

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

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**Abstract:** Dodecahedryl anion (**1a**) was generated in a Fourier transform mass spectrometer by deprotonation of dodecahedrane (**1**). Examination of the acid and base behavior of **1** and **1a**, respectively, enabled the acidity of **1** to be determined ( $\Delta H^{\circ}_{\text{acid}} = 402 \pm 2$  kcal/mol). Good agreement is found with the 298 K computed MP2/6-31+G(d)//HF/6-31+G(d) value of 405.1 kcal/mol. In a similar manner, the electron affinity of dodecahedryl radical was measured (EA =  $4 \pm 2$  kcal/mol). These results were combined in a thermodynamic cycle to afford the C–H bond dissociation energy of dodecahedrane (BDE =  $92 \pm 3$  kcal/mol), which is reasonably well reproduced (96.7 kcal/mol) at the MP2//HF level but leads to the suggestion that the reported heat of hydrogenation of dodecahedrane is in error. The DePuy kinetic method for measuring the acidity of **1** also was explored. It was found that this approach works well with triphenylsilyldodecahedrane but gives poor results with triethylsilyldodecahedrane. This latter failure is attributed to steric effects, and provides a rationale for several problem cases and a means to overcome these difficulties.

## Introduction

The synthesis of pentagonal dodecahedrane (**1**) with its perfectly symmetrical C<sub>20</sub>H<sub>20</sub> cage structure by the Paquette group was a much acclaimed achievement.<sup>1</sup> Yet, it was only with the advent of improved synthetic routes<sup>2,3</sup> that thermochemical data for **1** could be determined (heat of formation =  $18.2 \pm 1.0$  kcal/mol; strain energy =  $61.4 \pm 1.0$  kcal/mol).<sup>4</sup> More recently, the incorporation of a helium atom inside dodecahedrane<sup>5</sup> and the vibrational spectrum of **1** obtained via inelastic neutron scattering<sup>6</sup> were reported. Fundamental properties such as the acidity and carbon–hydrogen bond dissociation energy, however, are still unknown, and the dodecahedryl radical still has yet to be observed.<sup>7–9</sup> With the intriguing C<sub>20</sub> fullerene as an ultimate goal,<sup>10</sup> the installment of highly bent C=C double bonds into the dodecahedral skeleton has been explored. This provided an impetus for the present study, while ready access to the surprisingly persistent dodecahedrane<sup>11</sup> enabled the substrates of interest to be prepared.

In this work, we have obtained the homolytic carbon–hydrogen bond dissociation energy and acidity ( $\Delta H^{\circ}_{\text{acid}}$ ) of **1** by carrying out studies on dodecahedryl anion (**1a**) in a Fourier transform mass spectrometer. This ion represents one of a very few alkyl anions which have been generated and characterized in the gas phase; cubyl anion, the conjugate base of a second Platonic solid, is another.<sup>12–20</sup> Alkyl anions are difficult to prepare not only because they are extremely basic but because they often are unstable with regard to electron detachment (i.e., they often are energetically disfavored relative to their corresponding radicals). Consequently, kinetic methods have been employed to obtain thermochemical data for a number of these species. For example, the method developed by DePuy and co-workers has been shown to successfully provide the acidities of alkanes even in cases where the anion is unbound.<sup>21,22</sup> In this paper, we also will address the application of this approach for large substrates.

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## Experimental Details

**Synthesis.** In line with prior experience of the Paquette group,<sup>23</sup> attempts to prepare sterically congested silylated dodecahedranes such as **2** and **3** starting from bromododecahedrane via transmetalation have remained futile.<sup>24</sup> With the availability of dodecahedrene **1**, resort could be made to the method of catalytic addition of silanes to reactive olefins.<sup>25,26</sup> In fact, when a boiling solution of **1** and RhCl(PPh<sub>3</sub>)<sub>3</sub> catalyst was treated with (Et)<sub>3</sub>SiH or (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiH the desired silanes (**2** and **3**) were obtained in high yield (85–90%) after a relatively rapid (4 h) reaction. Dodecahedrene was prepared by a published method.<sup>11</sup> Reference silanes used for the kinetic acidity measurements were prepared by standard methods and purified by gas chromatography using a 10% SE 30 on Chrom W column in the case of the triethylsilyl compounds or by medium-pressure liquid chromatography using hexanes (100%) as the eluent for the triphenylsilanes. For the naphthalene derivative, 2.5% ethyl acetate in hexanes was used.

