

## Formation of the Radical Anion of Cubene and Determination of the Heat of Formation, Heat of Hydrogenation, and Olefin Strain Energy of Cubene

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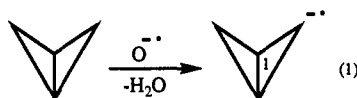
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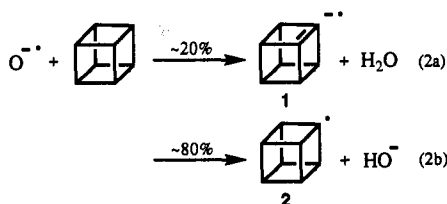
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Small strained ring compounds have fascinated chemists for generations and have been the subject of numerous investigations.<sup>1</sup> Many of these species are fleetingly stable, and as a result, thermodynamic information is usually unavailable. Gas-phase ion chemistry is of considerable value in this regard, and we report herein on the heat of formation, heat of hydrogenation, and olefin strain energy of cubene.

The atomic oxygen radical anion ( $O^{\bullet-}$ ) reacts with many organic compounds by abstracting both a proton and a hydrogen atom to afford a new radical ion and water.<sup>2</sup> For example, bicyclobutane reacts with  $O^{\bullet-}$  to produce the radical anion of bicyclobutene (eq 1).<sup>3</sup> We have found that cubane reacts with the atomic oxygen



ion in a home-built Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer<sup>4</sup> to afford hydroxide and a  $C_8H_6^{\bullet-}$  ion (**1**,  $m/z$  102) which we believe is the radical anion of cubene (eq 2).<sup>5</sup>



Our structural assignment is based, in part, upon analogy to other recent work, i.e., the formation of cubene<sup>6</sup> and the radical anions of bicyclobutene<sup>3</sup> and benzyne.<sup>7</sup> Ion **1** also undergoes five hydrogen/deuterium exchanges upon reaction with deuterium

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(1) For example, see: (a) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978. (b) *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley and Sons: New York, 1987; Parts 1, 2. (c) Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 973 and the rest of this issue.

(2) For a recent review on the gas-phase chemistry of the atomic oxygen ion, see: Lee, J.; Grabowski, J. J. *Chem. Rev.* **1992**, *92*, 1611.

(3) Chou, P. K.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 697.

(4) Koning, L. J. de; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, *109*, 1715 and references cited therein.

(5) A small amount ( $\leq 5\%$ ) of a  $M - 3$  ion is also formed. This species could be the conjugate base of cubene, but since it is formed in low yield it was not explored further. Cubane and  $O^{\bullet-}$  also react in a flowing afterglow device to afford a small signal of the  $M - 2$  ion, but the reaction is inefficient and precludes a thorough investigation of this ion.

(6) Eaton, P. E.; Maggini, M. J. *Am. Chem. Soc.* **1988**, *110*, 7230.

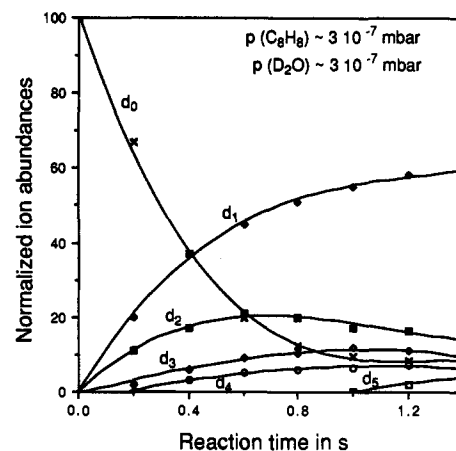


Figure 1. Hydrogen–deuterium exchange behavior of the radical anion of cubene (**1**) upon reaction with deuterium oxide.

oxide (Figure 1).<sup>8</sup> A sixth sequential exchange is not observed because of the falling intensity of the deuterium containing ions with time and the presence of a competitive deuterium transfer pathway, i.e.,  $DO^{\bullet-}$  formation. The only other  $C_8H_6^{\bullet-}$  isomer which would be expected to undergo at least five H/D exchanges is the radical anion of 1,2-dehydrocyclooctatetraene, but this species can be ruled out on thermodynamic grounds.<sup>9</sup>

