of a high-temperature limiting slope indicates both have reached pre-equilibrium where $T > 25$ °C. To what degree S_Δ may vary with temperature is dependent on the relative activation energies of at least four rate constants.

We believe that this is the first direct evidence of exciplex involvement in triplet state quenching by oxygen, and we are currently investigating the possibility that exciplexes are associated with oxygen quenching of triplet states of widely varying structure, energy, and S_Δ values.

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Registry No. Benzophenone, 119-61-9; oxygen, 7782-44-7.

Photoelectron Spectrum of *o*-Benzyne. Ionization Potentials as a Measure of Singlet–Triplet Gaps

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We report the experimental determination of ionization potentials (IP) for *o*-benzyne (o-C_6H_4). While o-C_6H_4 had been the subject of several studies[2,3] aimed at determining its IP, there nevertheless remained no clear, reliable number. In this paper, we report the photoelectron spectrum of o-C_6H_4 and demonstrate, for geometrically-constrained singlet biradicals (or biradical-like species), a relationship between ionization potentials and the singlet–triplet gap (Δ_{ST}) which we had recently shown for singlet ground-state carbenes.[4] We confirm the predicted identity:

$$\mathrm{IP}_\sigma[o\text{-}C_6H_4] - \mathrm{IP}_\sigma[C_6H_5] \approx \Delta_{ST}[o\text{-}C_6H_4] \tag{1}$$

This relationship, derived from valence bond (VB) promotion energy arguments,[4-6] can be applied to the prediction of singlet–triplet gaps and ionization potentials for *m*- and *p*-benzyne.

The time-of-flight (TOF) mass and photoelectron spectrometers have been previously described.[4,6-8] Laser light at 118.2 nm (10.49 eV) was produced by frequency-tripling the Nd^{3+}–YAG third harmonic in xenon. o-C_6H_4 was produced by supersonic jet flash pyrolysis of benzocyclobutene-1,2-dione,[9] synthesized by the procedure of South and Liebeskind.[10] Photoionization of the benzocyclobutenedione with 10.49-eV photons gave only mass peaks at $m/e = 132$ (M^+) and $m/e = 104$ ($M^+ - CO$). Pyrolysis of <1 Torr partial pressure of the dione, seeded in 1500 Torr of helium (1300 °C by optical pyrometry, 50–100 μs contact time), gives quantitative, clean conversion to o-C_6H_4 with *no secondary pyrolysis or detectable bimolecular reactions* and no other detectable products (IP[CO] > 10.49 eV) in the photoionization mass spectrum of the pyrolysate. Because $m/e = 76$ is the only large peak in the mass spectrum of the pyrolyzed benzocyclobutenedione, all of the peaks observed in a photoelectron spectrum (Figure 1) taken under the same conditions can be assigned to o-C_6H_4. At higher temperatures, a peak at $m/e = 50$ appears in the mass spectrum, accompanied by sharp peaks at ~1.25 eV kinetic energy in the photoelectron spectrum.

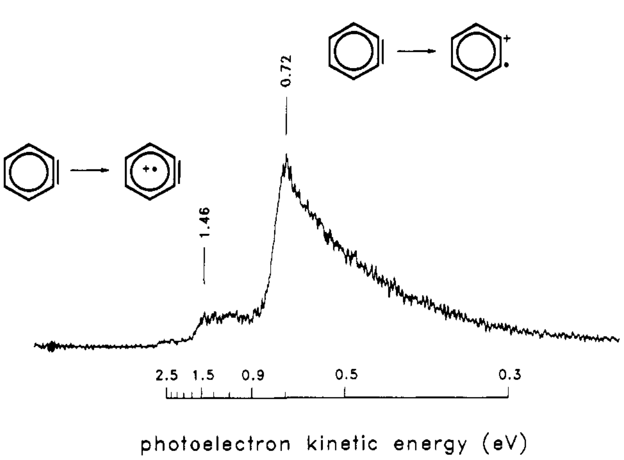

Figure 1. Time-of-flight photoelectron spectra (10.49 eV) of *o*-benzyne. Subtraction of the photoelectron kinetic energies from the 10.49-eV photon energy gives an ionization potential. The two marked ionization potentials come from removal of an electron from the out-of-plane and in-plane molecular orbitals, respectively (Koopmans' theorem). Splitting of the first band, assigned to $\mathrm{IP}_\pi[o\text{-}C_6H_4]$, is unresolved and may account for the broadness of that band.