**Triethylsilylundecacyclo[9.9.0.0<sup>2,9</sup>.0<sup>3,7</sup>.0<sup>4,20</sup>.0<sup>5,18</sup>.0<sup>6,16</sup>.0<sup>8,15</sup>.0<sup>10,14</sup>.0<sup>12,19</sup>.0<sup>13,17</sup>]icosane (**2**).** To a solution of dodecahedrene (10 mg, 0.038 mmol) in benzene (3 mL) was added HSiEt<sub>3</sub> (0.2 mL) under argon and the resulting mixture was stirred at room temperature for 2 min. A solution of Rh(PPh<sub>3</sub>)<sub>3</sub>Cl (3 mg) in benzene (2 mL) was added and the reaction mixture was refluxed for 3 h (the color changed from red to yellow during this time). The product mixture was filtered over silica gel and concentrated in vacuo to give a colorless crude product. After chromatography (CH<sub>2</sub>Cl<sub>2</sub>, silica gel) and crystallization from ether, **2** was obtained as colorless crystals (12 mg, 85%), mp > 300 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.40–3.30 (m, 19 H), 0.95 (t, 9 H, –CH<sub>2</sub>CH<sub>3</sub>), 0.56 (q, 6 H, –CH<sub>2</sub>CH<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 3.31 (m, 14 H), 3.28 (m, 5 H), 1.08 (t, 9 H, –CH<sub>2</sub>CH<sub>3</sub>), 0.61 (q, 6 H, –CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ 70.2 (C-1), 67.5 (C-3, C-4, C-9, C-10, C-12, C-19), 67.1 (C-5, C-7, C-8, C-13, C-14, C-18), 67.3 (C-2, C-11, C-20), 67.0 (C-6, C-15, C-17), 67.0 (C-16), 8.2 (–CH<sub>2</sub>CH<sub>3</sub>), 2.7 (–CH<sub>2</sub>CH<sub>3</sub>). HRMS-EI M<sup>+</sup> calcd for C<sub>26</sub>H<sub>34</sub>Si 374.2430, obsd 374.2422.

**Triphenylsilylundecacyclo[9.9.0.0<sup>2,9</sup>.0<sup>3,7</sup>.0<sup>4,20</sup>.0<sup>5,18</sup>.0<sup>6,16</sup>.0<sup>8,15</sup>.0<sup>10,14</sup>.0<sup>12,19</sup>.0<sup>13,17</sup>]icosane (**3**).** To a stirred solution of dodecahedrene (15 mg, 0.058 mmol) in benzene (4 mL) was added HSiPh<sub>3</sub> (16 mg, 0.061 mmol) under argon. A solution of Rh(PPh<sub>3</sub>)<sub>3</sub>Cl (3 mg) in benzene (2 mL) was added and the resulting reaction mixture was refluxed for 4 h (the color changed from red to yellow during this time). Filtration of the solution over silica gel gave a colorless residue which was purified by chromatography (CH<sub>2</sub>Cl<sub>2</sub>, silica gel). Crystallization from ether gave **3** as colorless crystals (27 mg, mmol, 90%), mp > 290 °C. IR (PTFE): 2946, 2907, 1626, 1430, 879, 801, 700, 643, 504 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.42 (m, 6 H), 7.31 (m, 6 H), 7.26 (m, 3 H), 3.70 (br m, 3 H, 2-, 9-, 11-H), 3.40–3.30 (br m, 15 H, 3-, 4-, 5-, 6-, 7-, 8-, 10-, 12-, 13-, 14-, 15-, 17-, 18-, 19-, 20-H), 2.93 (br m, 1 H, 16-H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ [136.2, 135.9, 135.9] (C<sub>aromat</sub>), 72.2 (C-1), 67.8 (C-3, C-4, C-9, C-10, C-12, C-19), 67.4 (C-2, C-11, C-20), 67.3 (C-16), 67.2 (C-6, C-15, C-17), 67.0 (C-5, C-7, C-8, C-13, C-14, C-18). HRMS-EI M<sup>+</sup> calcd for C<sub>38</sub>H<sub>34</sub>Si 518.2430, obsd 518.2432.

