α,3-Dehydrotoluene: Experimental and Theoretical Evidence for a Singlet Ground State

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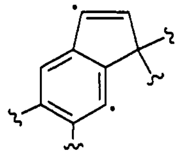
The α,3-dehydrotoluene biradical (**3**) has achieved recent notoriety for the relative ease with which it is formed by a thermal Bergman-type cyclization of (*Z*)-1,2,4-heptatrien-6-yne.[1] Biradical **3** serves as a model for the substituted 3,7-dehydroindene biradical (**1**) that has been implicated in the DNA-cleaving action of neocarzinostatin.[2] We report here a determination of absolute heats of formation for **3** and its isomers, α,2- and α,4-dehydrotoluene (**2** and **4**, respectively), from threshold collision-induced dissociation (CID) in a flowing afterglow–triple quadrupole apparatus.[3] The experimental results, interpreted with the aid of *ab initio* molecular orbital calculations, indicate a singlet ground state for **3**, as well as absolute energies for all three biradicals that are significantly lower than estimates based on bond energy additivity.



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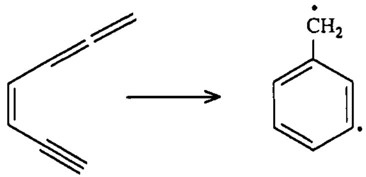

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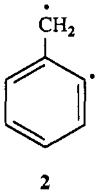

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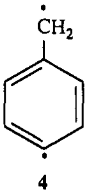

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We have previously shown how the measured threshold energies for collision-induced halide elimination from gas-phase halocarbanions can be used to derive accurate heats of formation for carbenes[4] and biradicals.[5] For the dehydrotoluenes, the procedure involves formation of isomeric *o*-, *m*- and *p*-halobenzyl anions from the corresponding halotoluenes in the flowing afterglow, followed by measurement of the CID threshold energies (E_T) for halide loss in the triple quadrupole analyzer. The heats of formation for the dehydrotoluene biradicals can then be obtained by combining the measured dissociation energies with the gas-phase acidities of the corresponding halotoluenes and other data according to a simple thermochemical cycle.[5]

Table I. CID Threshold Energies for Halobenzyl Anions, Halotoluene Acidities, and Derived Heats of Formation for α,2- α,3-, and α,4-Dehydrotoluene (kcal/mol)

halobenzyl anion	E_T[a]	$\Delta H_{acid}(XC_6H_4CH_3)$[b]	$\Delta H_f°_{298}(C_6H_4CH_2)$[c]
o-Cl	40.8 ± 2.1	374 ± 2	109 ± 3
m-Cl	33.6 ± 2.8	374 ± 2	102 ± 3
p-Cl	40.8 ± 1.2	374 ± 2	109 ± 3
o-Br	30.0 ± 1.6	374 ± 2	107 ± 3
m-Br	27.4 ± 2.8	374 ± 2	104 ± 3
p-Br	27.4 ± 2.0	374 ± 2	104 ± 3
o-I	20.0 ± 2.3	372 ± 2	103 ± 3
m-I	20.5 ± 2.3	372 ± 2	103 ± 3
p-I	20.5 ± 1.4	372 ± 2	103 ± 3

[a] Average threshold energy for halide elimination (±1 standard deviation, corrected to 298 K) determined by the methods outlined in refs 6 and 7. [b] Halotoluene acidities determined from acid–base bracketing experiments. [c] Dehydrotoluene heat of formation calculated from $\Delta H_f°_{298}(C_6H_4CH_2) = E_T + K + \Delta H_{acid}(XC_6H_4CH_3) + \Delta H_f°_{298}(XC_6H_4CH_3) - \Delta H_{acid}(HX) - \Delta H_f°_{298}(HX)$, where K is a factor for converting E_T to a 298 K enthalpy; indicated uncertainty estimated; supplemental thermochemical data taken from ref 8.

Absolute cross sections for dissociation of Cl^-, Br^-, or I^- from the corresponding *o*-, *m*- and *p*-halobenzyl anions are shown in Figure 1. The threshold energies for halide loss are obtained from these appearance curves using an analytical procedure, similar to that developed by Armentrout,[6] which explicitly accounts for the reactant ion thermal energy and kinetic shifts.[7] The average E_T values based on replicate measurements for each system are listed in the second column of Table I. The gas-phase acidities of the halotoluenes, $\Delta H_{acid}(XC_6H_4CH_3)$, were determined using standard bracketing procedures or were taken from the literature[8] and are listed in the third column. The apparent heats of formation derived from these data are listed in the last column of Table I.

