Supplementary Material Available: Analytical and spectral data for **1a–d**, **2a–d**, **3c**, and **4–11** and synthetic procedures for **2c**, **3c**, and **4–8** (4 pages). Ordering information is given on any current masthead page.

Large Protonated Water Clusters $H^+(H_2O)_n$ ($1 \le n >$ 60): The Production and Reactivity of Clathrate-like Structures under Thermal Conditions

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Received April 24, 1989

The nature of gas-phase water clusters has been of long-standing interest, impacting on a number of areas including elucidating transitions from the gas to condensed state, determining the nature of hydrogen bonded liquids and ice, noting the influence of solvation on proton transfer, and studying important problems in the atmospheric sciences, for example. Although the structure and reactivities of small proton hydrates [$H^+\cdot(H_2O)_n$; $n \le 10$] have been well explored[1-3] and large clusters up to $n = 22$ have been observed[4] under atmospheric pressure ionization, there has been little quantitative data to interpret particular features observed in larger clusters.[5,6] The focus of most work on special structures and magic numbers of large protonated water clusters has been based on supersonic beam and sputtering experiments[5-12] that have not been designed to elucidate the actual mechanisms of their production.

Herein, we report the first observation of magic numbers for proton hydrates corresponding to $n = 21$, 24, 26, and 28, produced and studied under thermal conditions, and also present the first information on trends in their reactivity with cluster size. The well-established fast-flow reactor technique,[13] equipped with a "poorman's" SIFT,[14] was used to produce large protonated water clusters containing more than 60 molecules and study their reactions with several molecules including acetonitrile, at well defined temperatures.

Figure 1 is a distribution spectrum of the protonated water clusters taken at $T \approx 120$ K, which clearly demonstrates that (1) a second envelope is formed, emerging with a cluster size about $n = 13$, and (2) a peak maximum appears with $n = 21$ with some weak maxima features at $n = 24$, 26, and 28 (the maxima at $n = 24$ and 26 are present under most but not all conditions). It is important to note that the magic numbers similar to those observed in various beam and sputtering experiments[5-12] do not depend on the source conditions. Although the envelope was shifted, the prominence of the magic numbered clusters did not vary with small changes in temperature and water vapor partial pressure.

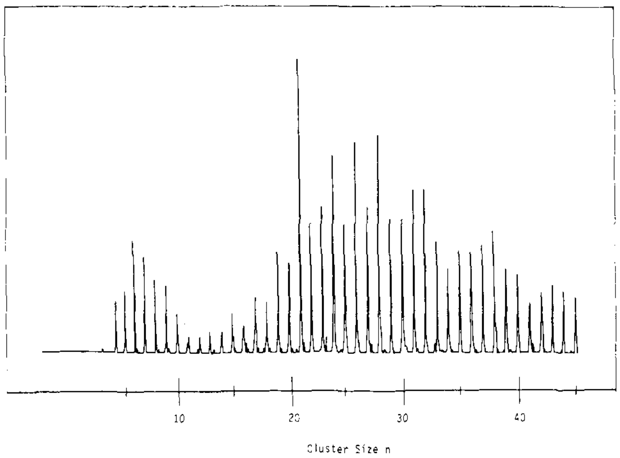

Figure 1. Mass spectrum of protonated water clusters $H^+(H_2O)_n$ (n = 4–45) at 119 K flow tube temperature and 0.3 Torr He.

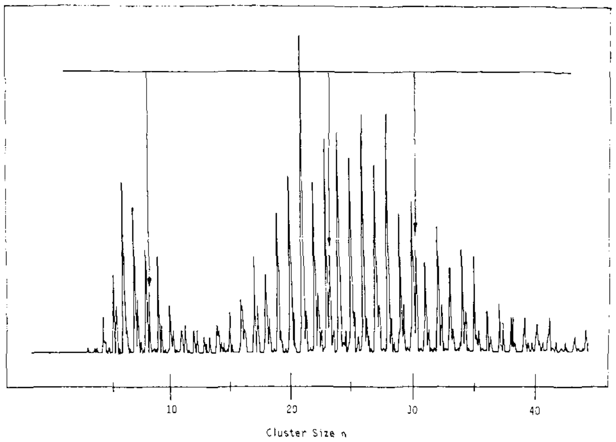

Figure 2. Product distribution of the reactions between protonated water clusters $H^+(H_2O)_n$ (n = 4–45) and acetonitrile at T = 119 K. The arrows point to the association products, e.g., $H^+(H_2O)_6\cdot CH_3CN$, $H^+(H_2O)_{21}\cdot CH_3CN$, and $H^+(H_2O)_{28}\cdot CH_3CN$.