The out-of-plane π-system in the phenyl radical, C_6H_5, was reported[11] to be almost unperturbed from that in benzene, as indicated by an observed threshold in the photoionization efficiency curve for C_6H_5, which we designated IP_π, close to $\mathrm{IP}[C_6H_6] = 9.24$ eV. Removal of an electron from the in-plane, nonbonding radical orbital of C_6H_5 gave a lower energy threshold, which we designated IP_σ, reported[11] to be $\mathrm{IP}_\sigma = 8.1 \pm 0.1$ eV. A simple Koopmans' theorem interpretation of Figure 1 finds, analogously, two ionization potentials for o-C_6H_4, corresponding to removal of an electron from out-of-plane and in-plane orbitals; $\mathrm{IP}_\pi[o\text{-}C_6H_4] = 9.03 \pm 0.05$ eV and $\mathrm{IP}_\sigma[o\text{-}C_6H_4] = 9.77 \pm 0.03$ eV. We assume, in our interpretation, that the splitting of the degenerate π-system HOMO in benzene, upon going from D_{6h} to C_{2v}, is small and results only in a broadening of the band associated with $\mathrm{IP}_\pi[o\text{-}C_6H_4]$. The relative ordering of ion states is consistent with both semiempirical[3] and ab initio[12] calculations for the ionization of *o*-benzyne.

That the VB promotion energy picture correctly describes o-C_6H_4 is seen below. We had noted[4] that $\Delta H_f[o\text{-}C_6H_4]$ differed from a simple bond additivity estimate (via cleavage of two C–H bonds in benzene) by VB promotion energy, which was approximately $\Delta_{ST}[o\text{-}C_6H_4]$. Recent reports[13-15] of $\Delta H_f[o\text{-}C_6H_4] = 106 \pm 3$ kcal/mol agree well with an estimate made assuming bond additivity, corrected by $\Delta_{ST}[o\text{-}C_6H_4]$:

$$\begin{aligned}\Delta H_f[o\text{-}C_6H_4] &\approx \Delta H_f[C_6H_6] + (2\mathrm{BDE}[C_6H_6]) - \\ &\qquad (2\Delta H_f[H^\bullet]) - \Delta_{ST}[o\text{-}C_6H_4] \\ &= 20 + (2 \times (113 \pm 3)^{\text{ref16}}) - (2 \times 52) - \\ &\qquad (38 \pm 0.7)^{\text{ref17}} = 104 \pm 4 \text{ kcal/mol}\end{aligned} \tag{2}$$

This is an especially favorable case because $\Delta_{ST}[o\text{-}C_6H_4]$ had been

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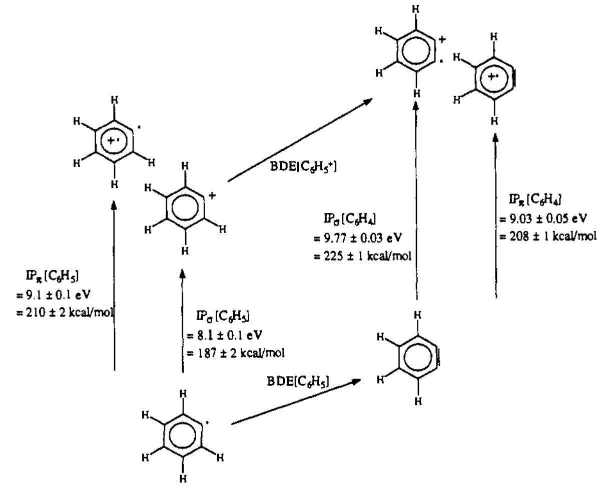
Scheme I. Thermochemical Cycle Relating Ionization Potentials to Bond Strengths and the Singlet–Triplet Gap (Phenyl Radical Data Taken from Reference 11)



previously determined by photodetachment of $C_6H_5^{\bullet-}$ and the carbocyclic skeleton is relatively rigid. This establishes that the hypothetical "noninteracting biradical" computed by additivity methods can be identified with triplet o-C_6H_4 and that the homolytic C–H bond dissociation energy (BDE) of phenyl radical (at the ortho position) is reduced from that in benzene by $\Delta_{ST}[o\text{-}C_6H_4]$.

