potential of the Cu/Cu⁺ redox system, thus preventing the large-scale deposition of Cu as well as the dissolution of the deposited Cu dots. An elliptical Pt wire about 50 μm in diameter was used as a tool, which is reflected in the elliptical shape of the dots. For the formation of Cu crystallites on the Au surface, a nucleation barrier has to be surmounted (22), requiring a critical Cu adatom concentration on the Au surface during the pulse. This kinetic constraint assists the strongly localized Cu deposition.

The versatility of electrochemical reactions, combined with spatial resolution down to the nanometer range, may provide new abilities for modern micromachining technologies. Electrochemical microstructuring is not restricted to sequential fabrication. Complicated structures could be molded directly onto a surface using an appropriately shaped tool. The theoretically achievable spatial resolution compares favorably with that of state-of-the-art lithographical techniques, with the additional advantage of fully 3D capabilities.

References and Notes


Taming Superacids: Stabilization of the Fullerene Cations HC₆₀⁺ and C₆₀⁺

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A new superacid, H(CB₁₁H₆X₆) (where X = chlorine or bromine), whose conjugate base is the exceptionally inert CB₁₁H₆X₆⁻ carbene anion, separates Brønsted acidity from oxidizing capacity and anion nucleophilicity in a manner not previously achieved. Reaction of this superacid with C₆₀ gives HC₆₀⁺ as a stable ion in solution and in the solid state. In a separate experiment, an oxidant was developed such that the long-sought C₆₀⁺ ion can be synthesized in solution. The preparation of these two fullerene carbenes is a notable departure from the prevalent chemistry of C₆₀, which is dominated by the formation of anions or the addition of nucleophiles. The H(CB₁₁H₆X₆) superacid overcomes the major limitations of presently known superacids and has potentially wide application. Superacids (those stronger than 100% sulfuric acid) have been of great value to chemistry. In organic chemistry, superacidity has been used to stabilize carbenes such as R₂C⁺ and HCO⁺ and to study acid-catalyzed processes (I, 2). In inorganic chemistry, the oxidizing capacity of superacids has been widely exploited to stabilize unusual reactive cations such as S₈²⁺, Ir(CO)₆³⁺, and Xe₂⁺ (3–6). Nevertheless, currently known superacids have limitations. For example, the anions of superacids (SbF₆⁻, HO⁻, CF₃SO₂⁻, and so forth) are too nucleophilic to allow the free silylium ion (R₃Si⁺) to exist (7), and attempts to protonate and/or oxidize C₆₀⁺ with superacids have led to its decomposition (8). Indeed, it is the combination of anion nucleophilicity and oxidizing capacity together with acidity that makes superacids corrosive and destructive, and limits many academic and industrial applications. Even the ostensibly nonoxidizing superacid triflic acid (CF₃SO₂H) decomposes C₆₀⁺ (9).

If a superacid could be developed which was oxidant-free and whose conjugate base was significantly less nucleophilic than presently available anions, many desirable protonation reactions might be carried out without decomposition. Here, we report the preparation of a superacid, H(CB₁₁H₆X₆) (X = Cl, Br), that meets these requirements and illustrate its use in stabilizing the previously unobserved HC₆₀⁺ ion. We also show that the oxidizing capacity of superacids can be separately harnessed to the conjugate base (CB₁₁H₆X₆)⁺ to prepare an oxidant capable of producing the C₆₀⁺⁺ cation. C₆₀⁺⁺ has been referred to as the “electrophile par excellence” (I0) because its dominant chemistry is the addition of nucleophiles or electrons (for example, C₆₀⁺⁺ for n = 1 to 6). Thus, the addition of an electrophile or the removal of an electron to form HC₆₀⁺ and C₆₀⁺⁺, respectively, presents a particular challenge for synthetic chemistry and an excellent test for the concept of strict separation of oxidation from acidity and nucleophilicity.

Superacidity can be generated from a non-superacidic Brønsted acid by addition of a strong Lewis acid. A typical example is the addition of SbF₅ to HF to generate the common superacid HSbF₆⁺, properly formulated as [H(FF)₅⁺][nSbF₅–] (4). Here, we exploit the potent Lewis acidity of the silylium ion (R₃Si⁺) to generate superacidity from HCl. Latent silylium ions are found in the silylium ion–like species R₃Si(CB₁₁H₆X₆) (7) where CB₁₁H₆X₆⁻ is the exceptionally inert and weakly nucleophilic anion shown in Fig. 1 (I1). Condensing liquid HCl onto solid (C₂H₅)₃Si(CB₁₁H₆X₆) at low temperature followed by removal of the volatiles under vacuum at room temperature yields the desired acid H(CB₁₁H₆X₆). In essentially quantitative yield (Eq. 1).