Although small water clusters undergo proton transfer or replacement reactions with molecules that have higher gas-phase proton affinities (PA),[3,15] this possibility becomes less likely at larger sizes, and it can become endoergic at large sizes where solvation affects the relative proton affinities in the cluster complex. As seen in Figure 2, larger clusters simply undergo an association reaction with CH_3CN (PA = 188.4 compared to 166.5 kcal/mol for H_2O)[16] as is evident from the shift in the water cluster spectrum to a nearly identical distribution, but one containing a single attached CH_3CN molecule. The reaction rates at 119 K are very close to the calculated collisional rates obtained by using the Su–Chesnovich method[17] and show a slow decrease proportional to the inverse square root of reduced mass. Most importantly, they do not display any abrupt variations at the cluster sizes corresponding to the magic numbers and no dependence on pressure over the range 0.3–0.5 Torr.

Several important implications of our new findings include the following: (1) the magic number proton hydrates can be produced by association reactions and survive the more than 10^5 collisions with helium during their 20-ms transient in the reactor, (2) simple addition of CH_3CN to these species does not display any abrupt variation with size in the vicinity of magic numbers, and (3) the CH_3CN directly attaches to larger water clusters. This strongly argues against the non-equilibrium growth kinetics being re-

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sponsible for their production and points to the role of ion stability. It has been found in beam studies[18] that upon electron impact ionization, protonated water clusters with slightly more than 21 molecules preferentially fragment to $n = 21$, leading to its net production. In the present work there is little available thermal energy in the collisions at 120 K, which can lead to dissociation. The new findings show that magic numbers arise due to thermodynamic stability of the cluster ions rather than effects due to selective growth kinetics or selective fragmentation. Water clathrates are the most plausible structures proposed to account for the proton hydrate cluster magic numbers.[6,19-21] The proton resides within the network of small clusters, and the smooth trend of reactivity argues against a sudden conformational change[21] at $n = 21$. Hence, the results of this study are consistent with the model proposed by Castleman and co-workers[5,6] that (1) the anomalous cluster involving 21 water molecules with a proton has a very stable clathrate structure with a proton on its surface and (2) other distorted clathrate structures explain those weak features with $n = 24$, 26, and 28.

Acknowledgment. Financial support by the National Science Foundation, Grant No. ATM-87-14095, is gratefully acknowledged. The authors also thank Xin Zhang for her assistance in performing the experiments and Dr. R. G. Keesee for helpful discussions during the course of the experiments.

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Short Synthesis and Structure of a Large Molecular Bowl

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Received April 27, 1989

Molecular mechanics calculations[1] indicate that compound **1**, a network of aryl thioethers that looks unpromising in a planar projection, may adopt any of several low-energy bowl-shaped conformations, such as **1b** and **1c**, which differ only slightly in steric energy. These structures are potential hosts for small nonpolar molecules, and a simple synthesis of such compounds might permit their incorporation into more complex ligands with the ability to bind larger guests. We report here a two-step synthesis of **1** and the molecular structure of its chloroform clathrate.

Treatment of a mixture of 1,3,5-trimercaptobenzene[2] (**2**) and excess 1,3,5-trifluorobenzene in dimethylacetamide with 3 equiv of $NaN(SiMe_3)_2$ (added in portions over 6 h) at 70–100 °C for 48 h gives 1,3,5-tris((3,5-difluorophenyl)thio)benzene[3] (**3**) in 65% yield. Similar treatment of a mixture of **3** and 1,3-dimercaptobenzene at moderate dilution (5 and 15 mM, respectively) in dimethylacetamide with 6 equiv (relative to **3**) of $NaN(SiMe_3)_2$ gives **1** in 1.5% yield[4] after purification by preparative TLC (1:1 CH_2Cl_2–hexanes, $R_f = 0.8$). Compound **1** was easily identified by its first-order 500-MHz ^1H NMR spectrum and a mass spectrum dominated by the singly and doubly charged molecular ions.[5] Since the two sulfur-containing starting materials, 1,3,5-trimercaptobenzene and 1,3-dimercaptobenzene, are most conveniently prepared by heating the appropriate halobenzenes with excess sodium isopropylthiolate followed by reductive removal of the alkyl groups,[2,6] all 18 carbon–sulfur bonds in **1** were pre-

