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 $Et_2NO\cdot$, based on the gas-phase acidity and O–H bond strength of Et_2NOH. This electron affinity is 35 kcal/mol lower than that of the corresponding alkoxy radical, $Et_2CHO\cdot$. The gas-phase basicity of Et_2NOH 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,[2] and some mass spectrometric ionization potentials are known.[3] There seems to be no quantitative information[4] 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 cycle[5,6] so that $EA(R_2NO\cdot) =$
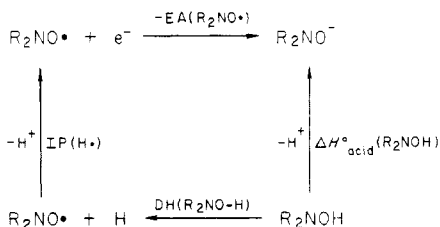
$DH(R_2NO–H) + IP(H\cdot) - \Delta H°_{acid}(R_2NOH)$. The O–H bond strength of diethylhydroxylamine is known to be 69.5 ± 2 kcal/mol[7] and $IP(H\cdot) = 313.6$ kcal/mol;[8] thus only its acidity is needed to complete the cycle. Using ICR spec-

trometry and standard techniques for measuring equilibrium gas-phase acidities,[6] we find that Et_2NOH is 0.4 kcal/mol more acidic than $PhCH_2OH$ and 0.9 kcal/mol less acidic than CH_3CN in $\Delta G°_{acid}$. Using $\Delta S°_{acid} = 22.0$ eu, as for the alcohols,[6] we obtained $\Delta H°_{acid}(Et_2NOH) = 369.9$ ± 2.5 kcal/mol. This gives $EA(Et_2NO\cdot) = 13.2 \pm 6$ 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,[6,7] this is a rather low value. The best comparison is with that of the carbon analog of DEHA, 3-pentanol. We find $\Delta H°_{acid}(3\text{-pentanol}) = 371.0 \pm 2.0$ kcal/mol and, using a standard $DH(RO–H)$ value of 104 ± 2 kcal/mol,[9] we derive $EA(Et_2CHO\cdot) = 45.9 \pm 4$ kcal/mol. The closest experimental homolog is $EA(i\text{-}PrO\cdot) = 42.4 \pm 0.7$ kcal/mol.[7c] 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 $EA(R_2N\cdot)$ is typically 10–20 kcal/mol.[6] The solution-phase reduction potentials of $(t\text{-Bu})_2NO\cdot$ and $CH_3O\cdot$ show a similar difference of 23 kcal/mol,[11] indicating comparable solvation effects. While the presence of the nitrogen lone pair adjacent to the oxy anion in Et_2NO^- might be predicted to reduce the acidity due to p–p electron repulsion, MO calculations[12] indicate that this is offset by a similar interaction in the acid form for little net acidity change of Et_2NOH vs. Et_2CHOH. In contrast to the acidity, we find that Et_2NOH is 0.4 kcal/mol less basic than 1-aminopropane, or 12.0 kcal/mol less basic than its carbon analog Et_2NCH_3.[13] 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 σ-acceptor effect of the α-OH group is expected to reduce basicity by ca. 10–12 kcal/mol based on $\sigma_I\rho_I$ calculations.[14]

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

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