While $\Delta_{ST}[o\text{-}C_6H_4]$ is known from the work of Leopold[17] et al., singlet–triplet gaps are usually difficult to infer. We therefore propose the relationship expressed in eq 1 as a measure of Δ_{ST} for geometrically-rigid singlet biradicals and check the proposition using o-C_6H_4 as the prototypical test case. Referring to Scheme I, we see that $IP_\sigma[o\text{-}C_6H_4] - IP_\sigma[C_6H_5] = BDE[C_6H_5^+] - BDE[C_6H_5]$ is an identity. While the VB promotion energy model that rationalized $\Delta H_f[o\text{-}C_6H_4]$ predicts a weakening of the ortho C–H bond in phenyl radical by $\Delta_{ST}[o\text{-}C_6H_4]$, the same picture finds no comparable weakening of the corresponding bond in phenyl cation. We therefore use the ortho C–H bond in $C_6H_5^+$ as the reference bond to which the bond in C_6H_5 is compared. It is this assumption that relates the difference in ionization potentials to the singlet–triplet gap of o-benzyne. The numerical test of the proposition is

$$BDE[C_6H_5^+] - BDE[C_6H_5] \approx \Delta_{ST}[o\text{-}C_6H_4] \approx IP_\sigma[o\text{-}C_6H_4] - IP_\sigma[C_6H_5]$$

This predicted relationship is tested with our spectroscopic measurements. We find

$$\begin{aligned} IP_\sigma[o\text{-}C_6H_4] - IP_\sigma[C_6H_5] &= (9.77 \pm 0.03) - (8.1 \pm 0.1) = 1.67 \pm 0.1 \text{ eV} \\ &= 38.5 \pm 2.4 \text{ kcal/mol} \end{aligned}$$

which is very close to the independently determined singlet–triplet gap of o-benzyne of $\Delta_{ST}[o\text{-}C_6H_4] = 38 \pm 0.7$ kcal/mol. *The remarkable agreement validates eq 1 and establishes ΔIP as a measure of a singlet biradical's singlet–triplet splitting.*

Because we identify triplet o-C_6H_4 with the "noninteracting biradical" whose ΔH_f is computed by additivity, and because a strict additivity estimate (which does not include the Δ_{ST} correction) does not distinguish[18] between ortho, meta, and para isomers, eqs 1 and 2, along with the recently determined[14] $\Delta H_f[m\text{-}C_6H_4] = 116 \pm 3$ kcal/mol and $\Delta H_f[p\text{-}C_6H_4] = 128 \pm 3$ kcal/mol, predict that $\Delta_{ST}[m\text{-}C_6H_4] \approx 26$ kcal/mol, $\Delta_{ST}[p\text{-}C_6H_4] \approx 14$ kcal/mol, $IP_\sigma[m\text{-}C_6H_4] \approx 9.2$ eV, and $IP_\sigma[p\text{-}C_6H_4] \approx 8.7$ eV. Experimental confirmation of these predictions is in progress.

We have observed a regularity in the thermochemistry of singlet biradicals that is confirmed by photoelectron spectroscopic measurements of biradical ionization potentials. Further work is underway to explore the generality of the relationship expressed in eq 1 as a way to determine biradical singlet–triplet gaps.

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[18] Ab initio calculations for **2**, **3**, and **4** predict correct relative energies among the singlet isomeric benzynes and also find that the triplet states of the three isomers are degenerate to within 3 kcal/mol. See: Noell, J. O.; Newton, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 51.

Unexpected Frequency Effects on the Rate of Oxidative Processes Induced by Ultrasound

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Sonication of water generates radicals which oxidize compounds in solution.[1] In this work we give evidence that in the presence of argon or oxygen these oxidative processes occur in enhanced yields when a high frequency (514 kHz) is used in comparison with the more commonly used low frequency (20 kHz).

In water cavitation bubbles are filled with vapor and dissolved gas. They oscillate with pressure and then collapse.[2] At the end of the compression phase, the internal temperature can reach several thousand degrees (K), and the pressure several hundred bars.[1,3] Under these extreme conditions, the water molecule is cleaved to H• and OH• (eq 1).[4] Molecular oxygen if present in the bubble can also decompose (eq 2).[5]

$$H_2O \rightarrow H^\bullet + OH^\bullet \qquad (1)$$

$$O_2 \rightarrow 2O \qquad (2)$$

Transient radicals can recombine or escape from the collapsed bubble to react with dissolved molecules.[6] In several cases a dependence is suggested among the rates of the sonochemical oxidative process, the frequency of the wave, and the nature of the dissolved gas.[7] As no extensive study has reported on the

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