C_4H_4 Negative Ions: Formation of the Bicyclo[1.1.0]but-1(3)-ene Radical Anion and an Experimental Determination of the Heat of Formation of Bicyclo[1.1.0]but-1(3)-ene

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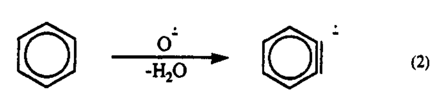
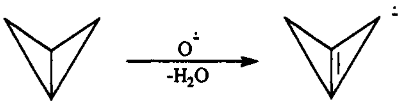
The atomic oxygen ion ($O^{\bullet-}$) is a marvelous reagent in the gas phase.[1] It is a reasonably strong base (PA = 382.2 kcal mol^{-1})[2] and readily undergoes proton transfer reactions. This ion also undergoes radical-type reactions, i.e., hydrogen atom abstraction and addition–fragmentation due to its unpaired electron. What makes $O^{\bullet-}$ unique, however, is its ability to undergo proton and hydrogen atom transfer at the same time ($-H_2^{\bullet+}$, presumably in the form of H_2O). The resulting radical anion (M − 2) often corresponds to a highly energetic neutral species. For example, ethylene reacts with $O^{\bullet-}$ to afford the radical anion of vinylidene (eq 1)[1o] while benzene reacts to give the radical anion of benzyne (eq 2).[1j] We now report that $O^{\bullet-}$ reacts with bicyclo[1.1.0]butane to afford the radical anion of bicyclo[1.1.0]but-1(3)-ene.

$$CH_2{=}CH_2 \xrightarrow[-H_2O]{O^{\dot{-}}} CH_2{=}C^{\dot{-}} \qquad (1)$$



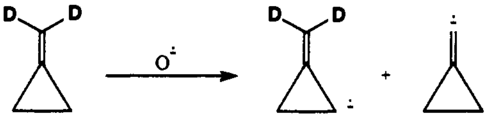
(2)

In our flowing afterglow apparatus,[3] $O^{\bullet-}$ (generated by electron impact on N_2O) reacts with bicyclo[1.1.0]butane (**1**) to afford a single C_4H_4, m/z 52, product ion. This species is highly reactive and is believed to be the radical anion of bicyclo[1.1.0]but-1(3)-ene (**2**, eq 3). The structural assignment is based on the following:



1 2 (3)

(1) Derivatives of bicyclo[1.1.0]but-1(3)-ene, but not the parent compound, have been reported by Szeimies and co-workers as transient intermediates in the liquid phase.[4] (2) Isotopic labeling of **1** with one deuterium at the bridgehead position[5] leads to the exclusive formation of a m/z 52 ion (M − HD). This result is consistent with the proposed structure but does not rule out the ring-opened methylenecyclopropylidene radical anion (**3**). An independent preparation of **3** as a ~3:1 mixture with **4** (eq 4), along with a study of their reactivity, indicates that both ions are distinct from **2**.[6] For example, the radical anion of bicyclo[1.1.0]but-1(3)-ene undergoes electron transfer to CS_2 whereas the (M − 2) ions derived from methylenecyclopropane do not. Furthermore, although all three ions react with CH_3OD via deuteron transfer, their reaction rates are significantly different ($k_2 = (3.89 \pm 0.74) \times 10^{-10}$, $k_3 = (1.11 \pm 0.07) \times 10^{-9}$, and $k_4 = (6.83 \pm 0.58) \times 10^{-11}$ cm^3 particle^{-1} s^{-1}). 3) Additional C_4H_4 ions were generated by the reaction of $O^{\bullet-}$ with 1,2-butadiene, 1,3-butadiene, 1-butyne, and 2-butyne. All of them react differently than **2** with reagents such as N_2O and/or CS_2. (4) Most hydrocarbons do not form stable radical anions in the gas phase because the loss of an electron is exothermic, i.e., the electron affinity (EA) is negative.[7] However, it has been shown experimentally and theoretically that bending an olefin out-of-plane lowers the energy of the lowest unoccupied molecular orbital (LUMO) and increases the EA.[8] The formation of **2**, the radical anion of a pyramidalized olefin, is therefore quite reasonable. Further support for this intuitive argument is obtained by examining the empirical relationship between LUMO energies and electron affinities.[9] In particular, the experimental EAs of 20 unsaturated hydrocarbons have been compared to their calculated LUMO energies using both semiempirical (AM1)[10] and ab initio (3-21G and 6-31G*/3-21G)[11] methods. In all three cases a linear relationship is observed which can be used to qualitatively predict whether a given olefin has a positive or negative EA.[12] All three correlations suggest that the radical anion of bicyclo[1.1.0]but-1(3)-ene is bound while those derived from vinylacetylene, cyclobutadiene, and methylenecyclopropene are not. Taken together, these four criteria strongly suggest that the bicyclo[1.1.0]but-1-(3)-ene radical anion (**2**) is indeed the product of the reaction of $O^{\bullet-}$ with **1**.



