PHOTOELECTRON SPECTROSCOPY OF SUBSTITUTED PHENYLNITRENES

NELONI R. WIJERATNE, MARIA DA FONTE and PAUL G. WENTHOLD, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084*.

Nitrenes are unusual molecular structures with unfilled electronic valences that are isoelectronic with carbenes. Although, both can be generated by either thermal or photochemical decomposition of appropriate precursors they usually exhibit different reactivities. In this work, we carry out spectroscopic studies of substituted phenylnitrene to determine how the introduction of substituents will affect the reactivity and its thermochemical properties. All studies were carried out by using the newly constructed time-of-flight negative ion photoelectron spectrometer (NIPES) at Purdue University. The 355 nm photoelectron spectra of the *o*-, *m*-, and *p*-chlorophenyl nitrene anions are fairly similar to that measured for phenylnitrene anion. All spectra show low energy triplet state and a high energy singlet state. The singlet state for the *meta* isomer is well-resolved, with a well defined origin and observable vibrational structure. Whereas the singlet states for the *ortho* and *para* isomers have lower energy onsets and no resolved structure. The isomeric dependence suggests that the geometry differences result from the resonance interaction between the nitrogen and the substituent. Quinoidal resonance structures are possible for the open-shell singlet states of the *o*- and *p*-chlorinated phenyl nitrenes. The advantages of this type of electronic structures for the open-shell singlet states is that the unpaired electrons can be more localized on separate atoms in the molecules, minimizing the repulsion between. Because the *meta* position is not in resonance with the nitrenes, substitution at that position should not affect the structure of the open-shell singlet state. The measured electron affinities (EA) of the triplet phenylnitrenes are in excellent agreement with the values predicted by electronic structure calculations. The largest EA, 1.82 eV is found for the *meta* isomer, with *para* being the smallest, 1.70 eV.