Electron Affinity of a Nitroxide Radical

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From a thermochemical cycle, an electron affinity of 13.2 ± 6 kcal/mol is derived for Et2NO, based on the gas-phase acidity and O-H bond strength of Et2NOH. This electron affinity is 35 kcal/mol lower than that of the corresponding alkoxy radical, Et2CHO. The gas-phase basicity of Et2NOH is also reported.

The nitroxide group finds wide use as a spin label, an oxidizing agent, a product of spin trapping, and as a hydrogen donor.1 There is little thermochemical data available for this functionality, however, and what is known is scattered throughout the literature. Heats of formation are available from several sources, and some mass spectrometric ionization potentials are known.2 There seems to be no quantitative information on the gas-phase electron affinity (EA) of the nitroxide functionality, even though the anion should be a stable closed-shell species. In conjunction with studies on the ion/molecule chemistry of the functionality series of hydroxylamines, nitroxides, and nitrones, we report an electron affinity for diethyl nitroxide.

We can indirectly obtain the EA of a nitroxide radical from the thermochemical cycle3-6 so that EA(R2NO•) = -DH(R2NOH) + IP(H•) - DHs(2NO2). The O–H bond strength of diethylhydroxylamine is known to be 9.5 ± 2 kcal/mol and IP(H•) = 131.6 kcal/mol, thus only its acidity is needed to complete the cycle. Using ICR spectra and standard techniques for measuring equilibrium gas-phase acidities, we find that Et2NOH is 0.4 kcal/mol more acidic than PhCH2OH and 0.9 kcal/mol less acidic than CH3CN in ΔS°acid. Using ΔS°acid = 22.0 eu, as for the alcohol, we obtained ΔHacid(Et2NOH) = 369.9 ± 2.5 kcal/mol. This gives EA(Et2NO•) = 13.2 ± 6 kcal/mol. The uncertainty given includes the ±2 kcal/mol uncertainty in anchoring the gas-phase acidity scale to such a cycle.6

When compared with typical alkoxyl radical EAs of 36-50 kcal/mol, this is a rather low value. The best comparison is with that of the carbon analog of DEHA, 3-pentanol. We find ΔHacid(3-pentanol) = 371.0 ± 2.0 kcal/mol and, using a standard DH(RO–H) value of 104 ± 2 kcal/mol, we derive EA(Et2CHO•) = 45.9 ± 4 kcal/mol. The closest experimental homolog is EA(t-PrO•) = 42.4 ± 0.7 kcal/mol.7 The decrease in adiabatic EA on going to the aza compound of 33 kcal/mol can be attributed either to resonance stabilization of the nitroxide radical or to the electron being added to a nitrogen, rather than oxygen, radical, since EA(R2N•) is typically 10-20 kcal/mol lower than its respective EAs. The solution-phase reduction potentials of t-BuNO• and CH3O• show a similar difference of 23 kcal/mol, indicating comparable solvation effects. While the presence of the nitrogen lone pair adjacent to the oxygen anion in Et2NO• might be predicted to reduce the acidity due to p-p electron repulsion, MO calculations2 indicate that this is offset by a similar interaction in the acid form for little net acidity change of Et2NO• vs. Et2CHO•. In contrast to the acidity, we find that Et2NOH is 0.4 kcal/mol less basic than 1-aminopropane, or 12.0 kcal/mol less basic than its carbon analog Et2NCH3.8 Once again, there are two possible rationalizations: (1) the p-p electron repulsion present in the neutral base is not present in the protonated conjugate acid form, due to the nitrogen lone pair being tied up by the proton, or (2) the p acceptor effect of the α-OH group is expected to reduce basicity by 10-12 kcal/mol based on σ+β calculations.14

Studies on other ion/molecule chemistry of these functional groups and pertinent molecular orbital calculations are in progress.

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