**Gas-Phase Experiments.** All work was carried out in a dual cell Finnigan Fourier transform mass spectrometer (FTMS) equipped with a 3 T superconducting magnet and controlled by a Sun workstation running the Odyssey Software 4.2 package. Dodecahedrene was sublimed into the FTMS from a glass capillary tube placed inside the heated (150 °C) solid inlet probe. Amide was prepared by electron ionization of ammonia at 6 eV. Dodecahedryl anion (**1a**) was isolated by application of a SWIFT waveform<sup>27</sup> and a chirp broad band excitation for low masses.<sup>28</sup> Argon was pulsed at a nominal pressure of 10<sup>-5</sup> Torr to collisionally cool the ions. Neutral reagents were introduced via slow leak valves and reactions with **1a** were examined over time.

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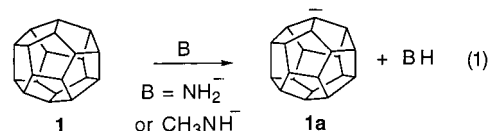
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For the DePuy kinetic acidity method, hydroxide was prepared by electron ionization (3 eV) of a 3:1 mixture of methane–nitrous oxide and allowed to react with a static pressure of the requisite silane. After a pulse of 10<sup>-5</sup> Torr of argon and a 500 ms delay period, all product ions were ejected. The reaction with thermalized hydroxide was then monitored over time (0.5 to 3 s) and the ratio of product ions was found to be constant. Triethylsilyldodecahedrane (**2**) was introduced by sublimation from a glass capillary tube inserted into the FTMS solid inlet probe (150 °C). For the triphenylsilyl derivative **3**, significant decomposition of the sample was noted if it was handled in this manner, as elevated temperatures (> 250 °C) were required to get enough vapor pressure into the FTMS cell. Therefore, **3** was dissolved in ether and deposited on a flat disk (9 mm diameter). After the solvent evaporated, the disk was mounted on the tip of the solid inlet probe which was inserted into the FTMS. The sample was rapidly heated to 200 °C and the experiments were executed in a timely fashion. A correction for the small amount of decomposition of **3** was made as described in the Results and Discussion section. For the kinetic acidity determination, an error analysis which accounts for the quality of the correlation as well as the uncertainties in the calibration data was carried out.<sup>29,30</sup>

**Computations.** All calculations were performed using Gaussian94<sup>31</sup> installed on IBM and SGI workstations. Geometries were optimized at the HF level of theory with the 6-31G(d) and 6-31+G(d) basis sets, and single point energy determinations were made at the MP2 level. The nature of each stationary point was investigated by a full vibrational analysis at the HF level. Bond energies come from MP2/6-31G(d)//HF/6-31G(d) calculations and the exact energy for hydrogen (–0.5 H). Acidities and bond dissociation energies were corrected from 0 to 298 K using scaling factors of 0.9135 and 0.8929 for the zero-point energies and harmonic frequencies, respectively.<sup>32</sup>

## Results and Discussion

Dodecahedrane (**1**) was found to react with amide in a Fourier transform mass spectrometer to afford its conjugate base (**1a**, eq 1). Dodecahedryl anion (**1a**) is rather basic and readily



deprotonates ethylamine, dimethylamine, and water (Table 1). In the case of methylamine, the reaction is considerably slower, but the reverse direction (methylamide with **1**) is fast indicating that **1** is slightly more acidic than this reference compound. These results enable us to assign  $\Delta H^\circ_{\text{acid}}(\mathbf{1}) = 402 \pm 2$  kcal/mol (eq 2a). In accord with this result, **1a** undergoes hydrogen–deuterium exchange with ammonia-*d*<sub>3</sub>. Up to 8 of the possible 19 hydrogen atoms are observed to exchange; further incorporation is precluded by the competitive loss of **1a** due to water in the system and the ammonia-*d*<sub>3</sub>. The bracketed acidity can be compared with a value of  $405 \pm 3$  kcal/mol obtained by the DePuy kinetic method using triphenylsilyl reference compounds (see below) and a 298 K computed value of 405.1 kcal/mol at the MP2/6-31+G(d)//HF/6-31+G(d) level of theory.<sup>33</sup>

