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The Photoelectron Spectrum of the α,3-Dehydrotoluene Biradical

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The α,3-dehydrotoluene biradical,[1] and related structures[2] have been recently the subject of considerable interest in relation to the proposed mechanism of action of neocarzinostatin.[3,4] In particular, the facile cyclization of (*Z*)-1,2,4-heptatrien-6-yne to **1** is expected to be exothermic,[1,5] in contrast to the comparable cyclization of (*Z*)-1,5-hexadien-3-yne to the *p*-benzyne biradical.[6] The heats of formation of biradicals have also been a longstanding problem[7] for both theory and experiment for which no globally applicable solution has been found. We report gas-phase preparation and the 10.49-eV laser photoelectron spectrum of **1** and apply the measured ionization potentials to the prediction of $\Delta H_{f,298}$[**1**] by an additivity scheme corrected by a valence promotion energy.[8,9] We find two photoelectron bands corresponding to ionization potentials at 7.29 and 8.27 ± 0.04 eV. Comparison of the ionization potentials of **1** to those of benzyl radical **2** and *m*-tolyl radical **3** suggests that the singlet–triplet splitting of **1** is less than 5 kcal/mol and that $\Delta H_{f,298}$[**1**] lies just a little below (≤5 kcal/mol) the additivity estimate[10] of 109 kcal/mol.

The α,3-dehydrotoluene biradical, **1**, was prepared, seeded in a supersonic jet of helium, by the flash pyrolysis of either *m*-nitrophenethyl nitrite **4** or (*Z*)-1,2,4-heptatrien-6-yne, **5**. Standard procedures were used to prepare **4** from the corresponding alcohol. The synthesis of **5** was performed according to the procedure of Myers *et al.*[1] The pyrolysis nozzle design, operating conditions, time-of-flight mass and photoelectron spectrometers, and vacuum–UV light generation have been previously described.[11] Pyrolysis conditions were chosen to optimize the photoelectron spectrum of the biradical. Pyrolysis of **4** (1500 K, 10 μs) produces only the expected NO, NO_2, formaldehyde, and a C_7H_6 species at $m/e = 90$, as evidenced by the 10.49-eV photoionization mass spectrum. Pyrolysis of **5** under conditions optimized for biradical production (considerably lower temperature than needed for **4**) gives no new mass peaks, indicating that the changes in the photoelectron spectrum are due to an isomer of **5**. We believe that the same species, the biradical **1**, was formed from the two different precursors.

The photoelectron spectrum of pyrolyzed **4** is shown in Figure 1. A retarding potential of ~1.7 V was applied to improve energy resolution for the fast electrons and to exclude photoelectrons due to nitric oxide (from the pyrolysis of **4**). Photoionization of **1**, *in principle*, could produce up to four observable photoelectron bands because **1** and $\mathbf{1}^{\bullet+}$ each have two low-lying electronic states. These are designated X^1A'' and a^3A'' for **1** and X^2A' and A^2A'' for $\mathbf{1}^{\bullet+}$, with the relative ordering of the states determined by *ab initio* calculations.[12] Qualitatively, the X^1A'' and a^3A'' states of **1** both derived from the "open-shell" biradical configuration, while the X^2A' and A^2A'' states of $\mathbf{1}^{\bullet+}$ come from removal of an electron from either the benzylic π-system or the in-plane sp^2 orbital of **1**, respectively. If the singlet–triplet splitting, ΔE_{ST}, of **1** were small (≤5 kcal/mol given the width of the observed photoelectron bands), then the $X^2A' + e^- \leftarrow X^1A''$ and $X^2A' + e^- \leftarrow a^3A''$ bands would overlap. Similarly, the $A^2A'' + e^- \leftarrow X^1A''$ and $A^2A'' + e^- \leftarrow a^3A''$ bands would not be separately resolved. If, on the other hand, ΔE_{ST}[**1**] were to be greater than 5 kcal/mol, the $X^2A' + e^- \leftarrow a^3A''$ and $X^2A' + e^- \leftarrow X^1A''$ photoelectron bands in particular, should be resolved, with the $X^2A' + e^- \leftarrow a^3A''$ ionization giving faster photoelectrons than $X^2A' + e^- \leftarrow X^2A''$. One would expect the $X^2A' + e^- \leftarrow a^3A''$ band to be of lower intensity than the $X^2A' + e^- \leftarrow X^1A''$ band because of a Boltzmann factor (assuming equilibration). Because supersonic jet expansions in helium do not cool electronic degrees of freedom efficiently,[13] the "temperature" used for an *estimate* of the Boltzmann factor (up to ~20%) would be the pyrolysis temperature (~1500 K), which would give a small but definitely observable peak.