(C₂H₅)₃Si(CB₁₁H₆Cl) → H(CB₁₁H₆Cl) + (C₂H₅)₃SiCl (1)

The absence of an AgCl precipitate when the product is dissolved in aqueous AgNO₃ shows that the possible alternative formulation of a R₃Si-solvated proton in [H(RCl)⁺][R₃SiCl]⁻ (I1) cannot be discounted. For X = Br, the acid can be successfully sublimed under vacuum (10⁻⁷ kPa) at 185°C to give a reasonable yield (45%) of white crystalline solid...
of high analytical purity [calculated (experimental) percentages for CH₃Br₂, C: 1.75 (1.94); H, 1.23 (1.14); Br, 18.95 (19.26); Br 76.90 (77.65)]. For an anion with hydric B–H bonds, the carborane shows remarkable resilience toward acid and thermal decomposition. Infrared (IR) spectra (KBr or Nujol mull) show only bands due to the carborane B–H bonds, the carborane shows remarkable resilience toward acid and thermal decomposition. The protonation of C₆₀ is reversible. Exposure of the solution to a base via aerobic moisture or by the addition of Na₂CO₃ returns the spectrum to that of C₆₀. The room-temperature 500-MHz NMR characterization of HC₆₀⁺ indicates fluxional behavior, with the proton “globe-trotting” rapidly over the C₆₀ sphere, presumably via 1,2 shifts. Thus, the ¹³C signal of C₆₀ at 142.85 ppm in ODCB remains a singlet upon addition of H(CB₁¹H₆Cl₆) and moves a mere 0.08 ± 0.01 ppm downfield (Fig. 4). This chemical shift is consistent with time-averaging of the spread of signals expected for a static structure, as observed with RC₆₀⁺ (14). Fluctuation persists down to −70°C. A singlet at 6.6 ppm in the ¹H NMR spectrum is assigned to the C–H resonance of HC₆₀⁺. This sp³-C-H proton is highly deshielded but is not unlike those of the fullerene hydrocarbon H₆C₆₀ (5.9 ppm in toluene) (16). It is −1 ppm downfield of comparable acidic protons in protonated benzene (5.6 ppm) (17). The resonance disappears upon addition of base and is absent in ODCB solutions of H(CB₁¹H₆Cl₆). (The superacid also collapses the resonances of the solvent at 7.2 and 7.4 ppm into a broad asymmetric peak at 7.4 ppm, indicating facile protonation of ODCB.)

Analytically pure samples of solid [HC₆₀]−[CB₁¹H₆Cl₆] can be produced by evaporating the solvent under vacuum. The four IR-active bands of C₆₀ (527 vs, 576 s, 1182 s, 1428 s) change their relative intensities in a manner typical of derivatization (vs, m, m, and m, respectively; see asterisk in Fig. 2C) but the frequencies are unchanged within spectral resolution (1 to 2 cm⁻¹). New weak bands appear at 545, 550, 560, and 612 cm⁻¹ that are also typical of C₆₀ derivatization. For example, in the [2+2] dimer (C₁₂₀₂) (18), weak bands are observed at 545, 551, 560, and 612 cm⁻¹. The proton-decoupled ¹³C MAS NMR spectrum of [HC₆₀][CB₁¹H₆Cl₆] (Fig. 5E) shows that the cation has a static structure in the solid state. A singlet at 56 ppm is assigned to the unique sp³ C atom at the protonated site, a singlet at 182 ppm to the carboxylate carbon, and a cluster of resonances in the 133 to 154 ppm range to the remaining 28 different sites expected from a C₆₀ symmetry structure. The proton attached to the 56 ppm C site must be isolated from other H atoms in the lattice because it can be observed at 6.6 ppm in the ¹H MAS NMR spectrum. Two-dimensional ¹H-¹³C correlation experiments identify the 56 ppm ¹³C resonance with this ¹H resonance. Using ¹H-¹³C cross-polarization experiments with short contact times, the C nuclei closest to this proton can be identified (Fig. 5, A and B). With longer contact times (Fig. 5, C and D), enhancement of the peak at 182 ppm occurs, indicating a 1,4 (rather than 1,2) disposition of the cationic center. A classical carboxylation of C₆₀ symmetry is suggested by these data (Scheme 1).

C₆₀ is very difficult to oxidize to C₆₀⁺⁺ in condensed media [the C₆₀⁺⁺ redox potential is +1.26 V versus ferrocene/ferroccenium in 1,1,2,2-tetrachloroethane (TCE) solution (19) (~1.7 V versus saturated calomel electrode or standard H electrode)].

