the porphyrin π-system to the metal. Furthermore the efficiency of this reaction is governed by the Marcus equation (eq 13), in particular, by the magnitude of the orbital overlap integral, $|V(r)|$. This implies that in these cofacial dimers, although there is a significant electrostatic interaction between the metal and the porphyrin π-system,[24] overlap of the metal orbitals of one porphyrin with the proximate π-orbitals of the other porphyrin is weak. If there were a significant interaction, we would expect demetalation to be increased in the cofacial dimers. These experimental results are in accord with assumptions of our electrostatic model for π–π interactions: except that in some special cases orbital overlap between two π-stacked systems is negligible.[24]

Conclusion

We have shown that metalloporphyrins may be used as subtle probes of the chemistry and physics of processes occurring in the FAB matrix. The behavior of the porphyrins investigated under FABMS mirrors remarkably their behavior in solution with respect to both the kinetics and thermodynamics of acid demetalation, electronic reduction, and electron transfer. We propose a model whereby the gas-phase and selvedge regions of the matrix are in a steady-state equilibrium with the liquid phase. This generates a small ambient concentration of protons (2×10^{-4} M), free electrons, and excited states in the bulk liquid matrix. For porphyrins, reactions of these species apparently dominate the appearance of the spectrum. We have also shown that excited states, probably electronically excited states, are generated in the collision cascade, and this leads to complex electron-transfer processes in the matrix.

By using a series of different matrices, we have shown that it is possible to investigate the complex series of events that occurs in FABMS essentially independently. Our results provide a new insight into the mechanism and kinetics of metalloporphyrin reduction and demonstrate a new approach to the study of ultrafast electron-transfer reactions. Studies of more complex dimeric porphyrins have thrown some light on the nature of the aromatic–aromatic interactions in these systems.[24] These interactions are biologically very important since they are the basis of structure and drug/substrate recognition properties of biomacromolecules such as nucleic acids.[43]

Now that these simple systems have been thoroughly investigated and their behavior explained, FABMS should prove a useful tool for the study of more complex multicomponent assemblies of biomimetic significance.[26]

Experimental Section

Materials and Samples. All solvents used were HPLC grade. The FABMS matrices glycerol, aminoglycerol, thiodiglycol, and 3-nitrobenzyl alcohol were all purchased from Aldrich Chemical Co., U.K. and were vacuum-distilled prior to use. Zinc acetate was purchased from Aldrich and used without further purification.

The syntheses of all porphyrins used in this work have been described previously.[44]

Mass Spectra. All positive ion FAB mass spectra were recorded on one of the following instruments. (1) The first instrument was the Kratos MS50 operating at full accelerating voltage of 8 keV with a mass range of 10 000 daltons. The instrument was equipped with a standard Kratos FAB source and an Ion Tech gun. Xenon was used as the primary atom beam accelerated to 8 keV with an ion current of 1 μA. Spectra were obtained with a magnet scan rate varying between 10 and 100 s per decade, and the data were outputted to a UV chart strip recorder. The source pressure was typically $\sim 1.3 \times 10^{-3}$ Pa (10^{-5} Torr). (2) The second instrument was the VG 70-SEQ of EBQQ geometry operating at full accelerating voltage of 8 keV with a mass range of 3000 daltons. The instrument was equipped with a standard VG FAB source and an Ion Tech gun. Xenon was used as the primary atom beam at 8 keV and 1 μA. Spectra were obtained at a scan rate of 5 s per decade, and the data were collected and processed by using a VG 11/250 system.

Porphyrins were first dissolved in CH_2Cl_2 (which had been passed through a basic alumina column to remove any trace amounts of acid) in order to improve their solubility in the FAB matrix.[26] Typically, ~ 5 nmol of porphyrin in 2 μL of CH_2Cl_2 was added to 2 μL of matrix on the FAB probe. The sample and matrix were thoroughly mixed and subjected to FAB mass spectrometry. The porphyrin samples in the FAB matrix were subjected to FABMS continuously for ~ 5 min, and the $(MetPH)^+$ and $(H_2PH)^+$ regions were scanned.

Acknowledgment. We thank the MRC (S.N. and J.H.L.), DENI (C.A.H.), and SERC (J.A.C. and J.K.M.S.) for financial support. J.K.M.S. is a member of the Cambridge Molecular Recognition Centre. We thank one of the reviewers for a number of interesting and valuable comments.

