molecular salt effects. While it is steric effects that are most often turned to when better stereocontrol is desired in a chemical process, this paper shows that dipolar effects, especially the large dipoles associated with ion pairs in nonpolar solvents, can be an important aspect of stereocontrol. Further applications of these concepts are under study.

Acknowledgment. This work was funded by the University of Pittsburgh and the Alfred P. Sloan Foundation. P.J.S. thanks the Department of Education for a graduate fellowship. We thank Dr. Mark Reddington for conductometric determinations.

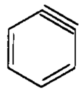
The Absolute Heats of Formation of *o*-, *m*-, and *p*-Benzyne

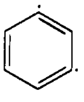
Paul G. Wenthold, Jose A. Paulino, and Robert R. Squires*

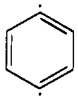
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received June 12, 1991

The dehydrobenzenes (benzynes), **1–3**, constitute a fascinating class of reactive organic intermediates that has inspired numerous experimental and theoretical investigations.[1] *o*-Benzyne (**1**) has been extensively studied over the last 40 years to establish its geometric and electronic structures, its chemical reactivity, and its thermodynamic properties.[2-12] Recently, derivatives of *p*-benzyne (**3**) have attracted considerable attention as intermediates in the DNA-cleaving action of calicheamicins and esperamicins.[13]


1


2


3

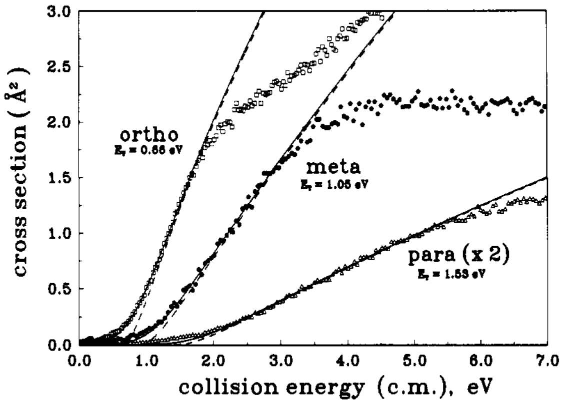
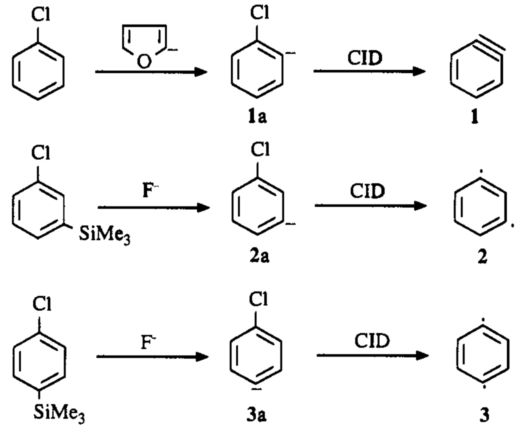


Figure 1. Cross sections for Cl^- dissociation from *o*-, *m*-, and *p*-chlorophenyl anions resulting from collisional activation with argon target at 4.0×10^{-5} Torr. The solid line is the optimized, fully convoluted model appearance curve, and the dashed line represents the unconvoluted excitation function. The uncertainty in the absolute cross sections is estimated to be ±50%, while the relative cross sections are accurate to within ±20%.

Scheme I



However, little is known about the physical properties of *m*- and *p*-benzyne,[14-16] and the thermochemistry of *o*-benzyne has been controversial. We report here an experimental determination of the absolute heats of formation of **1–3** as derived from energy-resolved collision-induced dissociation (CID) measurements in a flowing afterglow–triple quadrupole apparatus.[17]

We recently demonstrated the use of collision-induced α-elimination reactions of halocarbanions in the gas phase as a new method for obtaining carbene thermochemistry.[18,19] The basic

---

(1) (a) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967. (b) Levin, R. H. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; J. Wiley: New York, 1978; Vol. 1, pp 1–26; 1981; Vol. 2, pp 1–14; 1985; Vol. 3, pp 1–18. (c) Gilchrist, T. L. *Carbenes, Nitrenes, and Arynes*; Appleton-Century-Croft: New York, 1969. (d) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25.