Scheme 1.

Fig. 1. Structure of the hexahalocarborane anion, CB₁¹H₆X₆⁻ (X = Cl, Br).

Fig. 2. Infrared spectra (KBr disk) of (A) H(CB₁¹H₆Cl₆), (B) [C₆₀H₆⁺][CB₁¹H₆Cl₆]−, (C) [HC₆₀⁺][CB₁¹H₆Cl₆]−, and (D) [HC₆₀⁺⁺][CB₁¹H₆Cl₆]−. For meaning of asterisks, see text.

Fig. 3. Electronic spectra of (A) C₆₀ in ODCB, (B) HC₆₀⁺⁺ in ODCB, (C) (CH₂Cl₂)₅C₆₀ in CH₂Cl₂, and (D) C₆₀⁺⁺ in TCE solution.

Fig. 4. Solution ¹³C NMR spectra of (A) C₆₀ in ODCB, (B) HC₆₀⁺⁺ in ODCB, and (C) C₆₀⁺⁺ in TCE.
The ionization energy of C₆₀ is high because of σ character in the π system, induced by curvature (20). Chemically, electrophilic oxidants such as Br₂ and Cl₂ react with C₆₀ (21), but the products involve addition rather than oxidation because of the nucleophilicity of the halide ions that accompany the oxidizing equivalents. Thus, the characterization of C₆₀⁺⁺ to date has been restricted to the gas phase or to spectroscopy on transients (22). Attempts to prepare and characterize C₆₀⁺⁺ in oxidizing superacid media have met with limited indications of success (8, 9, 23).

The problem of oxidizing C₆₀ to C₆₀⁺⁺ is to find an oxidant that is strong enough (>1.26 V versus Fe/Fe⁺) but that does not bring along a reacting nucleophile. We recently solved this problem for C₆₀⁺⁺, which is ~0.5 V easier to oxidize (24), but the repertoire of practical oxidizing reagents for organic media has been limited to oxidants of ~0.7 V for quite some time (25). A new oxidant based on a triarylammonium radical cation can be prepared from the hexabrominated phenylcarbazole, I (Scheme 2). The bromine substitution pattern in I was established by x-ray crystallography, mass spectrometry, and ¹H and ¹³C NMR spectroscopy. Cyclic voltammetry in CHCl₃/Bu₄N⁺PF₆⁻ shows a reversible anodic wave at 1.34 V versus Fe/Fe⁺. Partnering the stable radical cation of I with the hexachlorocarborane anion CB₆H₅Cl₆⁻ via Cl₁ oxidation in the presence of a silver carborane salt gives the purple-brown reagent [I⁺][CB₆H₅Cl₆⁻] [νmax = 1163 in ODCB; electron paramagnetic resonance (EPR): g = 2.0107, ΔHpp = 40 G in ODCB at 5 K].

Treatment of C₆₀ with a slight molar excess of [I⁺][CB₆H₅Cl₆⁻] in carefully dried TCE or ODCB produces a dark red solution that is stable for several hours. The electronic absorption spectrum (Fig. 3D) shows minor changes in the visible region along with a diagnostic band at 980 nm in the near-IR region. This band has been identified with C₆₀⁺⁺ in low-temperature matrix isolation studies (22, 26). A weaker band appears at 847 nm with a shoulder at ~750 nm. The ¹³C NMR spectrum in TCE is consistent with a radical cation. A broad singlet is observed at 144.2 ppm (linewidth ~340 Hz at half height; Fig. 4C). The downfield shift and broadening relative to C₆₀ (142.83 ppm, linewidth ~21 Hz) are the expected result of paramagnetism in a radical cation. Mixtures of C₆₀ and C₆₀⁺⁺ show peaks of averaged chemical shift and linewidth indicating that intermolecular electron transfer between them is fast on the NMR time scale. The EPR spectrum in frozen ODCB solution (g = 2.002, ΔHpp = 8 G at 5 K) is typical of a delocalized organic radical cation, showing none of the complexity observed with the radical anion, C₆₀⁻ (22). Attempts to isolate pure crystalline salts have led to solids that contain both [C₆₀⁺⁺][CB₆H₅X₆⁻] (g = 2.0022, ΔHpp = 3 G at 105 K) and C₆₀⁺⁺. We hypothesize that concentration of the solution accelerates a bimolecular disproportionation reaction giving C₆₀ and the super-electrophile C₆₀⁺⁺, which is immediately attacked by the solvent, counterion, or errant nucleophiles. This mechanism is well established for the decomposition of radical cations of aromatic hydrocarbons (27). Otherwise, the redox reaction is entirely reversible. Treatment of solutions of [C₆₀⁺⁺][CB₆H₅X₆⁻] with (p-BrC₆H₅)₃N (E = 0.72 V) gives (p-BrC₆H₅)₃N⁺ and C₆₀⁺⁺. The preparation of stable solutions of C₆₀⁺⁺ (~λmax = 770 nm; g = 2.0012, ΔHpp = 4 G in ODCB at 10 K) can be carried out in a similar manner to C₆₀⁺⁺.