---

(43) See, for example: Wang, A. H.-J.; Ughetto, G.; Quigley, G.; Rich, A. *Biochemistry* **1987**, *26*, 1152. Burley, S. K.; Petsko, G. A. *Adv. Protein Chem.* **1988**, *39*, 125. Plus references cited therein.

(44) (a) Cowan, J. A.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. I* **1985**, 2435. (b) Cowan, J. A.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. I* **1987**, 2395.

(45) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925.

Comparison of the Calculated Acidity of Cubane with That of Other Strained and Unstrained Hydrocarbons

James P. Ritchie* and Steven M. Bachrach†

Contribution from Los Alamos National Laboratory, Mail Stop B214,
Los Alamos, New Mexico 87545. *Received September 5, 1989*

Abstract: Gas-phase acidities of some strained and unstrained hydrocarbons were calculated. The resulting deprotonation enthalpies (DPE's) are within 2-3 kcal mol^{-1} of those observed when extended basis sets are employed, some accounting of the correlation energy is made, and zero-point energy differences are considered. Our best calculated DPE for cubane (406.4 ± 3 kcal mol^{-1}) is significantly greater than that calculated for benzene (397 kcal mol^{-1}) and bicyclobutane (395.4 kcal mol^{-1}), but less than that for cyclopropane (413 kcal mol^{-1}). This result shows that the enhanced kinetic acidity of cubane is reflected in its thermodynamic acidity as well. It is noted that the quantity $\nabla^2\rho_c$(C–H) predicts cubane to be less acidic than cyclopropane, as would correlations against $J_{^{13}C-H}$. Changes of angles between bond paths at carbon upon ionization were calculated. It is found that the change for cubane is unusually large for formal sp^3 centers, thus corroborating the unusual hybridization in the cubyl anion as suggested by Luh and Stock.[1]

Luh and Stock suggested in 1974 on the basis of measured exchange rates that cubane is anomalously acidic.[1] They pointed out that its $J_{^{13}C-H}$ is 155 Hz, while that of cyclopropane is 161 Hz. Well-known hybridization arguments[2] and relationships

---

† Permanent address: Department of Chemistry, Northern Illinois University, Dekalb, IL 60115.

(1) Luh, T.-Y.; Stock, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 3712-3713.

Table II. Deprotonation Energies (kcal/mol) for Some Hydrocarbons (First Line Calculated as *E*($RH-R^-$))

molecule	AM1	6-31G	6-31G*	6-31+G	6-31+G*	MP2 6-31+G	Δ ZPE	best	obsd
methane	432.5	459.0	457.0	433.4	433.9	425.3	9.2	416.6	416.8 ± 1.7[a]
ethane	417.9	457.4	455.7	438.7	438.2	429.6	9.6	419.5	420.9 ± 1.9[a,f]
ethylene	417.3	440.3	438.5	423.1	421.6	417.0	9.0	406.5	406.1[a]
acetylene	400.3	403.4	402.8	384.8	384.6	382.9	7.7	375.0	376.7 ± 2.4[a]
cyclopropane	415.8	448.4	445.0	434.8	431.8	425.8	9.7	413.1	412.0 ± 1.9[a]
methylcyclopropane	406.9	445.9	442.7	433.4	430.3	422.2	9.4	409.5	409.2[b,d]
bicyclobutane	406.7	429.6	427.4	416.8	415.3	405.7	8.7	395.4	398 ± 2[e]
benzene	401.4	431.2	428.7	416.8	414.6	407.7	8.4	397.1	400.8 ± 0.5[b]
cubane	411.6	442.5	440.5	431.1	429.2	416.3	8.1	406.3	

[a] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data 17* (Supplement 1), 1–861. [b] Reference 15a. [c] $(CH_2)_2CHCH_2\text{-}\mathit{H}$. [d] $(CH_2)_2C\mathit{H}(CH_3)$. [e] Reference 15d. [f] Unstable with respect to ejection of an electron. See ref 16.

