

Gas-Phase Basicities of Cubane, Dodecahedrane, and Methyl- and 1,16-Dimethyldodecahedrane as Measured by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Ivan Santos,[†] Douglas W. Balogh,^{†§} Christopher W. Doecke,^{†§} Alan G. Marshall,^{*†‡} and Leo A. Paquette^{*†}

Contribution from the Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210. Received August 6, 1985

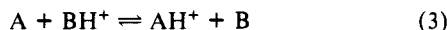
Abstract: The relative gas-phase basicities of eight reference compounds (α -methylstyrene, isopropyl ether, *n*-pentyl ether, 2,4-dimethyl-3-pentanone, methyl benzoate, *n*-butyl ether, methyl trimethylacetate, and methyl cyclopropanecarboxylate) have been redetermined by Fourier transform ion cyclotron resonance (FT/ICR) mass spectrometry and are now self-consistent to less than 0.8 kJ/mol (0.2 kcal/mol). For each binary mixture of two bases, equilibrium was approached from both sides via initial selective ejection of either of the two protonated bases. The gas-phase basicity of cubane was subsequently determined to be 840 kJ/mol (200.7 kcal/mol), at 155 °C, referred to *n*-propyl ether at 814 kJ/mol (194.5 kcal/mol), with ± 12 kJ/mol (3 kcal/mol) absolute and ± 0.8 kJ/mol (± 0.2 kcal/mol) relative errors. Similarly, the gas-phase basicity of dodecahedrane was determined to be 823 ± 12 kJ/mol (196.6 ± 3 kcal/mol), and the basicities of its monomethyl and 1,16-dimethyl derivatives were determined to be 824 ± 12 and 845 ± 21 kJ/mol (197 ± 3 and 202 ± 5 kcal/mol), respectively. These results are analyzed in terms of strain energy and polarizability effects for polyhedral hydrocarbons.

The gas-phase basicity of compound A (GB_A) is defined as the negative of the standard free energy change for the protonation reaction



$$GB_A = -\Delta G^\circ_A \quad (2)$$

When an ionized binary mixture of unknown compound A and a reference compound B is allowed to equilibrate, the standard free-energy change for the net proton-transfer reaction



may be evaluated from the experimentally determined partial pressures ($[A]$ and $[B]$) of the neutrals and the relative concentrations of the protonated parent ions ($[AH^+]/[BH^+]$) from their relative FT/ICR peak areas.

$$\Delta G^\circ_{\text{net}} = -RT \ln K_{\text{eq}} = -RT \ln \left[\frac{[B][AH^+]}{[A][BH^+]} \right] \quad (4)$$

Thus, the gas-phase basicity of A may be determined from $\Delta G^\circ_{\text{net}}$ and the previously established basicity of B.

$$GB_A = GB_B - \Delta G^\circ_{\text{net}} \quad (5)$$

A moderately self-consistent scale of gas-phase basicities for nearly 1000 compounds has recently been compiled.¹ Since gas-phase basicity can be related to bond strain, it is of interest to determine the gas-phase (i.e., "intrinsic") basicities of the known polyhedral hydrocarbons. In this paper, we report the determination by Fourier transform ion cyclotron resonance (FT/ICR) mass spectrometry^{2,3} of the gas-phase basicities of unsubstituted cubane and three dodecahedranes, referred to a recalibrated self-consistent set of eight reference bases (α -methylstyrene, isopropyl ether, *n*-pentyl ether, 2,4-dimethyl-3-pentanone, methyl benzoate, *n*-butyl ether, methyl trimethylacetate, and methyl cyclopropanecarboxylate).

Experimental Section

Cubane was prepared according to the Eaton-Cole procedure.⁴ Dodecahedrane and 1,16-dimethyldodecahedrane were prepared via a modification⁵ of Paquette's previously described routes.⁶ Monomethyldodecahedrane molecular ions were generated in the mass spec-

trometer via electron-ionization-induced fragmentation of dimethyldodecahedrane. The reference bases at $\geq 99\%$ purity were purchased from the Aldrich Chemical Company and used without further rectification. The purity of cubane and the dodecahedranes were shown by FT/ICR to be comparable to those of the reference compounds.