(2) Roberts, J. D.; Simmons, H. E., Jr.; Carlsmith, L. A.; Vaughan, C. W. *J. Am. Chem. Soc.* **1953**, *75*, 3290.

(3) (a) Berry, R. S.; Spokes, G. N.; Stiles, M. *J. Am. Chem. Soc.* **1962**, *84*, 3570. (b) Fisher, I. P.; Lossing, F. P. *J. Am. Chem. Soc.* **1963**, *85*, 1018. (c) Dewar, M. J. S.; Tien, T.-P. *J. Chem. Soc., Chem. Commun.* **1985**, 1243. (d) Dunkin, I. R.; MacDonald, J. G. *J. Chem. Soc., Chem. Commun.* **1979**, 772. (e) Brown, R. D.; Godfrey, P. D.; Rodler, M. *J. Am. Chem. Soc.* **1986**, *108*, 1296. (f) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 6134. Chapman, O. L.; Chang, C.-C.; Kole, J.; Rosenquist, N. R.; Tomioka, H. *J. Am. Chem. Soc.* **1975**, *97*, 6586. (g) Munzel, N.; Schweig, A. *Chem. Phys. Lett.* **1988**, *147*, 192. (h) Leopold, D. G.; Miller, A. E. S.; Lineberger, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 1379.

(4) Grutzmacher, H.-F.; Lohmann, J. *Justus Liebigs Ann. Chem.* **1967**, *705*, 81.

(5) Pollack, S. K.; Hehre, W. J. *Tetrahedron Lett.* **1980**, *21*, 2483.

(6) Riveros, J. M.; Ingemann, S.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1991**, *113*, 1053.

(7) Guo, Y.; Grabowski, J. J. *J. Am. Chem. Soc.* **1991**, *113*, 5923.

(8) Moini, M.; Leroi, G. E. *J. Phys. Chem.* **1986**, *90*, 4002.

(9) Gronert, S.; DePuy, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 9253.

(10) Noell, O. J.; Newton, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 51.

(11) (a) Hoffman, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Wilhite, D. L.; Whitten, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 2858. (c) Radom, L.; Nobes, R. H.; Underwood, D. J.; Li, W.-K. *Pure Appl. Chem.* **1986**, *58*, 75. (d) Guest, M. F.; Von Niessen, W. *Chem. Phys. Lett.* **1987**, *134*, 403. (e) Scheiner, A. C.; Schaefer, H. F., III; Liu, B. *J. Am. Chem. Soc.* **1989**, *111*, 274 and references therein.

(12) Dewar, M. J. S.; Li, W.-K. *J. Am. Chem. Soc.* **1974**, *96*, 5569. Dewar, M. J. S.; Ford, G. P.; Reynolds, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 3162.

(13) (a) Zein, N.; Sinha, A. M.; McGahren, W. J.; Ellestad, G. A. *Science (Washington, D.C.)* **1988**, *240*, 1198. (b) Golik, J.; Clardy, J.; Dubay, G.; Groenewold, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saitoh, K.; Doyle, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 3461. Golik, J.; Dubay, G.; Groenewold, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saitoh, K.-I.; Doyle, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 3462. (c) Lee, M. D.; Dunne, T. S.; Siegel, M. M.; Chang, C. C.; Morton, G. O.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3464. Lee, M. D.; Dunne, T. S.; Chang, C. C.; Ellestad, G. A.; Siegel, M. M.; Morton, G. O.; McGahren, W. J.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3466. (d) Nicolaou, K. C.; Ogawa, Y.; Zuccarello, G.; Kataoka, H. *J. Am. Chem. Soc.* **1988**, *110*, 7247.

(14) (a) Berry, R. S.; Clardy, J.; Schafer, M. E. *Tetrahedron Lett.* **1965**, 1011. (b) Bertorello, H. E.; Rossi, R. A.; De Rossi, R. H. *J. Org. Chem.* **1970**, *35*, 3332. (c) Washburn, W. N.; Zahler, R.; Chen, I. *J. Am. Chem. Soc.* **1978**, *100*, 5863. (d) Johnson, G. C.; Stofko, J. J., Jr.; Lockhart, T. P.; Brown, D. W.; Bergman, R. G. *J. Org. Chem.* **1979**, *44*, 4215.

(15) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660.

