Tetrahedron Letters Vol. 21, pp 2483 - 2486
© Pergamon Press Ltd. 1980. Printed in Great Britain

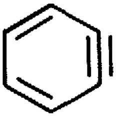
0040-4039/80/0622-2483$02.00/0

DETERMINATION OF THE HEAT OF FORMATION OF ORTHO-BENZYNE BY ION CYCLOTRON RESONANCE SPECTROSCOPY.

Steven K. Pollack[1] and Warren J. Hehre*
Department of Chemistry, University of California, Irvine, CA 92717

Summary: Ion Cyclotron Resonance Spectroscopy has been employed to obtain a value for the heat of formation of ortho-benzyne of 118 ± 5 kcal mol^{-1}.

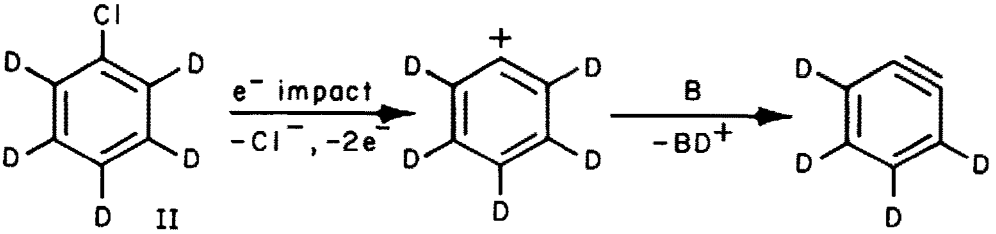
Ortho-benzyne (1,2-didehydrobenzene, I)



I

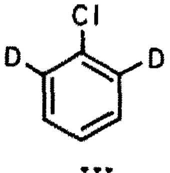
has long been postulated as an intermediate in many organic reactions.[2] In 1973, Chapman and his coworkers first observed the infrared spectra of what was presumed to be (I) in an argon matrix at $8^{o}K$[3]; more recent work has reinforced these findings[4]. Several groups[5,6,7] have made mass spectral determinations of the heat of formation of ortho-benzyne, their values ranging from 100 to 120 kcal mol^{-1}. The largest of these agrees quite well with a theoretical value of 122 kcal mol^{-1} obtained by Dewar and coworkers at the MINDO/3 level[8a] and the value of 120 kcal mol^{-1} obtained by Newton using ab initio molecular orbital theory.[8b] Further work by the Newton group[9] using higher levels of theory (including limited configuration interaction) concluded that the meta and para benzyne isomers were less stable than the ortho form by 14 and 22 kcal mol^{-1}, respectively.

Recently, we and others have employed Ion Cyclotron Resonance (ICR) spectroscopy to determine the relative thermochemical stabilities of a number of highly reactive species[10] by a method which involves the measurement of the proton affinity of the unstable neutral molecule using the double resonance bracketing technique[11,12]. The proton affinity of ortho-benzyne may be determined by way of the following reaction sequence.



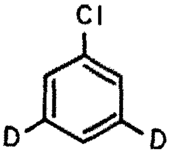
Here it is determined which of a series of bases of known proton affinity[14] will react with the labelled phenyl cation derived from chlorobenzene-d_5[15]. The proton affinity of the neutral product, in this case ortho-benzyne-d_4, is taken to lie midway between the proton affinity of the weakest base capable of deuteron abstraction (as confirmed by double resonance[11], and that of the strongest base incapable of reaction. All measurements were made with varying amount of argon as a buffer[12] to ensure that the proton transfers were not a function of excess energy in the phenyl cation. We find that tert-butyl sulfide (enthalpy of proton transfer 8.7 kcal mol^{-1} greater than our ammonia standard)[14c] is the strongest base considered which is not observed to abstract a deuteron from phenyl-d_5 cation; *N,N-dimethyl-O-ethyl carbamate* (ΔH^0 *of protonation* 9.5 kcal mol^{-1} above NH_3)[14c] is the weakest base for which deuteron transfer is observed. These results place the proton affinity of ortho-benzyne at 9.1 kcal mol^{-1} higher than ammonia. Combining this value with the absolute enthalpy of protonation of ammonia (205 kcal mol^{-1})[16], and the heats of formation of phenyl cation (270 ± 3 kcal mol^{-1})[17] and of H^+ (367.3 kcal mol^{-1})[18], we obtain a value of 118 ± 5 kcal mol^{-1} for the heat of formation of ortho-benzyne. This is in accord with the highest of the mass spectral determinations, and with the theoretical calculations of Dewar[8a] and of Newton[8b]. The main sources of error are the finite resolution of the gas phase proton *affinity scale, the uncertainty in the value of the heat of formation of* phenyl cation[17] and the likelihood that slightly endothermic proton transfer reactions, as well as thermoneutral and exothermic processes, will occur and will be detected. In addition, the requirement of an absolute basis for the proton affinity scale adds uncertainty (the absolute proton affinity of ammonia is not completely certain, estimates ranging from a low of 203 kcal mol^{-1} to a high of 209 kcal mol^{-1})[16]. These considerations place a total uncertainty of the heat of formation of the ortho-benzyne of no more than 5 kcal mol^{-1}.