between $J_{^{13}C-H}$ and exchange rates[3,4] would then suggest cubane to exchange hydrogen slower than cyclopropane. Nevertheless, Luh and Stock found that cubane undergoes deuterium exchange about 10^3 times faster than does cyclopropane. They, consequently, concluded that "the large enhancement of acid strength [in cubane] originates in the altered hybridization at the anionic carbon atom to an orbital with significantly enhanced s character". We have found no further additional experimental data concerning this anomaly, although INDO calculations tend to support this argument.[5] It is worthwhile noting, however, that $J_{^{13}C-H}$ for benzene is 159 Hz,[6] i.e., nearly equal to that of cyclopropane. Luh and Stock found its exchange rate, however, to be slightly faster than that of cubane. Thus, the foregoing analysis of the "unexpected" kinetic acidity of cubane based solely upon correlation of $J_{^{13}C-H}$ with exchange rates may be oversimplified and demonstrates that other factors may be important. It is, thus, unclear whether a comparison of cyclopropane with cubane is appropriate since, for example, one results in a secondary anion and the other a tertiary anion.

An interesting observation in light of the often discussed "acidic" character of cyclopropane and cubane is that, to the best of our knowledge, no direct lithiations have been reported to give synthetically useful quantities.[7] Since any reasonable conception of base strengths would place alkyl anions above those of strained rings, the failure to effect this reaction in solution is clearly not primarily due to the thermodynamic instability of the strained ring anions. Differences of stability arising from complexation with a single Li cation would also not seem responsible, as the calculated stabilities of bare anions and their monolithium salts are normally quite simply related.[8] Although differences in solvation and degree of complexation inherent in condensed-phase studies may be responsible, we are unable to evaluate these effects and, instead, examine the stabilities of the bare anions to provide some information regarding this puzzle.

Lithiation of both the cubane and cyclopropane nucleus has, however, recently been accomplished by using their carboxamide derivatives to activate adjacent hydrogens.[7,9] It also appears that the direct lithiation of benzene has never been directly observed, but it has been inferred.[10] Benzamides, like cubanecarboxamides, can also be readily metalated.[11] Theoretical studies[12] show that the amide group, in addition to facilitating the metalation kinetically,[13] also stabilizes the ion pair by complexing the lithium cation. On the other hand, bicyclobutane and its hydrocarbon derivatives can be lithiated and reacted with ease.[3,4,14] A comparison of the calculated thermodynamic acidities for some of the parent hydrocarbons would thus be interesting to provide information relating to the synthetic accessibility of cubane and to discover whether its conjugate base possesses an unusual anionic carbon.

Calculating the deprotonation enthalpies (DPE's) of these compounds is expected to be difficult. It will be necessary to establish that the theoretical model to be used yields accurate results and can be applied to molecules as large as cubane. The DPE's for benzene, bicyclobutane, and cyclopropane have, however, been measured[15] and are available for comparison with calculations. High-quality calculations of the gas-phase acidity of cyclopropane[16] and other organic acids[17] have shown good agreement with experiment, but systematic examination of the compounds of interest to us with similar high-quality calculations are not available.

Computational Methods

All ab initio calculations were carried out on the CRAY computers at Los Alamos with either GAUSSIAN82,[18a] HONDO,[18b] or CADPAC[18c] and standard basis sets.[19] The AM1 calculations were performed with MOPAC.[20] All geometries were optimized at the lower levels of theory (6-31G, 6-31+G, and 6-31G*). With the largest basis used in this work (6-31+G*), however, the geometries of the larger molecules were not optimized. In these cases, energies were obtained at the 6-31+G optimized geometry. This choice of geometry was made to give a proper description of the anions. MP2/6-31+G energy calculations were per-

---

(2) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic: New York, 1965.

(3) (a) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, *85*, 2022–2023. (b) Closs, G. L.; Larrabee, R. B. *Tetrahedron Lett.* **1985**, *6*, 287–296.

(4) Streitwieser, A., Jr.; Caldwell, R. A.; Young, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 529.

(5) So, S. P.; Wong, M. H.; Luh, T.-Y. *J. Org. Chem.* **1985**, *50*, 2632–2635.

(6) Levy, C. G.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980.

(7) An attempt to trap the elusive cubyl anion is reported in: Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724–726. For an electrochemical approach see: Abeywicrema, R. S.; Della, E. W. *J. Org. Chem.* **1981**, *46*, 2352.

(8) (a) Schleyer, P. v. R.; Chandrasekhar, J.; Kos, A. J.; Clark, T.; Spitznagel, G. W. *J. Chem. Soc., Chem. Commun.* **1981**, 882–884. (b) Schleyer, P. v. R.; Kaufman, E.; Spitznagel, G. W.; Jonoschek, R.; Winkelhofer, G. *Organometallics* **1986**, *5*, 79–85.