There are wider possibilities for the new oxidant and superacid reagents. The superacid H(CB₆H₅X₆⁻) is the rare example of a weigehable reagent for the stoichiometric delivery of exceptionally clean protons to organic solvents at superacidity levels. Previously unobservable primary protonation reactions may now be amenable to study, and reactive cations observed only in solution at subambient temperatures may now be accessible as room temperature–stable salts, suitable for x-ray crystal structure determination (12). Stepwise protonation and purposeful addition of a selected nucleophile should allow easier exploration of acid-catalyzed processes. These reagents should also find applications in mechanistic studies, where dissection of the sequence of protonation, oxidation, and nucleophilic attack is desired. Another mechanistically useful property may be the strict separation of Brunsted and Lewis acidity achieved in H(CB₆H₅X₆⁻). In contrast to many superacids such as HF/SbF₅, H(CB₆H₅X₆⁻) is not a mixture of Brunsted and Lewis acids.

Finally, we note that this chemistry is possible because of the exceptional stability of the icosahedral boron cluster, possibly the most stable cluster in chemistry (11). The three-dimensional σ aromaticity of the CB₆ framework resists disruption to the point that in the absence of good nucleophiles, the exohedral C–H, B–H, and B–X bonds are resistant to acid or oxidative cleavage. This inertness reduces the basicity and nucleophilicity of the anion to less than that of common halocarbon solvents such as ODCB. Superacidity, commonly associated with corrosive viscous liquids (e.g., “magic acid,” HSO₃F/SbF₅), is thereby brought into the realm of standard solution chemistry with understandable properties.

References and Notes
Subducted Seamount Imaged in the Rupture Zone of the 1946 Nankaido Earthquake

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The Nankai Trough is a vigorous subduction zone where large earthquakes have been recorded since the seventh century, with a recurrence time of 100 to 200 years. The 1946 Nankaido earthquake was unusual, with a rupture zone estimated from long-period geodetic data that was more than twice as large as that derived from shorter period seismic data. In the center of this earthquake rupture zone, we used densely deployed ocean bottom seismographs to detect a subducted seamount 13 kilometers thick by 50 kilometers wide at a depth of 10 kilometers. We propose that this seamount might work as a barrier inhibiting brittle seismogenic rupture.

Large subduction zone earthquakes have repeatedly occurred along the Nankai Trough, in southwest Japan, where the Philippine Sea Plate is subducting beneath Japan. Recurrence intervals and areas affected by these earthquakes have been documented since the seventh century (1). According to the historical literature, almost the entire length of the Nankai Trough (500 km) has been ruptured every 100 to 200 years by one or two successive large earthquakes. The most recent events, the 1944 Tonankai and 1946 Nankaido earthquakes, are the best studied of the large Nankai Trough earthquakes (2–5). The seismic data and geodetic data yield two conflicting results concerning the rupture process of the 1946 Nankaido earthquake. The seismic data show a rupture area of 2.5 × 10^4 km^2 with a slip of 5 to 18 m (3), whereas the seismic data show a rupture area of 1 × 10^4 km^2 with a slip of 3 m (4). The area of the fault derived from the seismic data corresponds to the 1-day aftershock area (5), which is located in the eastern half of the fault area determined by the geodetic data.

We performed a high-resolution deep seismic study in the proposed rupture zone (Fig. 1) to investigate the rupture process of the Nankaido earthquake. We used fraction data generated by a large air gun along a profile (Fig. 1) running in the center of the rupture zone (2) at the western edge of the 1-day aftershock area (5). To resolve the seismic velocity structure with high resolution to depths of 10 to 30 km, we deployed 98 ocean bottom seismographs (OBSs) with a spacing of 1.6 km on the 185-km-long profile. This spacing of the OBSs is closer than in conventional seismic refraction surveys by a factor of more than 10. All OBSs were positioned at sea bottom by means of a super short baseline (SSBL) acoustic positioning system.

All observed record sections (Fig. 2) showed first arrivals (P-wave refraction arrivals) throughout the entire profile, except for OBSs deployed in shallow water.