We find two low-energy bands in the photoelectron spectrum corresponding to ionization potentials of 7.29 and 8.27 ± 0.04 eV, which we designate as IP_π[**1**] and IP_σ[**1**], respectively. The same two bands appear in the photoelectron spectrum of pyrolyzed **5**, with some additional features attributable to the (*E*) isomer of **5**. Given the sharpness of the first photoelectron band and the similarity of the two ionization potentials to those of benzyl and *m*-tolyl radical, we believe the most likely interpretation of the observed spectrum is that ΔE_{ST}[**1**] is small and that the a^3A'' and X^1A'' bands are not separately resolved. The difference between IP_π[**1**] and IP_σ[**1**] is also consistent with the energy difference between the X^2A' and A^2A'' states of $\mathbf{1}^{\bullet+}$ based on orbital energies from an ROHF/6-31G* calculation.[14] Franck–Condon simulations[15] (using unmodified *ab initio* geometries) for the lowest energy ionization, which corresponds to a transition from the "open-shell" singlet ground-state geometry for **1** (X^1A'' in the calculation, but α^3A'' is predicted to have a very similar geometry

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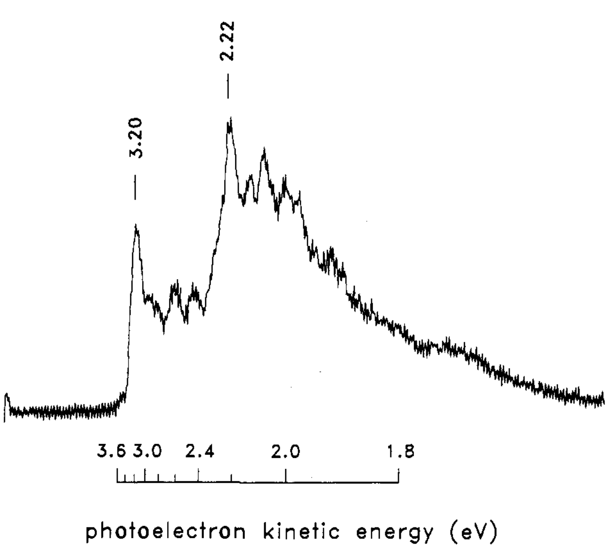

Figure 1. Time-of-flight laser photoelectron spectrum of the α,3-dehydrotoluene biradical **1** from the flash pyrolysis of *m*-nitrophenyl nitrite **4**. Subtraction of the photoelectron kinetic energies for the two observed bands at 3.20 and 2.22 ± 0.04 eV from the 10.49-eV photon energy gives the two ionization potentials of the biradical corresponding to removal of an electron from either the benzylic π-system or the in-plane sp² orbital. The two bands are assigned as $X^2\mathrm{A}' + \mathrm{e}^- \leftarrow \{a^3\mathrm{A}'', X^1\mathrm{A}''\}$ and $A^2\mathrm{A}'' + \mathrm{e}^- \leftarrow \{a^3\mathrm{A}'', X^1\mathrm{A}''\}$, respectively. A retarding potential of ~1.7 V was applied to improve energy resolution.

as well[12]) to the doublet ground state ($X^2\mathrm{A}'$) of $\mathbf{1}^{\bullet+}$, indicate that there should be a prominent, sharp origin band reminiscent of that in the photoelectron spectrum of the benzyl radical.[16] Accordingly, the adiabatic and vertical ionization potentials for the first photoelectron band are coincident and can be read directly from the spectrum. The second photoelectron band corresponds to a transition from singlet and/or triplet **1** to the first electronically-excited state ($A^2\mathrm{A}''$) of $\mathbf{1}^{\bullet+}$ and was not modeled because the prerequisite conditions for a valid Franck–Condon simulation were not satisfied.[17] The additional structure seen in Figure 1 is reproducible and corresponds to vibrational excitation in $\mathbf{1}^{\bullet+}$. However, without a more detailed knowledge of the vibronic interactions between vibrationally-excited $X^2\mathrm{A}'$ levels and those in $A^2\mathrm{A}''$, further assignments beyond the ionization potentials are problematic. Fortunately, the ionization potentials alone are needed to draw thermochemical conclusions.