(9) Eaton, P. E.; Daniles, R. G.; Casucci, D.; Cunkle, G. T.; Engel, P. *J. Org. Chem.* **1987**, *53*, 2100–2102.

(10) Eberhardt, G. G.; Butte, W. A. *J. Org. Chem.* **1964**, *29*, 2928–2932.

(11) (a) Gilman, H.; Bebb, R. L. *J. Am. Chem. Soc.* **1939**, *61*, 109–112. (b) Wittig, G.; Fuhrman, G. *Chem. Ber.* **1940**, *73*, 1197–1218. (c) Gshwend, H. W.; Rodriguez, H. R. *Org. React.* (*N.Y.*) **1979**, *26*, 1–361.

(12) Bachrach, S. M.; Ritchie, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 3134–3140.

(13) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356–363.

(14) Cohen, H. M. *J. Orgmet. Chem.* **1967**, *9*, 375–376.

(15) (a) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968–1973 and references therein. (b) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 607–608. (c) Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2853–2862. (d) Kass, S. R.; Chou, P. K. *J. Am. Chem. Soc.* **1988**, *110*, 7899–7900.

(16) (a) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051–4053. (b) Tumas, W.; Foster, R. F.; Brauman, J. I. *Ibid.* **1984**, 4053–4054. (c) Schleyer, P. v. R.; Spitznagel, G. W.; Chandrasekhar, J. *Tetrahedron Lett.* **1986**, *27*, 4411–4414.

(17) (a) Siggel, M. R. F.; Thomas, T. D.; Saethre, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 91–96. (b) DePuy, C. H.; Bierbaum, V. M.; Dramrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051–4053.

(18) (a) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. *GAUSSIAN82*; Carnegie-Mellon University: Pittsburgh, PA, 1982. The CTSS version was implemented by Dr. R. Martin, LANL. (b) Dupuis, M.; Rys, J.; King, H. F. *QCPE* **1981**, *No. 401*. (c) Amos, R. D.; Rice, J. E. CADPAC: The Cambridge Analytic Derivatives Package; issue 4.0, Cambridge, 1987.

(19) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(20) We thank J. J. P. Stewart, U.S. Air Force Academy, for providing us with a copy of his program.

formed at the HF/6-31+G optimized geometries. Topological electron density analysis was performed with EXTREME.[21]

Some computational difficulties were encountered in performing calculations for benzene, phenyl anion, cubane, and cubyl anion when basis sets with diffuse functions were used. These functions are necessary for the proper description of anions.[17a,22] In these cases, however, they are found to be very nearly linearly dependent and result in the difficult, if not impossible, convergence of the Hartree–Fock equations. The CADPAC program can remove the linearly dependent orbitals by defining a minimum acceptable eigenvalue of the overlap matrix. We set this minimum as 0.0001, which necessitated the removal of six orbitals for benzene, five orbitals for phenyl anion, and four each for cubane and cubyl anion. The deleted orbitals in benzene and phenyl anion were comprised of the diffuse s orbitals and the diffuse p orbitals in the molecular plane. The deleted orbitals in cubane and cubyl anion were formed predominantly from the diffuse s and p functions.

Results and Discussion

Energies. The calculated total energies from ab initio methods and heats of formation from AM-1 for all species examined are listed in Table I, which appears in the supplementary material. The derived DPE's from these energies are listed in Table II.

As was found in earlier studies, DPE's using standard basis sets (6-31G) are vastly too high, by an average of about 40 kcal mol^{-1}. Inclusion of polarization functions (HF/6-31G*//HF/6-31G*) reduces the DPE of all species by about 2 kcal mol^{-1}, but the inclusion of diffuse functions (HF/6-31+G//HF/6-31+G) has a much more dramatic effect, improving the calculated DPE's by 15–20 kcal mol^{-1}. Adding polarization and diffuse functions (HF/6-31+G*//HF/6-31+G* or HF/6-31+G*//HF/6-31+G for bicyclobutane, benzene, and cubane) results in DPE's that are closer to experiment but still systematically too large, ranging from an overestimation of 9.2 kcal mol^{-1} for acetylene to 21.1 kcal mol^{-1} for methylcyclopropane. Additional calculations were performed at the RMP2/6-31+G level to assess the effects of electron correlation. Results at this level show significant effects of electron correlation, but are still too high, as shown. Changes in ZPE, obtained from AM1 vibrational frequency calculations, are also shown in Table II and are found to be quite sizable.