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**Table 1.** Bracketing Results for the Acidity of Dodecahedrane

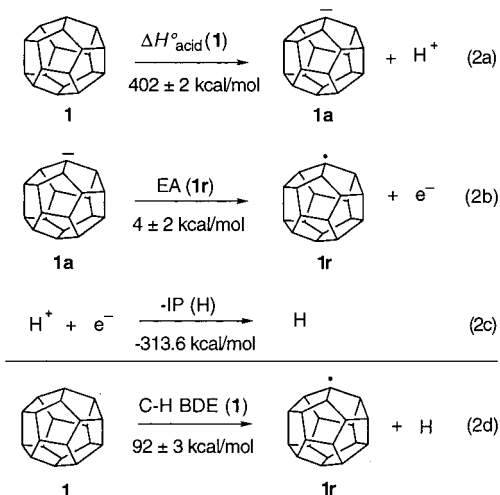
HA	$\Delta H^\circ_{\text{acid}}$ (kcal/mol) <sup>a</sup>	proton transfer <sup>b</sup>	
		forward	reverse
ammonia- <i>d</i> <sub>3</sub>	403.6 ± 0.8 <sup>c</sup>	no <sup>d</sup>	yes
methylamine	403.3 ± 0.8	yes, slow	yes
ethylamine	399.3 ± 1.1	yes	no
dimethylamine	396.5 ± 0.7	yes	no
naphthalene	394.2 ± 1.2	yes	no
water	390.7 ± 0.1	yes	no

<sup>a</sup> Acidity values taken from ref 54, except for naphthalene which comes from ref 55. <sup>b</sup> Forward and reverse directions correspond to the reaction of **1a** with different acids and **1** with different bases, respectively. <sup>c</sup> The value for NH<sub>3</sub> was used. <sup>d</sup> Up to eight hydrogen–deuterium exchanges are observed.

**Table 2.** Results for the Electron Affinity Bracketing of Dodecahedryl Radical (**1r**)

compound	EA (eV) <sup>a</sup>	electron transfer
nitric oxide	0.026 ± 0.005	no
phenanthrene	0.307 ± 0.012	yes
oxygen	0.451 ± 0.007	yes
carbonyl sulfide	0.46 ± 0.20	no <sup>b</sup>
carbon disulfide	0.51 ± 0.10	yes
sulfur dioxide	1.107 ± 0.087	yes

<sup>a</sup> Electron affinity values taken from ref 54. <sup>b</sup> Transfer of a sulfur atom and a small amount of clustering is observed.



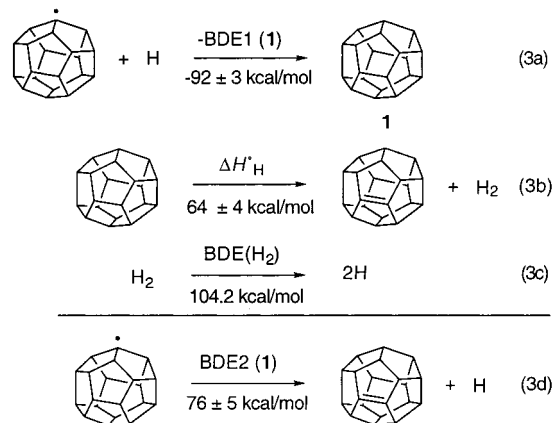
The stability of dodecahedryl anion also can be assessed by examining the electron affinity (EA) of its corresponding radical (**1r**, eq 2b). This quantity was obtained by monitoring electron-transfer reactions between **1a** and a series of reference compounds. In particular, **1a** transfers an electron to phenanthrene, molecular oxygen, carbon disulfide, and sulfur dioxide, but not to nitric oxide (Table 2). These data lead to an electron affinity of 0.17 ± 0.1 eV (4 ± 2 kcal/mol) for **1r**. This value indicates that **1a** is weakly bound as expected for an alkyl anion, and is near the threshold for being able to carry out experiments in our experimental setup. Dodecahedryl radical is an interesting bridgehead radical due to its fixed pyramidal configuration. Efforts to observe this “Platonic radical” spectroscopically, however, have been unsuccessful.<sup>7–9</sup> Nevertheless, the EA of **1r** can be combined with the  $\Delta H^\circ_{\text{acid}}$  of **1** and the known ionization potential of hydrogen atom in a thermodynamic cycle to afford the carbon–hydrogen bond dissociation energy of **1**