-3 : 1
3 4 (4)

The structure of **2** having been established, a great deal of thermodynamic information can be derived. Our previous mea-

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[2] All cited thermodynamic data, unless otherwise noted, comes from the following: Lias, S. G.; Bartmess, J. E.; Holmes, J. L.; Levin, R. D.; Liebman, J. F.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

[3] All of these experiments were carried out with He buffer gas, at room temperature, and pressures of ~0.4 Torr in an apparatus which has previously been described. For further details, see: Kass, S. R.; Guo, H.; Dahlke, G. D. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 366.

[4] (a) Harnisch, J.; Legner, H.; Szeimies-Seebach, U.; Szeimies, G. *Tetrahedron Lett.* **1978**, *19*, 3683. (b) Harnisch, J.; Baumgartel, O.; Szeimies, G.; Meerssche, M. V.; Germain, G.; Declercq, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 3370. (c) Zoch, H. G.; Schluter, A. D.; Szeimies, G. *Tetrahedron Lett.* **1981**, *22*, 3835. (d) Duker, A.; Szeimies, G. *Tetrahedron Lett.* **1985**, *26*, 3555.

[5] 1-Deuteriobicyclobutane was prepared as described by K. B. Wiberg and K. S. Peters (*Spectrochim. Acta* **1977**, *33A*, 261). The sample was >70% d_1 as determined by ^{1}H NMR.

[6] (Dideuteriomethylene)cyclopropane was synthesized as reported by G. N. LeFevre and R. J. Crawford (*J. Org. Chem.* **1986**, *51*, 747). The isotopic purity of our sample was >97% d_2 as ascertained by ^{1}H NMR and MS.

[7] Negative electron affinities can be measured by a scattering technique called electron transmission spectroscopy. For a recent review, see: Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, *87*, 557 and references therein.

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[9] Correlations of this type for several series of compounds with negative electron affinities have previously been reported. For example, see: (a) Howard, A. E.; Staley, S. W. *ACS Symp. Ser.* **1984**, *263*, 183. (b) Jordan, K. D.; Burrow, P. D. *ACS Symp. Ser.* **1984**, *263*, 165. (c) Heinrich, N.; Koch, W.; Frenking, G. *Chem. Phys. Lett.* **1986**, *124*, 20. (d) Younkin, J. M.; Smith, L. J.; Compton, R. N. *Theor. Chim. Acta* **1976**, *41*, 157.

[10] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

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[12] The electron affinities of bound hydrocarbons are not known very precisely, and quantitative predictions are not reliable. The least-squares fits of the data are as follows: $y = 1.26x - 0.29$ $r = 0.96$ (AM1); $y = 0.81x + 2.25$ $r = 0.99$ (3-21G); and $y = 0.84x + 2.41$ $r = 0.98$ (6-31G*/3-21G) where y is the experimental EA and x is the calculated LUMO energy (both in eV).