Gas-phase basicities were determined via FT/ICR mass spectrometry^{3,7,8} with a Nicolet FTMS-1000 instrument. The dodecahedranes were introduced via a solids probe; the remaining compounds were introduced via Varian Model 951 variable leak valves from a heated (130 °C) batch inlet after at least three freeze-pump-thaw cycles to remove volatile impurities. Pairs of bases were combined at approximately equal partial pressures of about 1.5×10^{-7} torr in a vacuum chamber whose background pressure was ca. 2×10^{-9} torr after overnight bakeout at 200 °C. Neutral pressures were determined with a nude Bayard-Alpert ionization gauge and corrected for differential sensitivity according to average molecular polarizability estimates.^{9,10} Under these conditions, the ratio of neutrals to ions is ca. $10^7:1$, with a neutral-wall collision rate of about 10^4 collisions/s. The neutral population should thus be well thermalized.^{11,12}

As soon as the pressure stabilized, the mixture was ionized by an electron beam (ca. 50 eV, 500 nA for 30 ms). The reaction (at 155 °C) was followed over time, typically 0.1–25 s, at about $3\text{--}5 \times 10^{-7}$ torr total pressure (including methane buffer gas when present). Equilibrium was typically reached after a few seconds (ca. 50–100 ion-neutral collisions), as evidenced by no further change in the ratio of protonated parent ion peak areas,^{11,13–15} as illustrated in Figure 1 (open circles) for 2,4-di-

(1) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695–808.

(2) (a) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *25*, 282; (b) **1974**, *26*, 489.

(3) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316–322.

(4) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157.

(5) Paquette, L. A.; Miyahara, Y.; Doecke, C. W. *J. Am. Chem. Soc.* **1986**, *108*, 1716.

(6) (a) Paquette, L. A.; Balogh, D. W.; Usha, R.; Kountz, D.; Christoph, G. G. *Science (Washington, D.C.)* **1981**, *211*, 575. (b) Paquette, L. A.; Balogh, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 774. (c) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503. (d) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *J. Am. Chem. Soc.* **1983**, *105*, 5446.

(7) Moylan, C. R.; Brauman, J. I. *Ann. Rev. Phys. Chem.* **1983**, *34*, 187–215.

(8) Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 247–350.

(9) Miller, K. J.; Savchik, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206–7213.

(10) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149–153.

(11) Wolf, J. F.; Stanley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417–5429.

(12) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046–6056.

(13) Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294–299.

[†] Department of Chemistry.

[‡] Department of Biochemistry.

[§] Current address: Research Laboratories, Eli Lilly and Company, Indianapolis, IN.

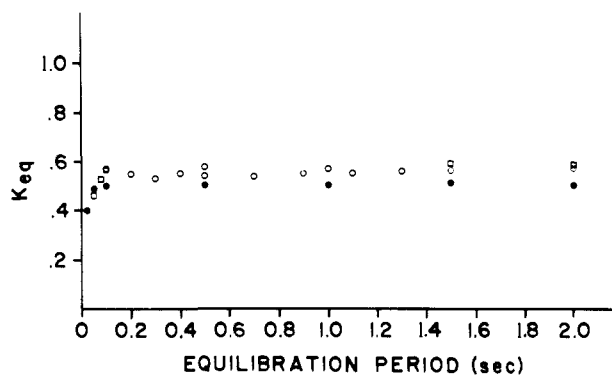


Figure 1. Approach to equilibrium for the proton-transfer reaction between 2,4-dimethyl-3-pentanone ($C_7H_{14}O$) and *n*-butyl ether ($C_8H_{18}O$). The apparent equilibrium constant, $K_{eq} = ([C_7H_{14}O][C_8H_{19}O^+])/([C_8H_{18}O][C_7H_{15}O^+])$, is plotted as a function of time following ion formation: (○) no ion ejection, (□) after ejection of protonated *n*-butyl ether, and (●) after ejection of protonated 2,4-dimethyl-3-pentanone.

Table I. Gas-Phase Basicities from Binary Mixtures of the Designated Compounds^a

compd	gas-phase basicity	
	kJ/mol	kcal/mol
1,16-dimethyldodecahedrane	845	202
α -methylstyrene	843	201.4
cubane	840	200.7
isopropyl ether	834	199.4
<i>n</i> -pentyl ether	830	198.4
2,4-dimethyl-3-pentanone	826	197.3
methyl benzoate	824	197.0
methyldodecahedrane	824	197
<i>n</i> -butyl ether	823	196.8
dodecahedrane	823	196.6
methyl trimethylacetate	819	195.7
methyl cyclopropanecarboxylate	815	194.9
<i>n</i> -propyl ether	814	194.5