(33) The directly computed value is 406.7 kcal/mol, but we have corrected this for the known errors at this level of theory in the acidities of methane (416.7 ± 0.7 (expt) vs 418.1 (calc) kcal/mol) and cubane (404 ± 3 (expt) vs 405.8 (calc) kcal/mol). An average value of -1.6 kcal/mol was used for the correction.

(92 ± 3 kcal/mol, eq 2). Corrected MP2/6-31G(d)//HF/6-31G-(d) calculations predict a 298 K value of 96.7 kcal/mol.<sup>34</sup>

The C–H bond energy in **1** is smaller than that of the tertiary C–H bond in isobutane (BDE = 96.5 ± 0.4 kcal/mol) by 4.5 ± 3 kcal/mol.<sup>35</sup> This difference can be accounted for by the loss of three hydrogen–hydrogen eclipsing interactions upon breaking the carbon–hydrogen bond.<sup>36</sup> In terms of the components of the employed thermodynamic cycle, the lower bond energy is primarily a reflection of the increased acidity of **1** relative to simple alkanes such as methane ( $\Delta H^\circ_{\text{acid}}$  = 416.6 kcal/mol), ethane ( $\Delta H^\circ_{\text{acid}}$  = 420.1 kcal/mol), propane ( $\Delta H^\circ_{\text{acid}}$  = 415.6 (primary CH) and 419.4 (secondary CH) kcal/mol), and isobutane ( $\Delta H^\circ_{\text{acid}}$  = 412.9 (primary CH) and 413.1 (tertiary CH) kcal/mol).<sup>21,22</sup> These differences can be accounted for by the ability of **1a** to distribute the negative charge over its carbon framework (i.e., polarizability). Consistent with this idea, calculations show the charge (Mulliken) to be spread over several atoms and only -0.38 e<sup>-</sup> reside at the anionic site.<sup>37</sup> Six additional carbon atoms each possess -0.08 e<sup>-</sup>; this is based on summing the contribution of the hydrogen atoms onto the carbon atoms to which they are attached. In contrast to other alkyl anions such as cyclopropyl, bicyclobutyl, or cubyl, an increased amount of s-character in the C–H bond does not appear to contribute to the stability of **1a**.<sup>12</sup> In particular, the latter quantity is predicted to be 27% for **1** which is just about what one would expect for a typical sp<sup>3</sup>-hybridized center.<sup>38</sup>

Our measurement of the carbon–hydrogen bond strength for **1** can be used along with a value for the heat of hydrogenation ( $\Delta H^\circ_{\text{H}}$  = 64 ± 4 kcal/mol)<sup>39</sup> of dodecahedrane and the bond energy (104.2 kcal/mol) for molecular hydrogen in a thermodynamic cycle to afford the second C–H bond energy (76 ± 5 kcal/mol) for **1** (eq 3). This value leads to a very weak  $\pi$  bond



(34) This value has been corrected by the average error for cubane (102 ± 4 (expt) vs 104.4 (calc) kcal/mol) and isobutane (96.5 ± 0.4 (expt) vs 96.8 (calc) kcal/mol) at this level of theory; no zero-point energy corrections were applied but this makes no difference in the final (averaged) answer. This result can be compared with the directly computed BDE of 98.0 kcal/mol, which is lowered to 89.7 kcal/mol by inclusion of the zero-point energies.

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(37) For comparison, cubyl anion has -0.86 e<sup>-</sup> at the anionic site.

(38) The percentage of s-character was obtained from the following relationship: 0.2J = % s-character, where J is the <sup>13</sup>C–H coupling constant (134.9 Hz) for **1**.