In an attempt to determine the heats of formation for the meta and para isomers of benzyne as well as the presumed more stable ortho form, compounds *III-V were synthesized.*[19] *Early mass* spectral work[20] indicates that phenyl cations undergo scrambling of the carbon framework. These studies were performed in conventional mass spectrometers with electron bombardment energies between 20 and 70 eV. In the absence of scrambling, dedeuteration of the phenyl cations resulting from the labelled halobenzenes (III-V) should give



III

IV



V

rise to ortho-, meta-, and para-benzyne, respectively, each formed at a different dedeuteration threshold. Even though the conditions under which the ICR experiments are performed are somewhat gentler than those normal to mass spectrometry; i.e. higher total pressures (10^{-5} torr versus 10^{-7} torr) and lower electron bombardment energies (10-15 eV), our results strongly imply that label scrambling has occurred. Thus, the thresholds for dedeuteration for phenyl cations formed from all three precursors are, within experimental error, the same as the value of 9.1 kcal mol^{-1} derived for the perdeuterated ortho-benzyne precursor. This assumes that phenyl cation is the most stable of the $C_6H_5^+$ isomers involved in the scrambling process. It is possible that the three isomeric benzynes are of approximately equal stability and hence have nearly identical proton affinities. This seems highly unlikely to us in view of the conclusions reached in Newton's theoretical study[9].

References and Notes

1. University of California Regents Dissertation Fellow, 1979
2. For reviews see, R.W. Hoffman, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, 1967; R.H. Levin in "Reactive Intermediates", M. Jones Jr. and R.A. Moss, ed., Wiley and Sons, New York, 1978, p. 1.
3. O.L. Chapman, K. Mattes, C.L. McIntosh, J. Pacansky, G.V. Calder and G. Orr, J. Am. Chem. Soc., 95, 6134 (1973).
4. O.L. Chapman, C.-C. Chang, J. Kole, N.R. Rosenquist, and H. Tomioka, J. Am. Chem. Soc., 97, 6586 (1975).
5. J.-F. Grützmacher and J. Lohmann, Liebigs Ann. Chem., 705, 81-90 (1967).
6. P. Natalis and J.L. Franklin, J. Phys. Chem., 69, 2943 (1965).
7. H.M. Rosenstock, J.T. Larkins and J.A. Walker, Int. J. Mass Spectrum. Ion Phys., 11, 309 (1973).
8. a) M.J.S. Dewar and W.-K. Li, J. Am. Chem. Soc., 96, 5569-5571 (1974); b) M.D. Newton and J.A. Fraenkel, Chem. Phys. Letters, 18, 244 (1973).
9. J.O. Noell and M.D. Newton, J. Am. Chem. Soc., 101, 51 (1979).
10. For examples of the use of similar techniques in the elucidation of the thermochemical stabilities of transient neutral molecules, see: free radicals, (a) D.J. DeFrees, W.J. Hehre, R.T. McIver, Jr., and D.H. McDaniel, J. Phys. Chem., 83, 232 (1979); enols of stable ketones, (b) S.K. Pollack and W.J.Hehre, J. Am. Chem. Soc., 99, 4845 (1977); singlet carbenes, (c) J. Vogt and J. Beauchamp, ibid., 97, 6682 (1975); (d) S.G. Lias and P. Ausloos, Int. J. Mass Spec. Ion Phys., 22, 135 (1976); (e) B.A. Levi, R.W. Taft and W.J. Hehre, J. Am. Chem. Soc., 99, 8454 (1977); (f) P. Ausloos and S.G. Lias, ibid., 100, 4594 (1978); methyleneimine, (g) D.J. DeFrees and W.J. Hehre, J. Phys. Chem. 82, 391 (1978); 1,1-Dimethylsilaethylene, (h) W.J. Pietro, S.K. Pollack and W.J. Hehre, J. Am. Chem. Soc., 101, 7126

(1979); Ethylidenimine and vinylamine, (i) M.R. Ellenburger, R.A. Eades, M.W. Thomsen, W.E. Farneth, and D.A. Dixon, ibid., 101, 7151 (1979).