^a The relative basicities for all but the dodecahedranes are self-consistent to within ± 0.8 kJ/mol (± 0.2 kcal/mol); the absolute errors are ± 12 kJ/mol (± 3 kcal/mol) relative to a basicity of 814 kJ/mol (194.5 kcal/mol) for *n*-propyl ether.¹ The origin of the larger imprecision for dodecahedrane (± 4 kJ/mol (± 1 kcal/mol)) and its methyl and dimethyl derivatives (± 12 kJ/mol (± 3 kcal/mol)) is discussed in the text.

methylpentanone ($C_7H_{14}O$) and *n*-butyl ether ($C_8H_{18}O$).

As a further check, equilibrium was approached from both sides, by initial selective ejection of either of the two protonated bases (e.g., squares and solid circles in Figure 1). The good agreement (to within 0.8 kJ/mol (0.2 kcal/mol)) between the $[AH^+]/[BH^+]$ ratios obtained via all three equilibration methods is strong evidence that equilibrium has been reached (after ca. 0.2 s in this example).¹⁶ The equilibrium constant was then calculated from the average of the values for the three equilibration methods. After each experiment, one of the leak valves was closed and the pressure remeasured. The initial and final pressures agreed to within 0.1×10^{-7} torr and were averaged in computing ΔG°_{net} . Each gas-phase basicity in Table I represents an average of at least five independent determinations, each from ca. 5 to 20 accumulated time-domain data sets. The FT/ICR peak area for each protonated parent ion was corrected for the carbon-13 contribution from the parent ion. Identical excitation and detection parameters were used for all FT/ICR experiments.

Results and Discussion

Self-Consistent Basicity Scale. A relative gas-phase basicity ladder (Figure 2) was first established for eight reference compounds whose basicities span the range of interest. *n*-Propyl ether was included as a secondary standard¹ to provide a reference

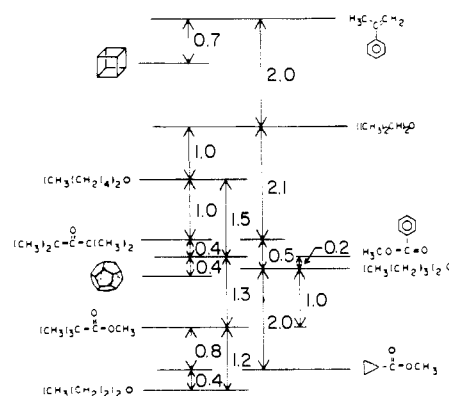


Figure 2. Self-consistent (to within ± 0.8 kJ/mol (± 0.2 kcal/mol)) ladder of gas-phase basicities, ΔG° , listed in kcal/mol.

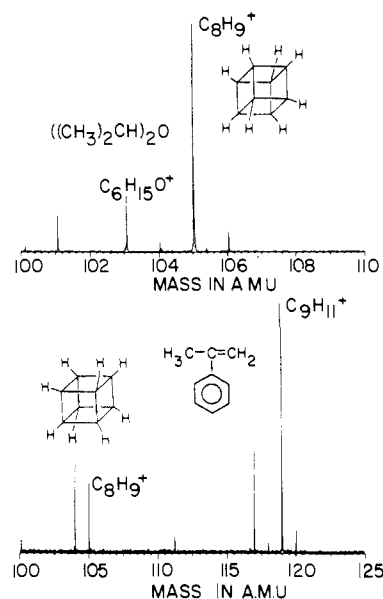


Figure 3. Fourier transform ion cyclotron resonance mass spectra of isobaric binary ionized mixtures of cubane and isopropyl ether (top) or α -methylstyrene (bottom), detected 45 s after ion formation via electron ionization. The relative peak heights of the protonated parent ions at m/q 105, 103, and 119 clearly show that cubane has a gas-phase basicity lower than that of α -methylstyrene and higher than that of isopropyl ether (see Table I). The m/q 101 and 117 peaks are $(M - H)^+$ from isopropyl ether and α -methylstyrene, respectively. The doublet at m/q 104 peaks was clearly resolved and quantitated as the cubane M^+ parent and a very small amount of $(M + 2H)^+$ from isopropyl ether.

anchor for the scale. Self-consistency between such apparent free-energy differences is a necessary condition for equilibrium. Thus, the high degree of self-consistency (to within ± 0.8 kJ/mol (0.2 kcal/mol)) shown in Figure 2 offers further evidence that equilibrium was indeed attained for each binary combination of reference bases.

