas phase, with four water molecules explicitly included in the first solvation-shell.[a]
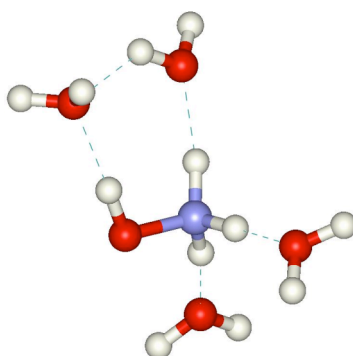
	H$_3$N$^+$OH
R (N-O)	1.418[b]
R (O-H)	0.990
R (N-H)	1.042
θ (N-O-H)	106.1
θ (H-N-O)	105.2, 109.2, 109.9
θ (H-N-H)	110.7, 110.9, 110.9

[a] Bond lengths in Å and angles in deg. [b] *Cf.* the value of 1.415(2) in the crystal

Table S4. Calculated energetics (kcal/mol) for the tautomeric process NH$_2$OH → NH$_3$O in the gas phase and in aqueous solution, at different levels of theory.

Method	Gas Phase		Aqueous solution	
	ΔE	ΔG	ΔG(*soln.*) Rigid charges[a]	ΔG(*soln.*) PCM polarized[b]
B3LYP[22]/6-311++G(d,p)[23]	24.33	24.45	5.69	-5.20
MP2//B3LYP/6-311++G(d,p)	27.69	27.82	9.06	-1.83
MP4(SDTQ)// B3LYP/6-311++G(d,p)	27.47	27.60	8.84	-2.05
CCSD(T)[24]// B3LYP/6-311++G(d,p)	25.93	26.06	7.30	-3.59

[a] ΔG(*soln.*) is the sum of ΔG(*g*) computed at the specified level of theory and $\Delta\Delta$G$_{solv}$(**NH$_2$OH → NH$_3$O**) calculated with the charges kept rigid on going from the gas phase to solution.
[b] ΔG(*soln.*) is the sum of ΔG(*g*) computed at the specified level of theory and $\Delta\Delta$G$_{solv}$(**NH$_2$OH → NH$_3$O**) calculated with free energy perturbation, using PCM polarized charges.

References.
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