11. L.R. Anders, J.L. Beauchamp, R.C. Dunbar, and J.D. Baldeschwieler, J. Chem. Phys., 45, 1062 (1966); J.L. Beauchamp, L.R. Anders, and J.D. Baldwschwieler J. Am. Chem. Soc., 89, 4569 (1967); R.T. McIver, Jr., and R.D. Dunbar, Int. J. Mass Spectrum. Ion Phys., 7, 471 (1971).

12. The ICR spectrometer used in these studies has been described previously (ref. 13). All organic materials were purified by preparative VPC. Argon (Linde - 99.9995%) was used as supplied. Gas mixtures were generally in the ratio of partial pressures 4:1:100, chlorobenzene: reagent base: argon, with total pressure of 1.0-5.0 x 10^{-5} torr. Ionization potentials of 15 eV were generally used, lower values producing an insufficient quantity of phenyl cation and higher values causing undesired contamination by fragment ions. Reactions were observed from 50 to 100 msec after the grid pulse to ensure sufficient time for the ions to come to thermal equilibrium. Double resonance experiments were performed first in the conventional fixed H_1-swept ω_2 mode, and then confirmed using a fixed ω_2-swept H_1 method (ref. 10a).

13. R.T. McIver, Jr., Rev. Sci. Instrum., 41, 55 (1970); R.T. McIver, Jr., ibid., 49, 111 (1978).

14. (a) J.F. Wolf, R.J. Staley, I. Koppel, M. Taagepera, J.L. Beauchamp, R.T. McIver, Jr., and R.W. Taft, J. Am. Chem. Soc., 99, 5417 (1977); (b) K.W. Hartman et al, "A Compendium of Gas Phase Basicity and Proton Affinity Measurements', National Bur. Stand., 1979; (c) Unpublished data of R.W. Taft.

15. Chlorobenzene-d_5 was employed in preference to the protio compound in order to distinguish (deuteron) transfer from the phenyl cation from possible (proton) transfer processes from acidic fragments of the reagent bases. Attempt to use bromobenzene as a neutral precursor proved unsuccessful due to the fact that electron impact on this compound leads primarily to loss of HBr rather than Br$^{\cdot}$.

16. The original value of 202.3 kcal mol^{-1} for the absolute proton affinity of ammonia as derived from ICR spectroscopy (ref. 14a) has been revised upward by more recent work: 203.6 kcal mol^{-1} (S.T. Ceyer, P.W. Tiedemann, B.J. Mahan and Y.T. Lee, J. Chem. Phys. 70, 14 (1979); 207 kcal mol^{-1} (F. A. Houle and J.L. Beauchamp, J. Am. Chem. Soc., 101, 4067 (1979)); 209.2 kcal mol^{-1} (R.G. McLoughlin and J.C. Traeger, J. Am. Chem. Soc., 101, 5791 (1979)).

17. J.L. Beauchamp, Adv. Mass Spectrum., 6, 717 (1975); T.C. McMahon, Ph.D. Thesis, California Institute of Technology, 1973.

18. D.R. Stull and J. Prophet, Nat. Stand. Ref. Data Ser., National Bur. Stand., No. 37 (1971).

19. Synthesis detailed in: S.K. Pollack, Ph.D. Thesis, University of California, Irvine, 1980.

20. D.H. Williams, S.W. Tam, and R.G. Cooks, J. Am. Chem. Soc., 90, 2150 (1968); W.O. Perry, J.H. Beynon, W.E. Baitinger, J.W. Any, R.M. Caprioli, R.N. Renard, L.C. Leitch, and S. Meyerson, J. Am. Chem. Sco., 92, 7136 (1979); R.J. Dickerson, K.H. Williams, J. Chem. Soc., (b) 249 (1971).

(Received in USA 7 January 1980)