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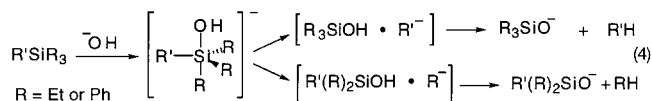
**Table 3.** DePuy Kinetic Acidity Measurement Data for Triethylsilyldodecahedrane (**2**) and Triphenylsilyldodecahedrane (**3**)

R'	R'SiEt <sub>3</sub>		R'SiPh <sub>3</sub>		$\Delta H^\circ_{\text{acid}}(\text{R}'\text{H})$ , kcal/mol
	ratio <sup>a</sup>	ln(3* ratio)	ratio <sup>a</sup>	ln(3* ratio)	
ethyl	1.00	0.00	0.0365	-2.17 <sup>b</sup>	420.1 ± 2.0
methyl	0.790	0.863	0.0209	-2.72 <sup>b</sup>	416.7 ± 0.7
cyclopropyl	2.75	2.11	0.0170	-2.97	411.5 ± 2.0
vinyl	6.11	2.91	0.0402	-2.12	409.4 ± 0.6
phenyl	19.9	4.09	1.00	0.00	401.7 ± 0.5
naphthyl			4.82	2.67	394.2 ± 1.2
dodecahedryl	2.41	1.98	0.124	-0.987	405.4 ± 3 <sup>c</sup>

<sup>a</sup> Ratio = (R<sub>3</sub>SiO<sup>-</sup>/R'(R<sub>2</sub>)SiO<sup>-</sup>) where R equals Et or Ph. Values have been isotopically corrected. <sup>b</sup> These data were not used in constructing the calibration curve, see text for details. <sup>c</sup> Value obtained from the triphenylsilyl calibration based on seven measurements taken on three separate days. With the triethylsilyl derivative, a value of 412 ± 2 kcal/mol was obtained based on the average of three measurements taken over 2 days.

strength (i.e., BDE1 – BDE2) for dodecahedrene of 16 ± 6 kcal/mol, and contrasts with values of 12 ± 7 and 58 ± 1 kcal/mol for cubene<sup>12,40</sup> and cyclopentene,<sup>41,42</sup> respectively. Given that incorporation of a double bond is much more difficult into cubane undoubtedly than dodecahedrane, we suggest that BDE2 (**1**) is too large because the heat of hydrogenation of dodecahedrene (obtained by examining the reactions of trifluoroacetyloxidodecahedrane with bases of varying strength)<sup>39</sup> is too big.<sup>43</sup> Therefore, a re-determination of the heat of hydrogenation of dodecahedrene is warranted.

As mentioned earlier, kinetic methods often have been used to obtain thermochemical data for ions, and we were interested in determining the proton affinity of **1a** using the DePuy method. In this approach, the acidity of an unknown is determined relative to that of an alkane, most often methane, based upon fragmentation of a siliconate anion (eq 4).<sup>22</sup> Specifically, the

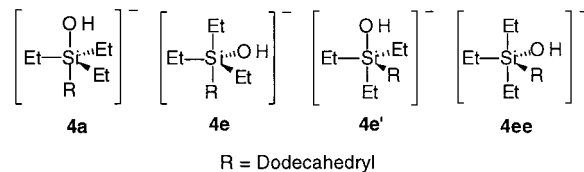


pentacoordinate species formed upon the reaction of hydroxide with a silane (R'SiR<sub>3</sub>) can dissociate by expulsion of RH or R'H and the formation of R'(R)<sub>2</sub>SiO<sup>-</sup> or R<sub>3</sub>SiO<sup>-</sup>, respectively. The natural logarithm of the statistically corrected ratio has been shown to correlate linearly with gas-phase acidities.

Since triethylsilyldodecahedrane (**2**) was available to us, we established a calibration curve using various triethylsilanes (Table 3):  $\Delta H^\circ_{\text{acid}}(\text{R}'\text{H}) = -4.42 \ln(3^* \text{Et}_3\text{SiO}^-/\text{R}'(\text{Et})_2\text{SiO}^-) + 420.7$ ,  $r^2 = 0.982$ . Our measurements with **2** afford an acidity for dodecahedrane which is 10 kcal/mol larger than our pseudoequilibrium number (412 ± 2 vs 402 ± 3 kcal/mol) because an insufficient amount of Et<sub>3</sub>SiO<sup>-</sup> is observed. To explore if the large difference in size between the ethyl and dodecahedryl groups could account for this result, we carried out an analogous experiment with triphenylsilyldodecahedrane (**3**). The following curve was constructed from reference triphenylsilanes (Table 3):  $\Delta H^\circ_{\text{acid}}(\text{R}'\text{H}) = -3.14 \ln(3^* \text{Ph}_3\text{SiO}^-/\text{R}'(\text{Ph})_2\text{SiO}^-) + 402.3$ ,  $r^2 = 0.996$ , and a value of 405 ±