Cubane. The FT/ICR mass spectra obtained for ionized binary isobaric mixtures of cubane with either α -methylstyrene or isopropyl ether are shown in Figure 3. The peaks at m/q 117 and 101 in Figure 3 represent $(M - H)^+$ from α -methylstyrene and isopropyl ether, respectively. The doublet at m/q 104 can be resolved and quantitated as the M^+ molecular ion from cubane and $(M + 2H)^+$ from isopropyl ether. (Our basicity determinations are unaffected by ejection of the above ions; thus, those ions do not affect our results.) It is qualitatively clear that protonated cubane is more abundant (i.e., higher basicity) than protonated isopropyl ether, but less abundant (i.e., lower basicity) than α -methylstyrene.

Once cubane had been bracketed between α -methylstyrene and isopropyl ether, the gas-phase basicity of cubane could be determined quantitatively with respect to (for example) α -methylstyrene as shown in Figure 4. As in Figure 1, equilibrium

(14) McDaniel, E. W. *Collision Phenomena in Ionized Gases*; Wiley: New York, 1964; pp 67-75.

(15) Davidson, W. R.; Bowers, M. T.; Su, T.; Aue, D. H. *Int. J. Mass Spectrom. Ion Phys.* 1977, 24, 83-105.

(16) Hodges, R. V.; Houle, F. A.; Beauchamp, J. L.; Montag, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* 1980, 102, 932-935.

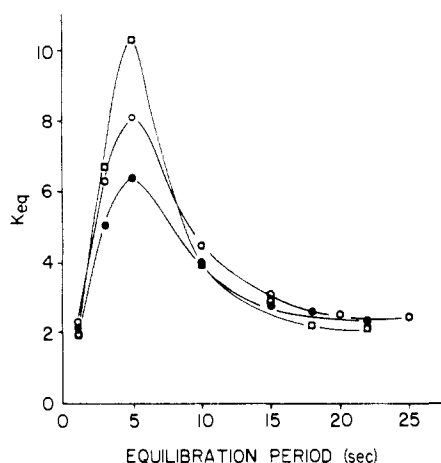


Figure 4. Approach to equilibrium for the proton-transfer reaction between cubane (C_8H_8) and α -methylstyrene (C_9H_{10}). The apparent equilibrium constant, $K_{eq} = ([C_8H_8][C_9H_{11}^+])/([C_9H_{10}][C_8H_9^+])$, is plotted as a function of time following ion formation: (O) no ion ejection, (\square) after ejection of protonated cubane, and (\bullet) after ejection of protonated α -methylstyrene.

Table II. Effect of Bond Angle Strain on Gas-Phase Basicity

compd	bond strain energy ¹⁵		gas-phase basicity ¹	
	kJ/mol	kcal/mol	kJ/mol	kcal/mol
cyclohexene	10	2.5	759	181.5
cyclobutene	128	30.6	766	183
cyclopropene	228	54.5	795	190

was approached without ion ejection (open circles) and following ejection of either protonated parent (squares and solid circles). From the equilibrium constant averaged (after >20-s equilibration) for the three routes to equilibrium, the gas-phase basicity of cubane was found to be 3 ± 0.8 kJ/mol (0.7 ± 0.2 kcal/mol) lower than that of α -methylstyrene. On the basis of an absolute gas-phase basicity of *n*-propyl ether as 814 ± 12 kJ/mol (194.5 ± 3 kcal/mol),¹ we can therefore assign the absolute gas-phase basicity of cubane as 840 ± 12 kJ/mol (200.7 ± 3 kcal/mol).

Dodecahedranes. The larger error (± 4 kJ/mol (± 1 kcal/mol) vs. 0.8 kJ/mol (0.2 kcal/mol)) reported for dodecahedrane (Figure 2) is due to the larger uncertainty in measurement of its partial pressure. The dodecahedranes were introduced via a solids probe, from which the sample pressure in the high-vacuum chamber was controlled by heating the probe tip. Because there is no valve between the ICR excitation/detection cell and the sample tip, no fine control of pressure is possible. Moreover, the small amount of sample on the probe tip is exhausted at a partial pressure of ca. 5×10^{-8} torr, at which the rate of approach to equilibrium is inconveniently slow. Therefore, methane was added to the reaction as a buffer gas to increase the chamber pressure to ca. $3-5 \times 10^{-7}$ torr and to provide a source of protons. In this way, it was possible to equilibrate a binary mixture of dodecahedrane and methyl benzoate to give a relative basicity difference of 0.4 kcal/mol, leading in turn to an absolute gas-phase basicity of 823 ± 12 kJ/mol (196.6 ± 3 kcal/mol) for dodecahedrane.