The above result strongly suggests that the acidity of cubyl radical (**2**) is similar to that of deuterium oxide ( $\Delta H^{\circ}_{acid} = 392.0$  kcal mol<sup>-1</sup>).<sup>11</sup> In accord with this observation, **1** does not react with weaker acids such as ammonia- $d_3$  or dimethylamine ( $\Delta H^{\circ}_{acid} = 403.6$  and  $396.2$  kcal mol<sup>-1</sup>, respectively), but is protonated by fluorobenzene and methanol ( $\Delta H^{\circ}_{acid} = 387.2$  and  $381.5$  kcal mol<sup>-1</sup>, respectively). Consequently,  $\Delta H^{\circ}_{acid}(\mathbf{2}) = 392 \pm 3$  kcal mol<sup>-1</sup>, which corresponds to a 12 kcal mol<sup>-1</sup> acidity enhancement over the calculated value for cubane ( $404.3$  kcal mol<sup>-1</sup> at the MP2/6–31+G(d)//6–31+G(d) level). This difference is the same as between bicyclobutane and the 1-bicyclobutyl radical<sup>3</sup> but somewhat smaller than the benzene/phenyl radical acidity differential (22 kcal mol<sup>-1</sup>).<sup>7a,b</sup>

The cubene radical anion undergoes electron transfer upon reaction with  $m\text{-CF}_3\text{C}_6\text{H}_4\text{CN}$ ,  $\text{C}_6\text{F}_6$ , or  $\text{CS}_2$  (EA = 0.67, 0.52, and 0.51 eV, respectively) but not with  $\text{CH}_3\text{NO}_2$  (EA = 0.48

(7) (a) Guo, Y.; Grabowski, J. J. *J. Am. Chem. Soc.* **1991**, *113*, 5923. (b) Matimba, H. E. K.; Crabbendam, A. M.; Ingemann, S.; Nibbering, N. M. M. *J. Chem. Soc., Chem. Commun.* **1991**, 644. (c) Guo, Y.; Grabowski, J. J. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 299.

(8) The slight increase in the relative abundance of the  $d_1$  ions at reaction times exceeding 0.8 s may be a result of the presence of another species with the same mass as the  $d_1$  ion. The present experiments do not give insight into the origin or structure of this species. Initially, it cannot be anything more than a minor ion, but it can become more pronounced at longer times because the sum of the abundances of the  $d_0$ – $d_5$  cubene radical anions decreases as a result of deuterium transfer ( $DO^{\bullet-}$  formation) and possibly some electron detachment. In any case, the H–D exchange results are inconsistent with the 1,3- and 1,4-dehydrocubane radical anions since these species should undergo two and zero exchanges, respectively.

(9) If the radical anion of 1,2-dehydrocyclooctatetraene was formed and one assumes a vinyl C–H BDE of 110 kcal mol<sup>-1</sup> for 1,3,5,7-cyclooctatetraene, then one can derive a heat of hydrogenation for the neutral dehydrocyclooctatetraene going to cyclooctatetraene using our experimental data and a thermodynamic cycle similar to the one shown in eqs 3–7. The heat of hydrogenation would be 98 kcal mol<sup>-1</sup>, which is unreasonably large given that the hydrogenation energy of 2-butyne going to *cis*-2-butene is 37 kcal mol<sup>-1</sup>,<sup>10</sup> and that of 1,5-cyclooctadien-3-yne going to 1,3,5-cyclooctatriene is only 48 kcal mol<sup>-1</sup>.<sup>11</sup> Moreover, several stable dehydrocyclooctatetraenes have been prepared.<sup>12</sup>

(10) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

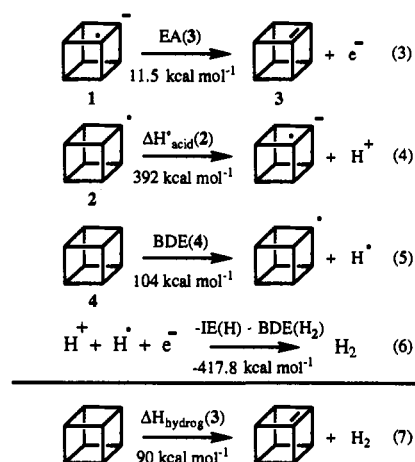
(11) All thermodynamic information including gas-phase acidities and electron affinities, unless otherwise noted, comes from Lias et al.: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(12) See: Huang, N. Z.; Sondheimer, F. *Acc. Chem. Res.* **1982**, *15*, 96 and references therein.