Our best estimate for DPE's was finally obtained by assuming an additivity of the extension of the basis set and calculated correlation energies;[23] ZPE differences were also explicitly accounted for. Thus, the difference of the DPE's at HF/6-31+G and HF/6-31+G* is a measure of the error arising from a lack of polarization functions, while that of the DPE's at HF/6-31+G and RMP2/6-31+G is an estimate of the neglect of correlation energy. The estimates obtained from the use of these quantities are listed in Table II as DPE (best).

The best previous estimates of the DPE values (in kilocalories per mole) for the unstrained hydrocarbons we use as references are as follows: methane (MP4/6-31++G(2d,p)), 418.5;[17a] ethane (HF/4-31+G//HF/4-31+G) (note: the ethyl anion is expected to be unstable with respect to electron loss), 422.2;[16,17b] ethene (HF/4-31+G//HF/4-31+G), 406.9;[16] ethyne (HF/4-31+G//HF/4-31+G), 368.7;[16] [1.1.0]bicyclobutane (AM1), 400.0.[15c] Our best estimates for the DPE values of methane, ethane, ethene, and ethyne are all within 1.0 kcal mol^{-1} of the measured values. Results for strained-ring compounds show larger, but nonetheless reasonably small, differences. Our estimate of the DPE for cyclopropane (413.1 kcal mol^{-1}) is in good agreement with that obtained at the higher MP2/6-31+G*//HF/6-31+G* level (412.6 kcal mol^{-1})[16] and shows that our use of the HF/6-31+G geometry is not a significant source of error. The DPE's for cyclopropane and methylcyclopropane differ by 1.1 and 0.3 kcal mol^{-1}, respectively, from the experimental values. The result for bicyclobutane is somewhat below the lower limit of the measured number and a previous "corrected" AM1 estimate.[15c] The DPE (best) for benzene is 3.6 kcal mol^{-1} below the experimental value. Although these calculated results show larger differences from measured values (ca. ±3 kcal mol^{-1}) than might be desired (±1 kcal mol^{-1}), the relative ordering of the DPE's is qualitatively reasonable even at the HF/6-31+G* level. We note, however, that in the case of cubane correlation effects are unusually large and the difference in DPE values between cyclopropane and cubane is 2.6 kcal mol^{-1} at HF/6-31+G*, but 9.5 kcal mol^{-1} at MP2/6-31+G.

Table III. Calculated R(C–H), ρ_c(C–H), $\nabla^2\rho_c$(C–H), and Electron Population (n(H)) for the Hydrocarbons Studied.[a]

hydrocarbon	R_e, Å	ρ_c(C–H)	$\nabla^2\rho_c$(C–H)	n(H)
methane	1.084	0.277	−0.977	1.007
ethane	1.086	0.278	−0.982	1.024
ethylene	1.076	0.287	−1.078	0.976
acetylene	1.058	0.295	−1.267	0.812
cyclopropane	1.076	0.285	−1.041	0.993
methylcyclopropane	1.078	0.286	−1.040	1.006
bicyclobutane	1.065	0.289	−1.095	0.943
benzene	1.073	0.290	−1.098	0.979
cubane	1.082	0.281	−1.015	1.007
r vs DPE(6-31+G*)	0.94	−0.88	0.98	0.97
r vs DPE(obsd)	0.96	−0.91	0.99	0.97

[a] The value of the correlation coefficient (r) of DPE(6-31+G*) and DPE(obsd) from Table II vs the calculated quantities at 6-31+G* are given. Correlation vs DPE(6-31+G*) was performed for all nine compounds. Correlation vs DPE(obsd) was performed for the eight compounds where data were available.

Thus, our best DPE for cubane is 406.3 kcal mol^{-1}. The results above suggest that this value may differ from a measured value by ±3 kcal mol^{-1}, but a definite error bar is impossible to assign because the results depend upon hard to predict systematic errors. This result is of sufficient accuracy, however, to state that cubane is thermodynamically more acidic than cyclopropane; the unexpected kinetic acidity of cubane relative to cyclopropane from considerations of $J_{^{13}\mathrm{C-H}}$ is reflected in its thermodynamic acidity as well.

