

## Cubyl Anion Formation and an Experimental Determination of the Acidity and C–H Bond Dissociation Energy of Cubane

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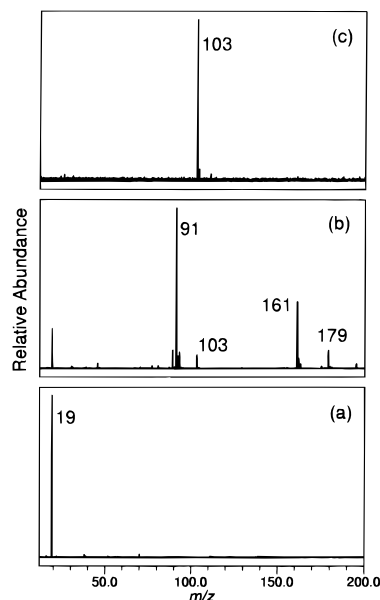
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Cubane (**1**) and its derivatives have been the subject of numerous investigations ever since Eaton's synthesis of the parent compound in 1964.<sup>1,2</sup> Kinetic measurements indicate that **1** is an unusually acidic alkane<sup>3</sup> and that its carbon–hydrogen bond dissociation energy (BDE) is considerably greater than that for a typical tertiary C–H bond.<sup>4</sup> The thermodynamic values for these quantities, however, are unknown. Cubane's acidity along with the electron affinity of cubyl radical could be used to derive the homolytic C–H BDE via a thermodynamic cycle (eq 1).

$$\text{BDE}(\text{cubyl-H}) = \Delta H_{\text{acid}}(\text{cubane}) - \text{IP}(\text{H}^{\bullet}) + \text{EA}(\text{cubyl radical}) \quad (1)$$

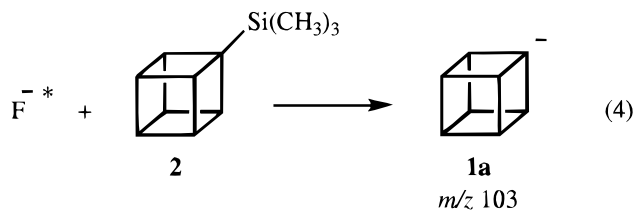
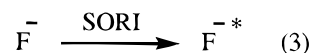
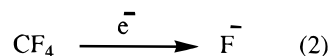
This bond energy is of special interest since it could be used in conjunction with our previous results on the radical anion of cubene to derive a purely experimental value for the heat of formation of cubene.<sup>5</sup> In this paper we report the formation of cubyl anion, a rare example of a stable gas phase alkyl anion, and the first determination of the acidity and C–H BDE of cubane.

Alkyl anions are difficult to generate in the gas phase typically, because of their extreme basicity and lack of stability relative to their radicals.<sup>6</sup> Cubyl anion ( $\text{C}_8\text{H}_7^-$ , **1a**) was prepared, nevertheless, by reacting (trimethylsilyl)cubane (**2**) with fluoride ion (i.e., the DePuy reaction)<sup>7</sup> in a Finnigan Fourier transform mass spectrometer (FTMS).<sup>8</sup> The yield of **1a** was poor but the efficiency of the reaction could be improved considerably by slightly increasing the kinetic energy of the fluoride ion.<sup>9</sup> This was accomplished by using the sustained off-resonance irradiation (SORI) technique developed by



**Figure 1.** (a) Generation and isolation of  $\text{F}^-$  ( $m/z$  19) via electron ionization of  $\text{CF}_4$ . (b) Formation of cubyl anion (**1a**,  $m/z$  103); the ions at  $m/z$  91, 161, and 179 presumably correspond to  $^-\text{CH}_2(\text{CH}_3)_2\text{SiF}$ ,  $\text{C}_8\text{H}_7(\text{CH}_3)_2\text{Si}^-$ , and  $^-\text{CH}_2(\text{C}_8\text{H}_7)(\text{CH}_3)\text{SiF}$ , respectively. (c) Isolation of cubyl anion.

Jacobson (eqs 2–4).<sup>10</sup> Subsequent isolation of **1a** (Figure 1) enabled us to unambiguously explore this ion's reactivity.



Acids, such as  $\text{H}_2\text{O}$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $\text{CH}_3\text{CH}_2\text{NH}_2$ ,  $\text{CH}_3\text{NH}_2$ , and  $\text{NH}_3$ , protonate **1a**, although the latter reaction is very inefficient. Ammonia- $d_3$  slowly transfers a deuteron to cubyl anion; it also induces up to five hydrogen/deuterium exchanges (Figure 2). The fifth deuterium appears only after a long reaction time ( $\sim 15$ – $20$  s), and it is this sluggishness which precludes the observation of the last two H/D exchanges. The acidity of cubane can be confidently assigned on the basis of these

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(8) A dual cell model 2001 Finnigan FTMS equipped with a 3.0 T superconducting magnet was used to carry out these studies.