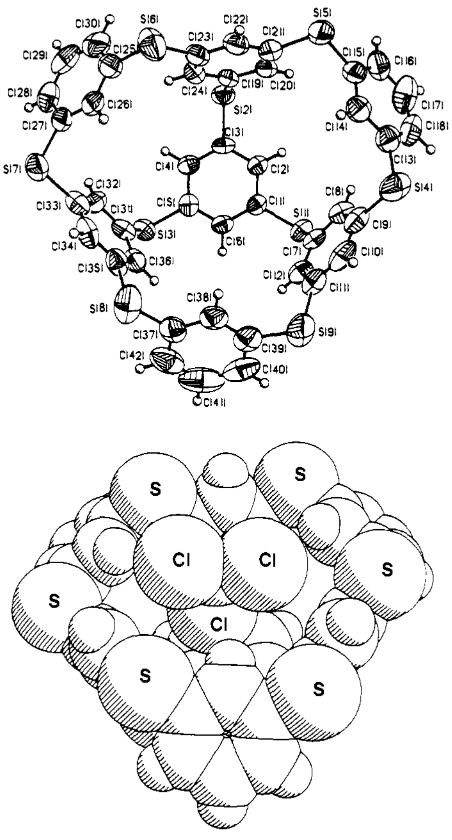
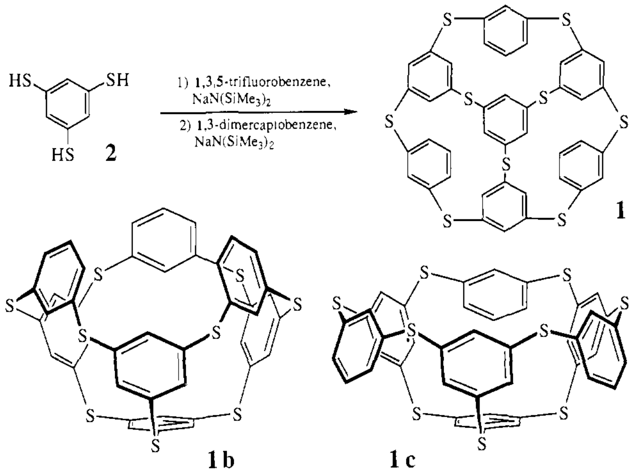


Figure 1. Two views of the molecular structure of compound **1**. In the upper illustration, the chloroform of crystallization is omitted in the interest of clarity.

Scheme I



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(1) MMPI [Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893–3907] was used for the calculations by including ad hoc parameters for aryl thioethers.

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(3) For **3**: mp 102–105 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 6.72 (tt, $J_{HF} = 9$ Hz, $J_{HH} = 2$ Hz, 3 H), 6.80 (m, 6 H), 7.24 (s, 3 H); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 103.3 (t, $J_{CF} = 25$ Hz), 113.4 (d, $J_{CF} = 27$ Hz), 132.7, 137.1, 138.0 (t, $J_{CF} = 10$ Hz), 163.1 (dd, $J_{CF} = 252$, 12 Hz); MS, m/z 510 (M^+, 50%), 398 ($M - C_6H_2F_2$, 26), 366 (26), 332 (13), 252 (28), 220 (100); exact mass 510.0008, calcd for $C_{24}H_{12}F_6S_3$ 510.0005.

(4) Neither prolonged reaction times nor addition of CsCl to the reaction mixture improved the yield of compound **1**.

(5) For **1**: ^1H NMR (500 MHz, CD_2Cl_2) δ 7.00 (d, $J = 2$ Hz, 6 H), 7.27 (t, $J = 2$ Hz, 3 H), 7.478 (t, $J = 8$ Hz, 3 H), 7.481 (t, $J = 2$ Hz, 3 H), 7.51 (s, 3 H), 7.60 (dd, $J = 8$, 2 Hz, 6 H); MS, m/z 816 (M^+, 100%), 408 (M^{2+}, 27%); exact mass 815.9371, calcd for $C_{42}H_{24}S_9$ 815.9364.

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