Hybridization. Although NMR coupling constants are frequently linearly related to the kinetic acidity of strained-ring compounds, any suspected correlation[15d] of $J_{^{13}\mathrm{C-H}}$ with observed DPE's appearing in Table II shows obvious problems. Benzene ($J_{^{13}\mathrm{C-H}}$ = 159 Hz) and cyclopropane ($J_{^{13}\mathrm{C-H}}$ = 161 Hz), for example, have similar $J_{^{13}\mathrm{C-H}}$'s, but quite different DPE's. On the other hand, bicyclobutane ($J_{^{13}\mathrm{C-H}}$ = 205.0 Hz) and benzene have similar DPE's, but quite different coupling constants. The original studies showing a relation between $J_{^{13}\mathrm{C-H}}$ and exchange rates (that is, kinetic acidities) were performed for closely related series of compounds, and it is perhaps too much to expect that this relationship differentiate between thermodynamic acidities of different classes of compounds to within a few kilocalories per mole. Nevertheless, $J_{^{13}\mathrm{C-H}}$ certainly does possess medium resolution for rank-ordering DPE's comparing very different carbon types, or quite fine resolution when comparing closely related hydrocarbons, e.g., small-ring cycloalkanes.[3,4] More simply stated, the systematic error of the correlation is larger than the differences we wish to distinguish between.

A more fundamental question is whether any ground-state property of the acid can correlate with DPE, with the desired accuracy. To assess this, some possible correlations of other ground-state parameters with DPE's were investigated. As a probe of hybridization effects, the equilibrium C–H bond length and ρ_c(C–H) were examined. The C–H bond length should reflect the hybridization of the carbon, while ρ_c(c–H) is the minimum value of electron density along the bond and is expected to be sensitive to the hybridization of carbon.[24] Also, examined were the quantities $\nabla^2\rho_c$(C–H), which is expected to be a measure of

---

(21) (a) Biegler-Konig, F. W.; Nguyen-Dang, T. T.; Tal, Y.; Bader, R. F. W.; Duke, A. J. *J. Phys. B: At. Mol. Opt. Phys.* **1981**, *14*, 2739–2751. (b) Biegler-Konig, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317–328. We thank Prof. Bader for a copy of EXTREME.

(22) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609–5612.

(23) (a) Gordon, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 4352–4357. (b) Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 1922–1930.

(24) (a) Bader, R. F. W.; Tang, T. H.; Tal, Y.; Biegler-Konig, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 946–952. (b) Knop, O.; Boyd, R. J.; Choi, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 7299–7301.

Table IV. Internuclear Angles and Angles between Bond Paths at Carbon (α) for the Indicated Hydrocarbon and Its Conjugate Base

R		RH	R-		RH	R-
methyl	α(HCH)	109.5	110.4			
	$\angle$(HCH)	109.5	109.2			
ethyl	α(CCH)	110.2	108.4	α(HCH)	108.7	107.9
	$\angle$(CCH)	111.2	109.8	$\angle$(HCH)	107.7	106.8
ethenyl	α(CCH)	122.6	104.2			
	$\angle$(CCH)	121.7	108.7			
phenyl	α(CCC)	120.6	103.0			
	$\angle$(CCC)	120.0	112.4			
cyclopropyl	α(CCC)	78.3	72.0	α(CCH)	113.8	107.4
	$\angle$(CCC)	60.0	59.4	$\angle$(CCH)	118.1	109.4
methylcycloprop-1-yl	$\alpha(C_2C_1C_3)$	79.9	73.4	$\alpha(C_2C_1C)$	116.0	104.9
	$\angle(C_2C_1C_3)$	60.2	60.2	$\angle(C_2C_1C)$	120.5	112.9
bicyclo[1.1.0]but-1-yl	$\alpha(C_2C_1C_3)$	76.4	68.0	$\alpha(C_2C_1C_4)$	104.8	91.2
	$\angle(C_2C_1C_3)$	60.4	57.3	$\angle(C_2C_1C_4)$	97.8	91.0
cubyl	α(CCC)	97.4	83.1			
	$\angle$(CCC)	90.0	86.5			

the ionic character in the bond,[25] and n(H), the integrated Bader electron population associated with the hydrogen atom. These quantities were correlated against calculated DPE's (at 6-31+G*) and, where available, observed DPE's. Correlation of calculated versus observed DPE's gives $r = 0.99$. Thus, these two quantities are highly correlated.