eV).<sup>11,13</sup> This data indicates that the electron affinity of cubene (3) is  $0.50 \pm 0.1$  eV ( $11.5 \pm 2$  kcal mol<sup>-1</sup>), which is similar to that of bicyclobutene ( $8 \pm 4$  kcal mol<sup>-1</sup>)<sup>3</sup> and in accord with the expectation for a highly bent out-of-plane olefin. Most hydrocarbons do not have bound radical anions; the loss of an electron is exothermic. However, the LUMO energy drops and the binding energy increases as an alkene is distorted from planarity.<sup>14</sup>

Our data can be combined with the C–H bond dissociation energy (BDE) of cubane (4) and some well-known ancillary thermochemical data to derive the heat of hydrogenation of cubene. Unfortunately, the C–H BDE of cubane has not been measured, and thus we have used ab initio calculations to obtain this quantity. Three methods were used: direct calculation of the bond energy (104 kcal mol<sup>-1</sup>),<sup>15</sup> anisodesmic reaction giving the relative BDEs of cubane and isobutane (104 kcal mol<sup>-1</sup>),<sup>16</sup> and a thermodynamic cycle relating the acidity of cubane and the electron affinity of cubyl radical to the bond dissociation energy of interest (104 kcal mol<sup>-1</sup>).<sup>17</sup> All three procedures were carried out using second-order Møller–Plesset perturbation theory and 6–31+G(d) or 6–31G(d) optimized geometries (e.g., MP2/6–31+G(d)//6–31+G(d))<sup>18</sup> and gave the same result, 104 kcal mol<sup>-1</sup>, to within 1 kcal mol<sup>-1</sup>. This value is in accord with the limited available experimental data and seems quite reasonable.<sup>19</sup> Combining this quantity with  $\Delta H^\circ_{\text{acid}}(2)$ , EA(3), IE(H<sup>+</sup>), and BDE(H<sub>2</sub>) leads to a heat of hydrogenation for cubene of  $90 \pm 4$  kcal mol<sup>-1</sup> (eqs 3–7), a heat of formation of  $238 \pm 4$  kcal mol<sup>-1</sup>, a strain energy of  $227 \pm 4$  kcal mol<sup>-1</sup>, and an olefin strain energy (OSE) of  $63 \pm 4$  kcal mol<sup>-1</sup>.<sup>20,21</sup> These values are in very good

accord with an OSE of 58.9 kcal mol<sup>-1</sup> and a heat of hydrogenation of 82.5 kcal mol<sup>-1</sup> previously calculated by Hrovat and Borden with a two-configuration wave function (6–31G(d)/3–21G TCSCF).<sup>14c</sup>



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**Supplementary Material Available:** Calculated structures, energies, and the three procedures used to calculate the bond dissociation energy of cubane (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(20) The strain energies of cubane (163.9 kcal mol<sup>-1</sup>) and cubene were calculated by subtracting their strain-free heats of formation (obtained using Benson's group equivalents) from their experimental heats of formation. The OSE was obtained by taking the difference in the strain energies of cubene and cubane. (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley and Sons: New York, 1976. (b) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

(21) The specified uncertainties are independent of the calculated C–H BDE of cubane as long as it is accurate to within 7 kcal mol<sup>-1</sup>. We anticipate that it is much more reliable ( $\pm 2$ –3 kcal mol<sup>-1</sup>).

(13) Proton transfer takes place with CH<sub>3</sub>NO<sub>2</sub> and competes with electron transfer with *m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN (60% proton transfer and 40% electron transfer).

(14) (a) Smith, J. M.; Hrovat, D. A.; Borden, W. T.; Allan, M.; Asmis, K. R.; Bulliard, C.; Haselbach, E.; Meier, U. C. *J. Am. Chem. Soc.* **1993**, *115*, 3816. (b) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095. (c) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710. (d) Yin, T. K.; Miyake, F.; Renzoni, G. E.; Borden, W. T.; Radziszewski, J. G.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 3544. (e) Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, *87*, 557. (f) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

(15) For a recent discussion on the calculation of C–H bond dissociation energies of alkanes, see: Wiberg, K. B.; Hadad, C. M.; Sieber, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 5820.

(16) This method has been used previously with a smaller basis set (6–31G(d)/3–21G). The results are quite similar. See: Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 3227.

(17) See the supplementary material for additional details.

(18) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

(19) (a) Choi, S.-Y.; Eaton, P. E.; Newcomb, M.; Yip, Y. C. *J. Am. Chem. Soc.* **1992**, *114*, 6326. (b) Della, E. W.; Head, N. J.; Mallon, P.; Walton, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 10730. (c) Luh, T.-Y.; Stock, L. M. *J. Org. Chem.* **1978**, *43*, 3271.