(16) (a) Berry, R. S.; Clardy, J.; Schafer, M. E. *Tetrahedron Lett.* **1965**, 1003. (b) Chapman, O. L.; Chang, C.-C.; Kole, J. *J. Am. Chem. Soc.* **1976**, *98*, 5703. (c) Lockhart, T. P.; Comita, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4082. (d) Lockhart, T. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4091.

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

(18) Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 1845.

0002-7863/91/1513-7414$02.50/0

approach can be extended to more remote "α,ω"-eliminations that produce unsaturated or diradical products. For benzynes **1–3**, the procedure involves regioselective formation of isomeric chlorophenyl anions (**1a–3a**) followed by measurement of the activation energies for chloride loss resulting from collisional activation (Scheme I). Barring any reverse activation energies or kinetic shifts, the measured activation energies can be directly equated with the enthalpies of bond cleavage by means of a simple thermochemical cycle to obtain heats of formation for the neutral benzyne products.[20]

m-Chlorophenyl and *p*-chlorophenyl anions (**2a** and **3a**) are readily generated from the reactions between fluoride and the corresponding (chlorophenyl)trimethylsilanes.[21] The *o*-chlorophenyl anion (**1a**) can be prepared in isomerically pure form by proton abstraction from chlorobenzene by furanide ion. The CID behavior described below, as well as the characteristic reactivity displayed by each ion, shows that they are distinct, noninterconverting structures. Proton transfer reactions of **2a** and **3a** with various reference acids indicate that the meta and para positions of chlorobenzene have similar acidities, lying between that of H_2O ($\Delta G_{acid} = 384.1 \pm 0.2$ kcal/mol)[22] and furan ($\Delta G_{acid} = 380.0 \pm 3.0$ kcal/mol).[22] Bracketing experiments with chlorobenzene and its conjugate base anion locate the gas-phase acidity of the ortho position between that of fluorobenzene ($\Delta G_{acid} = 378.9 \pm 2.0$ kcal/mol)[23] and furan. From the bracketed acidities and estimates for the entropy contributions,[24] we assign ΔH_{acid} values to the ortho, meta, and para positions of chlorobenzene to be 388 ± 2, 390 ± 2, and 390 ± 2 kcal/mol, respectively.

Each of the chlorophenyl anion isomers undergoes efficient fragmentation under single-collision conditions with argon target in the triple quadrupole analyzer to produce Cl^- as the only ionic product. Monitoring the chloride yield as a function of the center-of-mass collision energy gives an ion appearance plot from which the dissociation activation energy can be obtained using an analysis procedure that has been described previously.[19,25] Figure 1 illustrates the characteristic Cl^- appearance curves for the three isomers, along with the analytical fit for each.[26] The final average values of the CID threshold energies, E_T, for the ortho, meta, and para isomers obtained from replicate measurements are 15.7 ± 3.0, 24.2 ± 3.0, and 35.3 ± 3.0 kcal/mol, respectively, where the indicated uncertainty is at least two standard deviations.

The heats of formation of the neutral benzyne products are related to the measured chloride dissociation energies according to eq 1, where $\Delta H_{acid}(C_6H_5Cl)$ is the appropriate ortho, meta, or para acidity of chlorobenzene from this work, and the auxiliary data for HCl and C_6H_5Cl are taken from the literature.[22] The

$$\Delta H^\circ_{f,298}(C_6H_4) = (E_T + 0.6) + \Delta H_{acid}(C_6H_5Cl) - \Delta H_{acid}(HCl) + \Delta H^\circ_{f,298}(C_6H_5Cl) - \Delta H^\circ_{f,298}(HCl) \quad (1)$$

0.6 kcal/mol factor is an expansion-work term for converting the activation energies to enthalpies.[19] The final heats of formation derived in this manner are the following: $\Delta H^\circ_{f,298}$(*o*-benzyne) = 106 ± 3, $\Delta H^\circ_{f,298}$(*m*-benzyne) = 116 ± 3, and $\Delta H^\circ_{f,298}$(*p*-benzyne) = 128 ± 3 kcal/mol, where the assigned uncertainty represents the root-square sum of the component uncertainties. Adiabatic dissociation to give the ground states of the benzyne products is assumed; all three isomers are either known or predicted to be singlets.[3,10,11]