Apart from the natural decrease in dissociation energies expected for the heavier halides, Figure 1 also shows that the *differences* in the E_T values for each series appear to be dependent upon the halide ion. The *o*- and *p*-chlorobenzyl anions exhibit identical CID thresholds that are *ca.* 0.3 eV (7 kcal/mol) higher than that obtained for the *meta* isomer (Figure 1a), while the thresholds for the three isomeric iodobenzyl anions are essentially identical (Figure 1c). Of greater significance are the trends in the apparent heats of formation for **2**–**4** derived from these data. The value for $\Delta H_f(\mathbf{3})$ is invariant, within error, with changes in the halide leaving group used in the CID experiments. In contrast, the higher ΔH_f values obtained for **3** and **4** from the chlorobenzyl anion results both decrease to become the same as $\Delta H_f(\mathbf{3})$ derived from the iodobenzyl anion results.

A complete understanding of this behavior requires consideration of the electronic structures of the dehydrotoluene biradicals as well as the dynamics involved in the dissociation reactions that produce them. To this end we have carried out molecular orbital calculations of the structures and energies of **2**–**4** using an MCSCF procedure wherein the eight valence electrons were distributed in an active space consisting of the seven π orbitals and the nonbonding σ orbital.[9] Optimized geometries for **2**–**4** were obtained with a 3–21G basis set, and total energies were computed with use of a pVDZ basis set[10] in order to obtain more reliable energy orderings for the open-shell singlet and triplet states, *i.e.*, MCSCF(8,8)/pVDZ//MCSCF(8,8)/3-21G. At this level of theory, **3** is calculated to have a $^1A''$ ground state lying 3.0 kcal/mol below the triplet state ($^3A''$). Biradicals **2** and **4** are ground-state triplets ($^3A''$ and $^3B_1$, respectively), with the corresponding

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(1) (a) Myers, A. G.; Dragovich, P. S. *J. Am. Chem. Soc.* **1992,** *114,* 9369 and references therein. (b) Nagata, R.; Yamanaka, H.; Murahashi, E; Saito, I. *Tetrahedron Lett.* **1990,** *31,* 2907.

(2) Myers, A. G.; Proteau, P. J. *J. Am. Chem. Soc.* **1989,** *111,* 1146 and references therein.

(3) Graul, S. T.; Squires, R. R. *Mass Spectrom. Rev.* **1988,** *7,* 263.

(4) Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991,** *113,* 5573.

(5) (a) Wenthold, P. G.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991,** *113,* 7414. (b) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.*, submitted for publication.

(6) (a) Schultz, R. H.; Crellin, K. C.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991,** *113,* 8590. (b) Khan, F. A.; Clemmer, D. E.; Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1993,** *97,* 7978.

(7) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.*, in press.

(8) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988,** *17* (Suppl. 1).

(9) Nachtigall, P.; Jordan, K. J. *J. Am. Chem. Soc.* **1992,** *114,* 4743; **1993,** *115,* 270.

(10) Dunning, T. H. *J. Chem. Phys.* **1989,** *90,* 1007.

0002-7863/93/1515-12611$04.00/0

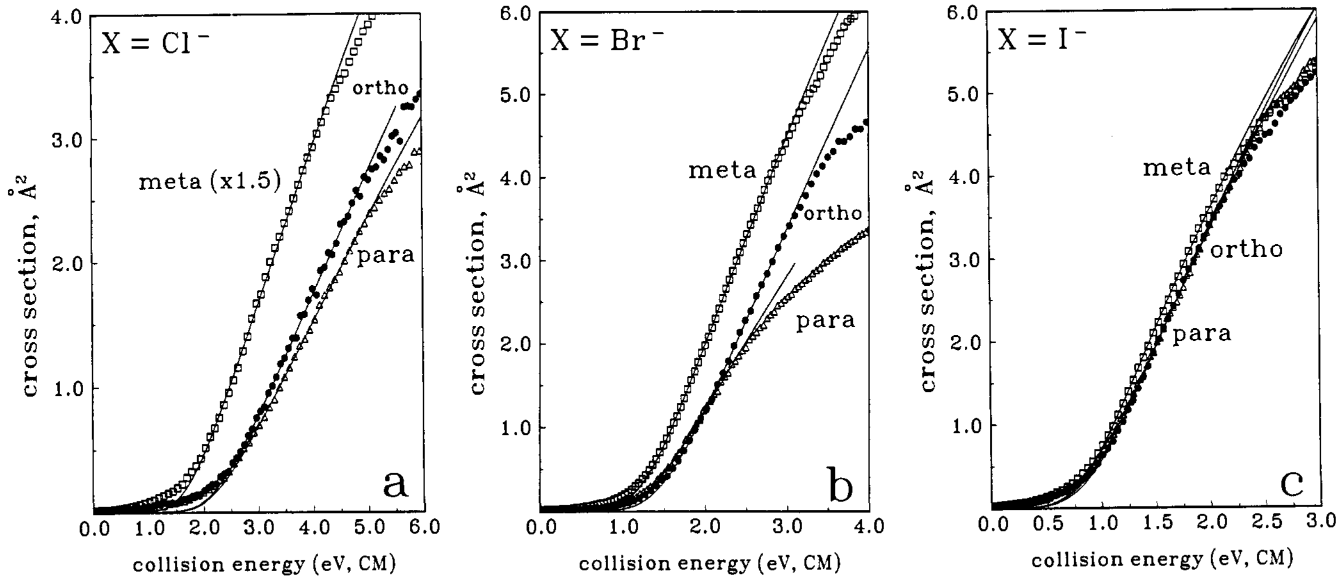

Figure 1. Cross sections for Cl^-, Br^-, and I^- dissociation from *o*-, *m*-, and *p*-halobenzyl anions resulting from collisional activation with argon target at (3–5) × 10^{-5} Torr. The solid line is the optimized, fully convoluted model appearance curve obtained by the methods described in refs 6 and 7.