(9) It is interesting to note that vinyl anion ( $\Delta H_{\text{acid}}(\text{C}_2\text{H}_4) = 409.4$  kcal/mol) can be generated without increasing the kinetic energy of the fluoride ion, but cyclopropyl anion ( $\Delta H_{\text{acid}}(\text{C}_3\text{H}_6) = 411.5$  kcal/mol) requires an energetic boost to be formed. For further information, see: ref 18.

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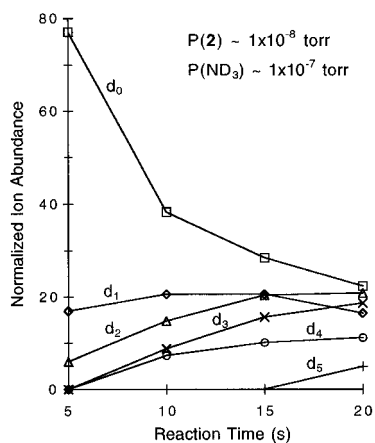
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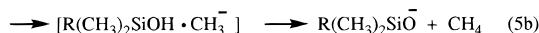
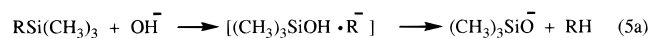
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**Figure 2.** Hydrogen/deuterium exchange behavior of cubyl anion (**1a**) upon reaction with ammonia- $d_3$ .

observations. In particular, its acidity must be very similar to that of ammonia; hydrogen/deuterium exchange would not take place if cubane was less acidic than ammonia- $d_3$ , and  $\text{ND}_2^-$  would not be observed if **1** was more acidic than  $\text{ND}_3$ . Therefore,  $\Delta H_{\text{acid}}(\mathbf{1}) = 404 \pm 3$  kcal/mol, which is in accord with the prediction of Ritchie and Bachrach that cubane is thermodynamically more acidic than cyclopropane ( $\Delta H_{\text{acid}} = 411.5$  kcal/mol).<sup>11,12</sup> This result is also in good agreement with our ab initio value of 404.7 kcal/mol (MP2/6-31+G(d)//MP2/6-31+G(d) + (0.96)ZPE).<sup>13</sup> In contrast, the conjugate base of cyclooctatetraene (**3a**) is not protonated by any of the acids listed above ( $\Delta H_{\text{acid}}(\text{cyclooctatetraene}) = 386 \pm 5$  kcal/mol),<sup>14</sup> and it readily undergoes seven H/D exchanges with  $\text{D}_2\text{O}$ .<sup>15</sup>

The acidity of cubane was also examined using a kinetic method developed by DePuy, Bierbaum, and Damrauer.<sup>16</sup> In this approach a trimethylsilane ( $\text{RSi}(\text{CH}_3)_3$ ) is reacted with hydroxide ion and a transient alkyl anion is formed ( $\text{R}^-$  and/or  $\text{CH}_3^-$ ), which subsequently abstracts the hydroxyl proton to afford  $(\text{CH}_3)_3\text{SiO}^-$  or  $\text{R}(\text{CH}_3)_2\text{SiO}^-$  (eq 5). The logarithm of



(11) All thermodynamic data, unless otherwise noted, comes from the following: 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*, Supplement 1 (or the slightly updated form available on a personal computer, *NIST Negative Ion Energetics Database* (Version 3.00, 1993); NIST Standard Reference Database 19B).

(12) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1990**, *112*, 6514.

(13) The acidity of methane is well reproduced at this level of theory (i.e., 416.6 (MP2/6-31+G(d) + (0.96)ZPE) and 416.6 (expt)). Note, in both cases the calculated values have not been corrected to 298 K. For scaling of MP2 zero-point energies, see: Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

(14) The acidity of cyclooctatetraene lies between water and methanol.

(15) The reactivity of **3a** also is different with some probe reagents. For example, **1a** reacts with  $\text{CS}_2$  to afford  $\text{HC}\equiv\text{CS}^-$  ( $m/z$  57),  $\text{CS}_2^-$  ( $m/z$  76), and  $\text{C}_8\text{H}_7\text{S}^-$  ( $m/z$  135) in a ~1:2:8 ratio while **3a** gives  $\text{HCS}_2^-$  ( $m/z$  77) and  $\text{C}_8\text{H}_7\text{S}^-$  ( $m/z$  135) in a ~1:10 ratio. The mechanism for the formation of thioetene enolate presumably is similar to the cubylcarbinyl radical cleavage, see: ref 4b.