The available quantities of methyl- and dimethyldodecahedrane were too small to permit multiple quantitative equilibrations with reference bases. Therefore, their reported basicities (824 ± 12 , 845 ± 21 kJ/mol (197 ± 3 , 202 ± 5 kcal/mol) for methyl and dimethyl derivatives, respectively) were based on bracketing experiments (with corresponding larger errors) to establish whether or not proton transfer to a reference base took place.

Bond Angle Strain. Table II shows the direct relation between gas-phase basicity and bond angle strain energy for representative cycloalkenes. On the basis of bond strain alone, cubane (ca. 694 kJ/mol (166 kcal/mol) strain energy) would be expected to exhibit much greater basicity than other hydrocarbons, including the dodecahedranes (ca. 292 kJ/mol (70 kcal/mol) corresponding to

Table III. Gas-Phase Basicities of Primary Amines, $n-(C_xH_{2x+1})NH_2$ ^a

x	gas-phase basicity	
	kJ/mol	kcal/mol
1	861	205.7
2	872	208.5
3	879	210.1
4	881	210.6
5	883	211.1
6	883	211.1
7	884	211.2
8	887	212.0

^a Basicity increases directly with polarizability, which in turn varies directly with alkyl chain length.

only about 17% as much strain energy per carbon as cubane).¹⁷⁻²⁰ Although the experimental cubane basicity is indeed higher than for other hydrocarbons, it is only slightly higher than those of dodecahedrane and methyldodecahedrane and is actually lower than that of 1,6-dimethyldodecahedrane.

Polarizability. Gas-phase basicity also varies directly with molecular polarizability, as seen for the series of primary amines in Table III.^{1,20} Since the calculated polarizabilities of the dodecahedranes are much larger than for cubane (ca. 2.5:1), the increased polarizability of the dodecahedranes evidently offsets their lower strain energies (relative to cubane) in determining the gas-phase basicities. The relative basicity order among the unsubstituted, methyl-, and 1,16-dimethyldodecahedranes is consistent with the predicted small increases in polarizability and torsional strain introduced by the attachment of methyl groups.

Summary and Suggestions for Future work. In conclusion, the gas-phase basicities of cubane (840 kJ/mol (200.7 kcal/mol)) and the dodecahedranes ($823-845$ kJ/mol ($196.6-202$ kcal/mol)) are strikingly higher than for most saturated hydrocarbons (e.g., cyclohexane 674 kJ/mol (161 kcal/mol)).¹ Although the high basicity of cubane is consistent with its high bond strain energy, the remarkably high basicity of dodecahedrane cannot arise from bond strain alone and at present must be ascribed to its high polarizability. We are currently endeavoring to reinforce these conclusions via the effects of deuterium substitution and temperature upon ΔG_{net}° values, in order to determine the site of protonation in both cubane and dodecahedrane. We are also working to establish more precise basicities for the dodecahedranes, with extension to trimethyl and other derivatives, as well as polyhedral molecules similar to cubane but with one or two bridging carbons across the edges. The latter compounds should be less strained than cubane; hence their basicities should be lower. We will also look at cubane-like compounds with deuterated methyl groups on some of the bridging carbons, in order to probe the site of proton abstraction in reactions with compounds of higher basicity. Finally, we plan to measure the gas-phase acidities of cubane and dodecahedrane as well.

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Note Added in Proof. Preliminary semiempirical (MNDO)²¹ and ab initio (HF/3-21G)²² calculations predict the relative energies for cubane protonated at different sites: corner < edge < face < center. Thus, the most likely site for protonation of cubane is a corner.

(17) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978.

(18) Schulman, J. M.; Venanzi, T.; Disch, R. L. *J. Am. Chem. Soc.* **1975**, *97*, 5335-5339.

(19) Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189-2223.

(20) Ferguson, L. N. *Organic Molecular Structure*; Williard Grant: Boston, 1975; pp 77-79, 484, 494.

(21) Bartmess, J. E., private communication.

(22) DeFrees, D., private communication.