3 kcal/mol was obtained for  $\Delta H^\circ_{\text{acid}}(\text{1})$ . The larger error in this instance arises from a correction of the Ph<sub>3</sub>SiO<sup>-</sup> ion intensity since this species also comes from the reaction of triphenylsilane with hydroxide. Upon heating, **3** was found to decompose to a small extent to **1** and triphenylsilane. In an independent experiment, the latter compound was found to yield three products upon reaction with hydroxide: Ph<sub>3</sub>SiO<sup>-</sup>, H(Ph)<sub>2</sub>SiO<sup>-</sup>, and Ph<sub>3</sub>Si<sup>-</sup>. Moreover, H(Ph)<sub>2</sub>SiO<sup>-</sup> also reacts with triphenylsilane to give Ph<sub>3</sub>SiO<sup>-</sup>. The ratio of Ph<sub>3</sub>Si<sup>-</sup> to Ph<sub>3</sub>SiO<sup>-</sup> (2.8:1.0) was monitored over time while H(Ph)<sub>2</sub>SiO<sup>-</sup> was continually ejected from the cell, and the Ph<sub>3</sub>SiO<sup>-</sup> ion intensity in experiments with **3** accordingly was corrected based on the observed Ph<sub>3</sub>Si<sup>-</sup> signal. Decomposition of **3** was minimized by modifying the method for introducing the sample into the FTMS. Overall, the correction led to a less acidic value for  $\Delta H^\circ_{\text{acid}}(\text{1})$  by 2 kcal/mol. Analogous decomposition products were not detected in experiments with **2**.

We attribute the failure of the kinetic method with triethylsilyldodecahedrane to steric effects and insufficient loss of dodecahedrane from the energetically favorable pentacoordinate siliconate **4a** in which the electronegative hydroxyl group and bulky alkyl substituent both occupy axial positions; it is known that electronegative substituents are apicophilic and MP2/6-31+G(d)//HF/6-31+G(d) computations on a model system (RSi(Me)<sub>4</sub><sup>-</sup> where R = Et, *i*-Pr, Ph, and *t*-Bu) indicate that the same is true for bulky groups.<sup>44</sup> Expulsion of a substituent from



pentacoordinate second row atoms is known to take place from the axial position<sup>45–47</sup> and, in the case of H<sup>-</sup> or CH<sub>3</sub><sup>-</sup>, the barrier can be lowered if the elimination takes place in conjunction with deprotonation of a pseudoequatorial hydroxyl group (i.e., formation of H<sub>2</sub> or CH<sub>4</sub> instead of H<sup>-</sup> or CH<sub>3</sub><sup>-</sup>).<sup>48</sup> In accord with this, we have found an enthalpy of activation of 23 kcal/mol (MP2//HF) for the direct loss of methyl anion from [(Me)<sub>4</sub>SiOH]<sup>-</sup> when the OH group is in an axial position (**5** to **6**, Figure 1) and a barrier of only 10–12 kcal/mol when the expulsion of methyl anion is concerted with abstraction of the proton from the hydroxyl group (**5** or **7** to **8**, Figure 1).<sup>49</sup> For **4a** to lose dodecahedrane and take advantage of the latter pathway, it must undergo an initial pseudorotation to **4ee** followed by a subsequent transformation to **4e** or **4e'**. Steric congestion is known to increase the energetic cost of stereomutation (i.e.,  $\Delta G^\ddagger = 12.8$  kcal/mol (condensed phase) for [2,4,6-tris((CH<sub>3</sub>)<sub>3</sub>C)C<sub>6</sub>H<sub>2</sub>SiF<sub>4</sub>]<sup>-</sup> versus a predicted value of 3 kcal/mol for SiF<sub>5</sub><sup>-</sup> (gas phase) at the MP4/6-311++G(d,p)//MP2/6-31++G(d,p) level of theory,<sup>50,51</sup> and thus could retard

(44) The *tert*-butyl group favors the axial position by 2.4 kcal/mol and the preference for the bulkier dodecahedryl group should be larger.