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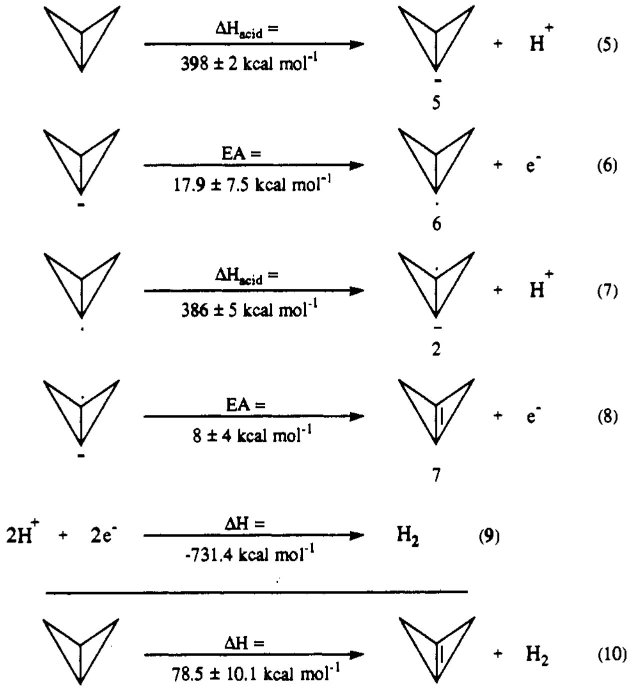
surements of the acidity of bicyclo[1.1.0]butane and the electron affinity of its corresponding radical (eqs 5 and 6)[13] can be combined with our current determination of the proton and electron affinity of **2** and **7** (eqs 7 and 8)[14] in a thermodynamic cycle (eqs 5–10) to afford the heat of hydrogenation for bicyclo[1.1.0]but-1(3)-ene (**7**). The experimentally derived value is 78.5 ± 10.1 kcal mol^{-1} and is in excellent agreement with recent computations by Hrovat and Borden, Schaefer et al., and Wiberg, Bonneville, and Dempsey (82.3 (TCSCF 6-31G*), 76.1 (DZP 2R CIDVD//6-31G* 2R CISD), and 91 kcal mol^{-1} (6-31G*), respectively).[8b,15] In addition, the heats of formation of **5**, **6**, **2**, and **7** (84 ± 2, 102 ± 8, 122 ± 9, and 130 ± 10 kcal mol^{-1}, respectively) have been derived.



Examination of a variety of additional compounds, including several strained ring systems, reveals that the formation of (M – 2) ions is a fairly general process. The structure and reactivity of these radical anions are currently being explored and should provide a wealth of thermodynamic information on a variety of reactive intermediates.

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Supplementary Material Available: Electron affinities and LUMO energies for all structures and a plot of their correlation (2 pages). Ordering information is given on any current masthead page.

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(14) Proton transfer is observed between **2** and *t*-BuOH, EtOH, and MeOH but not with H_2O (ΔH_{acid} = 375, 377, 381, and 391 kcal mol^{-1}, respectively). The proton affinity is therefore assigned a value of 386 ± 5 kcal mol^{-1}. Electron transfer occurs between **2** and SO_2, biacetyl, CS_2, cyclooctatetraene, and O_2 (EA = 25.6, 16.2, 13.8, 13.1, and 10.4 kcal mol^{-1}, respectively), and therefore 10.4 kcal mol^{-1} can be taken as an upper limit for the electron affinity of **7**. A reasonable lower limit is 5 kcal mol^{-1} since ions with electron affinities below this value rapidly undergo electron detachment and are difficult to observe, at room temperature, in a flowing afterglow device (He buffer gas). Consequently, the electron affinity is taken to be 8 ± 4 kcal mol^{-1}. References for the EAs are as follows. SO_2: (a) Celotta, R. J.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740. (b) Nimlos, M. R.; Ellison, G. B. *J. Phys. Chem.* **1986**, *90*, 2574. Biacetyl: (c) Grimsrud, E. P.; Caldwell, G.; Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 4627. CS_2: (d) Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 45. Cyclooctatetraene: (e) Wentworth, W. E.; Ristau, W. *J. Phys. Chem.* **1969**, *73*, 2126. O_2: (f) Travers, M. J.; Cowles, D. C.; Ellison, G. B. *Chem. Phys. Lett.* **1989**, *164*, 449.