The ionization potentials of **1** fit into a predictive thermochemical scheme we had previously proposed[9] for singlet carbenes and biradicals. In this context, the triplet biradical is identified with the "noninteracting" biradical of thermochemical additivity calculations. The single–triplet gap of a singlet biradical is identified as the correction (the valence promotion energy) to strict additivity estimates of $\Delta H_{\mathrm{f},298}$[biradical]. A direct test of the prediction requires an experimental measurement of $\Delta H_{\mathrm{f},298}[\mathbf{1}^{\bullet+}]$ so that the present $\mathrm{IP}_\pi[\mathbf{1}]$ can be used to determine $\Delta H_{\mathrm{f},298}[\mathbf{1}^{\bullet+}]$. Unfortunately, no data are available for $\mathbf{1}^{\bullet+}$ for a direct test. We therefore use an alternate thermochemical cycle, which we have applied successfully[9] to propadienylidene, propargylene, and *o*-benzyne, which is related to the valence promotion energy scheme by one additional approximation. Again, the "noninteracting biradical" is identified with the triplet biradical with the valence promotion energy approximately equal to ΔE_{ST} for ground-state singlets. The further approximation is an assumption that the difference in C–H bond dissociation energy between a reference radical and the corresponding cation is also the valence promotion energy of the biradical produced by that C–H bond scission. The difference in bond energies, in turn, equals the difference in ionization potential between the biradical and the reference radical (see Figure 2). Experimentally determined ionization potentials are, therefore, a semiquantitative predictor of the singlet–triplet gap and heat of formation of **1**. Using benzyl radical **2** as the reference against which **1** is compared (IP[**2**] = 7.2484 ± 0.0006 eV[18]), the ionization potentials indicate that **1** is either a ground-state triplet or a singlet with a small (≤5 kcal/mol or up to 0.2 eV given small deviations for geometric changes) singlet–triplet gap because $\mathrm{IP}_\pi[\mathbf{1}] \approx \mathrm{IP}[\mathbf{2}]$. Accordingly, $\Delta H_{\mathrm{f},298}[\mathbf{1}]$ should be close to, or just slightly below (again ≤5 kcal/mol), the additivity estimate of ≈109 kcal/mol.[19] A check of the conclusion can be made by using the ionization potential of a second radical, *m*-tolyl **3**, as the reference against which $\mathrm{IP}_2[\mathbf{1}]$ would be compared. IP[**3**] has not been reported, but it can be expected to be only slightly lower than the ionization potential of phenyl radical, C_6H_5, which was found to be 8.32 ± 0.04 eV by photoelectron spectroscopy[20] and 8.1 ± 0.1 eV by photoionization mass spectroscopy.[21] The observed $\mathrm{IP}_\sigma[\mathbf{1}] \approx \mathrm{IP}[\mathbf{3}]$ reinforces the thermochemical conclusions reached above. A further check of our thermochemical picture would be afforded by parallel studies of the isomeric α,2- and α,4-dehydrotoluenes. A study of the latter is in progress and will be the subject of subsequent reports.

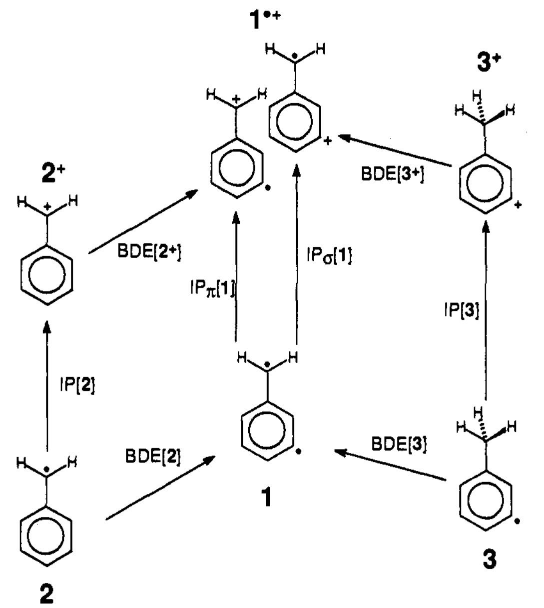

Figure 2. Two thermochemical cycles relating IP[**1**] to IP[**2**] and IP[**3**]. If $\mathrm{IP}_\pi[\mathbf{1}] \approx \mathrm{IP}[\mathbf{2}]$, then $\mathrm{BDE}[\mathbf{2}] \approx \mathrm{BDE}[\mathbf{2}^+]$. Similarly, if $\mathrm{IP}_\sigma[\mathbf{1}] \approx \mathrm{IP}[\mathbf{3}]$, the $\mathrm{BDE}[\mathbf{3}] \approx \mathrm{BDE}[\mathbf{3}^+]$. From ref 9, the singlet–triplet gap of **1** is related to the bond energies by $\mathrm{BDE}[\mathbf{2}^+] - \mathrm{BDE}[\mathbf{2}] \approx \Delta E_{\mathrm{ST}}[\mathbf{1}] \approx \mathrm{BDE}[\mathbf{3}^+] - \mathrm{BDE}[\mathbf{3}]$. Therefore, because $\mathrm{IP}_\pi[\mathbf{1}] \approx \mathrm{IP}[\mathbf{2}]$ and $\mathrm{IP}_\sigma[\mathbf{1}] \approx \mathrm{IP}[\mathbf{3}]$, $\Delta E_{\mathrm{ST}}[\mathbf{1}]$ must be small, and $\Delta H_{\mathrm{f},298}[\mathbf{1}]$ is close to the additivity estimate.

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