open-shell singlets lying 7.4 and 9.6 kcal/mol higher in energy. Especially noteworthy is the fact that the absolute energies of the ground states of the three biradicals are found to be essentially the same (within 0.3 kcal/mol). This is consistent with the results from the iodobenzyl anion experiments which gave identical heats of formation for **2**–**4**. The triplet ground state assignments for **2** and **4** are in accord with previous studies of these and related species in condensed phases.[11] That biradical **3** possesses a singlet ground state is a consequence of the orthogonal, disjoint orientation of the singly occupied $\pi(A'')$ and $\sigma(A')$ orbitals.[12] The π spin polarization of the benzylic radical system and the preference for local high-spin coupling of σ and π electrons at the dehydro ring carbon of each diradical result in a triplet ground state for **2** and **4** but a singlet ground state for **3**.

The calculated enthalpies of the hypothetical isodesmic reaction shown in eq 1 can be used in conjunction with auxiliary thermochemical data to derive absolute heats of formation for the three biradicals. Using the ZPE-corrected energies computed

$$C_6H_4CH_2\ (\mathbf{2},\ \mathbf{3},\ \text{or}\ \mathbf{4}) + C_6H_6 \rightarrow C_6H_5 + C_6H_5CH_2 \qquad (1)$$

for the ground states of **2**–**4**, C_6H_6, C_6H_5, and $C_6H_5CH_2$ at analogous MCSCF levels of theory, and experimental values for $\Delta H_f(C_6H_5)$ and $\Delta H_f(C_6H_5CH_2)$ from the literature,[13,14] the theoretically-predicted heats of formation for **2**–**4** are all 104 kcal/mol, in excellent agreement with the values determined from the iodobenzyl anion experiments.

Given these ground-state assignments for the three biradicals and the agreement with theory on the thermochemistry, we can now understand the origins of the halide ion dependence of the measured energies for **2** and **4**, and its absence for **3**. Although dissociation of a halobenzyl anion to produce a (σ,π)-dehydrotoluene biradical is formally symmetry-forbidden, it becomes "allowed" for nonplanar transition states. For *o*- and *p*-halobenzyl anions to form ground-state triplet biradicals the reaction is also spin-forbidden, and it necessarily involves a curve-crossing mechanism since the halide ion/triplet biradical interaction is repulsive at normal bonding distances. If intersystem crossing occurs at energies *above* the triplet asymptote, or if it is slow on the experimental time scale (*ca.* 30 μs), then either a reverse activation energy or a kinetic shift, respectively, would result that could ultimately translate into an erroneously high biradical heat of formation. Both effects would be expected to be diminished or to disappear altogether with the heavier halides as a result of either the less precipitous potential energy surfaces or heavy-atom-induced spin–orbit coupling.[15] In contrast, because dissociation of a *m*-halobenzyl anion to give singlet **3** is *spin-allowed*, it can occur at the true thermochemical limit with all three halides.

The measured heats of formation can be compared with the value predicted by bond energy additivity. Using the experimental heats of formation for benzyl and phenyl radicals,[13,14] the heat of formation of a "generic" dehydrotoluene is calculated to be 108 ± 3 kcal/mol. The experimental and theoretical heats of formation for **2**–**4** are all lower than this estimate by 4–5 kcal/mol. The electronic and geometric origins of this apparent stabilization are currently under investigation and will be described elsewhere.

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[11] (a) Closs, G. L.; Kaplan, L. R. Bendall, V. I. *J. Am. Chem. Soc.* **1967**, *89*, 3376. (b) Sander, W.; Müller, W.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 572.

[12] (a) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. (b) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 1.

[13] $\Delta H_f(C_6H_5)$ = 79.1 ± 1.5 kcal/mol derived from the benzene C–H bond strength of 111.5 ± 1.5 kcal/mol obtained from the relation: $DH[C_6H_5\text{–}H] = \Delta H_{acid}(C_6H_6) + EA(C_6H_5) - IP(H)$; $\Delta H_{acid}(C_6H_6)$ = 399.8 ± 1.5 kcal/mol (Meot-Ner, M.; Kafafi, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 6297; adjusted to 298 K); $EA(C_6H_5)$ = 25.3 ± 0.1 kcal/mol (Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601); IP(H) = 313.6 kcal/mol (ref 8).

[14] $\Delta H_f(C_6H_5CH_2)$ = 48 ± 2 kcal/mol: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[15] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publ. Co.: Menlo Park, CA, 1978.