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(49) It is possible that transition state **8** could arise from **7** and/or **5**. We have not carried out an intrinsic reaction coordinate calculation to probe this matter.

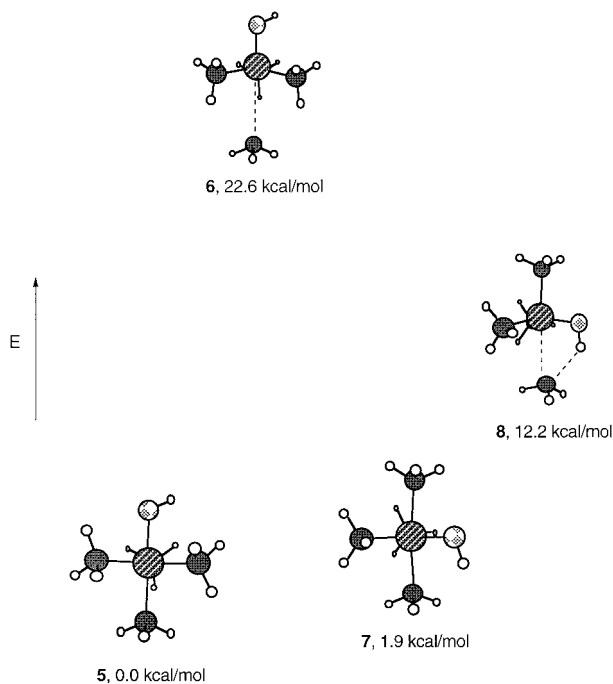
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(43) The computed difference in heats of hydrogenation of cubene and dodecahedrene is 39.3 kcal/mol at the CASSCF(2,2)/6-31G(d) level of theory.



**Figure 1.** Relative Energies (MP2/6-31+G(d)//HF/6-31+G(d)) for the isomers of  $[\text{Me}_4\text{SiOH}]^-$  (**5** and **7**) and the transition states **6** and **8** for loss of methyl anion and methane, respectively.

the loss of dodecahedrane and the observation of  $\text{Et}_3\text{SiO}^-$ . In the triphenylsilyl derivative the size difference between the ligands is much less and the energy difference between the various siliconate structures diminishes, so the  $\text{Ph}_3\text{SiO}^-/\text{R}'(\text{Ph})_2\text{SiO}^-$  ratio more accurately reflects the acidity of dodecahedrane.

The explanation given above accounts for the previously reported failure of the kinetic method for cubane (i.e., loss of cubane was too small and the resulting acidity was 9 kcal/mol too large).<sup>12</sup> The deviation from linearity for the ethyl- and methyltriphenylsilane data (Table 3) also can be rationalized

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in the same way, although electronic effects are probably important as well. Computational studies on siliconates are rife in the literature and a couple of these have addressed species generated in the DePuy kinetic method, but none have examined the impact of a ligand which does not closely resemble the reference.<sup>48,52</sup> Our experimental results suggest that such an investigation is warranted, that the application of this kinetic method requires new found care, and that the acidities of several bridgehead alkanes could be in error.<sup>53</sup>

## Conclusion

Dodecahedryl anion (**1a**) represents a rare example of a stable alkyl anion in the gas phase. The proton affinity of **1a** ( $402 \pm 2$  kcal/mol) and its electron binding energy ( $4 \pm 2$  kcal/mol) were used in a thermodynamic cycle to afford the C–H bond dissociation energy ( $92 \pm 3$  kcal/mol) for dodecahedrane. The stability of **1a** results from polarization of the charge onto its carbon framework. Determination of the acidity of dodecahedrane by the DePuy kinetic method was found to be successful using triphenylsilyldodecahedrane but not triethylsilyldodecahedrane. The large size difference of the alkyl groups in the latter case is the probable source of the discrepancy and should serve as a cautionary note in future applications of this method.

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