(16) (a) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051. (b) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968. (c) Damrauer, R. In *Selective Hydrocarbon Activation: Principles and Progress*; Davies, J. A., Watson, P. L., Greenberg, A., Liebman, J. F., Eds.; VCH Publishers: New York, 1990.

the statistically corrected ratio of these two ions, along with a calibration line derived from compounds with known acidities, can be used to obtain  $\Delta H_{\text{acid}}(\text{RH})$ . We employed  $\text{RSi}(\text{CH}_3)_3$ , where  $\text{R} = \text{CH}_3\text{CH}_2$ ,  $\text{CH}_3$ ,  $\text{c-C}_3\text{H}_5$ ,  $\text{C}_2\text{H}_5$ , and  $\text{C}_6\text{H}_5$ , as our standards and then measured the  $(\text{CH}_3)_3\text{SiO}^-/(\text{C}_8\text{H}_7)(\text{CH}_3)_2\text{SiO}^-$  ratio from **2** to derive an apparent acidity of 413 kcal/mol for cubane.<sup>17</sup> This result is in agreement with a preliminary value of 412 kcal/mol obtained using a flowing afterglow device,<sup>16c</sup> but clearly is incorrect. This failing of the kinetic method may be due to a steric effect or the fact that none of the reference compounds have a tertiary center as does **2**. However, it seems more likely that rehybridization upon forming the cubyl anion retards the expulsion of **1a** and the subsequent loss of cubane (eq 5a).<sup>3b,12,18</sup> This leads to an apparent acidity for **1** which is considerably too weak (i.e.,  $\Delta H_{\text{acid}}$  is too large).

Cubyl anion undergoes electron transfer upon reaction with  $\text{SO}_2$ ,  $m\text{-CF}_3\text{C}_6\text{H}_4\text{CN}$ ,  $\text{C}_6\text{F}_6$ , or  $\text{CS}_2$  (EA = 1.11, 0.67, 0.52, and 0.51 eV, respectively) but not with  $p\text{-FC}_6\text{H}_4\text{CHO}$ ,  $\text{CH}_3\text{NO}_2$ ,  $\text{COS}$ , or 2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CHO}$  (EA = 0.49, 0.48, 0.46, and 0.44 eV, respectively).<sup>11,15,19</sup> These data suggest that the electron affinity of cubyl radical ( $\text{C}_8\text{H}_7\cdot$ ) is  $0.50 \pm 0.1$  eV (11.5  $\pm$  2 kcal/mol), which is in good accord with our previous estimate of 13.2 kcal/mol based upon ab initio calculations<sup>5</sup> and is similar to the experimental electron affinity of cyclopropyl radical (8.4 kcal/mol).<sup>16b</sup>

The electron affinity of cubyl radical can be combined with the acidity of cubane in a thermodynamic cycle (eq 1) to derive the C-H BDE for cubane. This value,  $102 \pm 4$  kcal/mol, is consistent with the increased s-character in the exocyclic carbon orbital and previous experimental (kinetic) observations. It also is in accord with several ab initio calculations including our recently predicted bond dissociation energy of 104 kcal/mol.<sup>5,20</sup> By combining this BDE with previous measurements on the radical anion of cubane one can derive a heat of hydrogenation for cubane of  $88 \pm 5$  kcal/mol, a heat of formation of  $236 \pm 5$  kcal/mol, a strain energy of  $225 \pm 5$  kcal/mol, and an olefin strain energy of  $61 \pm 5$  kcal/mol.<sup>5</sup> This last quantity is within the experimental uncertainty of the Hrovat and Borden TCSCF/6-31G(d) prediction of 58.9 kcal/mol.<sup>21</sup>

**Acknowledgment.** Support from the National Science Foundation, the donors of the Petroleum Research Foundation, as administered by the American Chemical Society, and the Minnesota Supercomputer Institute are gratefully acknowledged.

**Supporting Information Available:** Preparation of (trimethylsilyl)cubane; calculated structures (xyz coordinates) and energies for cubane and cubyl anion (2 pages). See any current masthead page for ordering and Internet access instructions.

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(17) The statistically corrected  $(\text{CH}_3)_3\text{SiO}^-/\text{R}(\text{CH}_3)_2\text{SiO}^-$  ratios and the reference acid acidities are as follows:  $\text{R} = \text{C}_2\text{H}_5$  (0.42, 420.1),  $\text{CH}_3$  (1.00, 416.7 (Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744),  $\text{c-C}_3\text{H}_5$  (2.25, 411.5),  $\text{C}_2\text{H}_5$  (6.63, 409.4), and  $\text{C}_6\text{H}_5$  (21.66, 401.7 (Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590); the resulting correlation equation is  $\gamma (\ln \text{ratio}) = -0.216(\text{acidity}) + 90.1$  ( $r^2 = 0.977$ ). The corresponding ratio for (trimethylsilyl)cubane is 2.22. These results are in excellent agreement with those reported in ref 16c.

(18) This kinetic measurement is consistent with the data in ref 9 and the fact that suprathreshold  $\text{F}^-$  is needed to afford **1a** (i.e., the difficulty in forming cubyl anion makes it appear more basic than it really is). These data indicate that there is a significant barrier to the formation of **1a**.

(19) Proton transfer takes place with all of the Brønsted acids while  $\text{COS}$  reacts to afford  $\text{HC}\equiv\text{CS}^-$  ( $m/z$  57) and  $\text{C}_8\text{H}_7\text{S}^-$  ( $m/z$  135) in a ~10:1 ratio.

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