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Unsymmetrical Dicopper Complexes. Direct Observation of Reversible O_2 Binding in a Copper Monooxygenase Model System

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In modeling metalloenzyme Cu^I/O_2 interactions, the design and investigation of species containing unsymmetrically disposed dicopper ion centers is of interest, since there is good evidence for the inequivalence of copper sites in some proteins.[2,3] Here, we report the purposeful design, synthesis, and reactivity of a dinuclear complex $[Cu_2(UN)]^{2+}$ (**1**), containing unsymmetrically coordinated copper(I) ions.[8] In a transformation closely modeling that of copper monooxygenases,[9–11] **1** reacts with O_2 reversibly to give a stabilized and directly observable $\{Cu_2–O_2\}^{2+}$ species $[Cu_2(UN)(O_2)]^{2+}$ (**3**); upon warming, **3** further reacts to give hydroxylated complex $[Cu^{II}_2(UN\text{-}O\text{-})(OH)]^{2+}$ (**4**). This contrasts with the reactivity of the symmetric parent compound $[Cu^I_2(XYL)]^{2+}$ (**2**, derived from *m*-xylene diamine), where a reversibly formed $Cu_2–O_2$ intermediate was inferred only from a kinetic analysis.[10,11] Thus, within a single reaction sequence **1** → **4**, the elements of chemically reversible O_2 binding, spectroscopic identification of the $\{Cu_2–O_2\}^{2+}$ species, and O_2 activation are present (Scheme I).

Unsymmetrical compound **1**[12] displays an essentially featureless

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(3) The unsymmetrical nature of dicopper sites is evidenced in an X-ray structure of deoxyhemocyanin (Hc, O_2 carrier),[4] in the 2 Cu:1 CO binding ratio observed for deoxy-Hc,[2] and is seen from amino acid sequence comparisons.[5] The inequivalence of nearby copper ion centers may have functional consequences in tyrosinase (Tyr, *o*-phenol monooxygenases) and dopamine β-hydroxylase activity.[2,6,7]

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(11) A kinetic study reveals that **2** reacts reversibly with O_2 giving a $\{Cu_2–O_2\}$ intermediate; in a second intramolecular step, hydroxylation occurs. Cruse, R. W.; Kaderli, S.; Karlin, K. D.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 6882–6883.

(12) $[Cu_2(UN)]^{2+}$ (**1**) was generated by addition of 2 equiv of $[Cu^I(CH_3CN)_4](PF_6)$ with the UN[13] in CH_2Cl_2 (Ar). The ^1H NMR spectra of both the UN free ligand and **1** reflect the difference in chemical environment of the two ligand arms.[13] Anal. for $[Cu_2^I(UN)(PF_6)_2$ [**1-(PF_6)$_2$**]. Calcd for $C_{35}H_{38}Cu_2F_{12}N_6P_2$: C, 43.79; H, 3.96; N, 8.74. Found: C, 44.28; H, 4.25; N, 8.74. ^1H NMR (300 MHz) (CD_3NO_2): δ 8.70 (d, 2 H), 8.45 (d, 2 H), 8.0 (m, 2 H), 7.85 (m, 2 H), 7.52 (d, 4 H), 7.40 (m, br, 4 H), 7.20 (m, 2 H), 6.92 (d, 1 H), 6.76 (s, 1 H), 3.6–3.8 (br, 6 H), 3.0–3.2 (br, 12 H).

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