The measured heat of formation for *o*-benzyne is in excellent agreement with the recent estimates by Riveros, Ingemann, and Nibbering (105 ± 3 kcal/mol)[6] and by Guo and Grabowski (105 ± 5 kcal/mol)[7] and further confirms the claims made by these investigators that the older values in the literature (ca. 117 kcal/mol)[4,5] are too high. The quantitative accord for *o*-benzyne also supports our contention that the Cl^- dissociation reactions depicted in Scheme I occur at the thermochemical limit, i.e., with no reverse activation energy or kinetic shifts.[20] The bicyclic isomers of **2** and **3** are calculated to lie higher in energy by 32 and 77 kcal/mol, respectively.[10] Moreover, although the measured heat of formation of **3** is close to that of (*Z*)-3-hexene-1,5-diyne at 127 kcal/mol,[22] formation of this isomer as the product of Cl^- loss from **3a** at threshold by either a direct or concerted (Grob-like) fragmentation mechanism is considered unlikely in view of the substantial activation energy (>30 kcal/mol) for cyclization of the enediyne to **3**.[15] Multireference GVB calculations by Noell and Newton suggest that *m*- and *p*-benzyne (singlets) are higher in energy than the (singlet) ortho isomer by 14.5 and 23.3 kcal/mol, respectively,[10] in good agreement with the present results.

The currently accepted value for the first C–H bond energy in benzene, DH°[C_6H_5–H], is 110.9 ± 0.7 kcal/mol.[22] From the benzyne thermochemistry determined in this study we calculate the ortho, meta, and para C–H bond energies in phenyl radical to be 79 ± 3, 89 ± 3, and 101 ± 3 kcal/mol, respectively. The differences between the first and second C–H bond energies for benzene provide a quantitative measure of the extent of interaction between radical centers in the benzynes and, at the same time, expose the limitations of simple bond additivity approaches to estimating biradical thermochemistry.[27]

Acknowledgment. This work was funded by the National Science Foundation (CHE-8815502). P.G.W. is grateful to the Department of Education and Phillips Petroleum for a National Needs Fellowship.

---

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

(20) The presence of substantial long-range electrostatic interactions between the dissociating chloride ion/biradical pair should effectively eliminate any barriers associated with their exothermic recombination.

(21) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 6443.

(22) 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.

(23) Meot-ner, M.; Kafafi, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 6297.

(24) Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

(25) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2517.

(26) Standard exponential excitation function, $\sigma(E) = \sigma_0[(E - E_T)^n/E]$,[19,25] with an optimal *n* of 1.5–1.8, convoluted with Doppler broadening (Chantry, P. J. *J. Chem. Phys.* **1971**, *55*, 2746) and a 2.0-eV FWHM Gaussian distribution for the ion kinetic energy.

(27) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1991**, *113*, 1907.

Gas-Phase Molecular Recognition: Gas-Phase Crown Ether–Alkali Metal Ion Complexes and Their Reactions with Neutral Crowns

Hong Zhang, In-Hou Chu, Sam Leming, and
David V. Dearden*

The University of Texas at Arlington
Chemistry Department, Box 19065
Arlington, Texas 76019-0065

Received June 7, 1991

The ability of crown ethers to selectively form complexes with alkali metal ions is well-known. The model originally proposed by Pedersen[1] and quantified by Izatt and co-workers,[2] that crowns with a given cavity size are selective for cations with radii matching that of the cavity, is now generally accepted,[3] although faults of the model have been pointed out.[4–6] Arguments against the

---

(1) (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495; **1967**, *89*, 7017. (b) Pedersen, C. J.; Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 16.

(2) (a) Izatt, R. M.; Rytting, J. H.; Nelson, D. P.; Haymore, B. L.; Christensen, J. J. *Science* **1969**, *164*, 443–444. (b) Izatt, R. M.; Nelson, D. P.; Rytting, J. H.; Haymore, B. L.; Christensen, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 1619–1623.

(3) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, 1989; pp 4–6, 185–191.

(4) (a) Poonia, N. S. In *Progress in Macrocyclic Chemistry*; Izatt, R. M., Christensen, J. J., Eds.; Wiley: New York, 1979; Chapter 3. (b) Bajaj, A. V.; Poonia, N. S. *Coord. Chem. Rev.* **1988**, *87*, 55–213.