Examination of the correlation analysis results in Table III shows that quantities from the topological analysis, $\nabla^2\rho_c$(c–H) and n(H), correlate well with both calculated and observed DPE's. It is particularly interesting that these quantities provide DPE ordering of bicyclobutane, benzene, and cyclopropane closer to that observed than does $J_{^{13}C-H}$. It must be noted, however, that the values of these quantities would suggest that cubane is a weaker acid than cyclopropane. This disagrees with our "best" DPE's in Table II. It thus appears that these correlations also possess systematic errors larger than the acidity differences being examined.

To probe the rehybridization occurring upon deprotonation, additional quantities describing the topology of the charge distributions were calculated. A bond path is the path of maximum electron density between bonded atoms.[26] The angle between initial bond path directions in traveling away from an atom (α) may differ from geometric bond angles in strained rings, for example, and the bond paths are found to be bent in such cases. This angle is expected to be especially sensitive to hybridization effects because it is determined near the nucleus. We, thus, calculated this quantity at the ionized carbon for the neutrals and conjugate bases under consideration, except for acetylene, where it is determined by symmetry. The results are shown in Table IV.

As can be seen from these results, significant changes may occur upon ionization. For methane and ethane, the change in α is only a few degrees, indicating very similar hybridization in the neutral and ion. Changes of α in the range of 16–17° are found for ethylene and benzene. Thus, the two sp^2 centers undergo a similar and significant rehybridization upon ionization. For the cyclopropanes and bicyclobutane, $\alpha(C_2C_1C_3)$, the angle between "strained" bond paths at the ionized carbon, changes are consistently in the range of 6–9°. These are larger than the changes in methane and ethane. Finally, in cubane, the change in α accompanying ionization is 14.3°. This is larger than the changes found for other formal sp^3 centers and even larger than the more acidic bicyclobutane. Furthermore, α(ccc) is less than $\angle$(ccc) indicating that the bond paths are bent inward rather than outward, as is usually the case in strained rings. Thus, compared with other formal sp^3 centers, cubane behaves anomalously and much more like a formal sp^2 center. This is in keeping with the proposed "altered hybridization at the anionic carbon".[1,5]

Summary and Conclusions

The calculated DPE of cubane is less than that calculated for cyclopropane, contrary to expectations based upon correlation of kinetic acidity with $J_{^{13}C-H}$. Our calculations put the DPE of cubane at least 2 kcal mol^{-1} below that of cyclopropane. Both these hydrocarbons are thus more acidic than methane, and it is thermodynamically possible to deprotonate cubane and even cyclopropane with alkyl anions. Previous failures to observe this reaction in solution with lithium reagents may be due to alteration of the reaction thermodynamics by some external factor, such as solvent, ion pairing, etc., or simply from kinetic factors. Perhaps use of activated "super-bases" would be useful in this regard, as they have been claimed capable of deprotonating cyclopropanes.[27]

It is noted that correlations between $J_{^{13}C-H}$ and DPE cannot account adequately for the gas-phase acidity order benzene $\cong$ bicyclo[1.1.0]butane > cyclopropane. Quantities from the topological analysis of the electron-density distribution, however, do show this qualitative trend. Additional topological analysis of several hydrocarbon neutrals and their conjugate bases shows anomalous changes in hybridization of the deprotonated carbon upon ionization for cubane, in agreement with the previous suggestion of Luh and Stock.

Acknowledgment. This work was jointly funded by the Department of Defense, Office of Munitions, and the Department of Energy. S.M.B. greatly acknowledges the receipt of an Associated Western Universities Faculty Participation Award. We acknowledge helpful conversations with Dr. Scott Gronert. Helpful comments from the reviewers are greatfully acknowledged.

Supplementary Material Available: Table I showing calculated energies and geometries (1 page). Ordering information is given on any current masthead page.

---

(25) (a) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061–5068. (b) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. N. *J. Am. Chem. Soc.* **1984**, *106*, 1594–1605. (c) Bader, R. F. W.; Essen, H. *J. Chem. Phys.* **1984**, *80*, 1943–1960.

(26) Runtz, G. R.; Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* **1977**, *55*, 3040–3045.

(27) Schlosser, M.; Hartmann, J.; Stahle, M.; Kramar, J.; Walde, A.; Mordini, A. *Chimia* **1986**, *40*, 306–308.