Title
The structure of the H3O+ hydronium ion in benzene

Permalink
https://escholarship.org/uc/item/30k253n8

Journal
Journal of the American Chemical Society, 127(21)

ISSN
0002-7863

Authors
Stoyanov, ES
Hoffmann, SP
Kim, KC
et al.

Publication Date
2005-06-01

DOI
10.1021/ja050401k

Peer reviewed
The Structure of the H$_3$O$^+$ Hydronium Ion in Benzene

Evgenii S. Stoyanov,*† Stephan P. Hoffmann,§ Kee-Chan Kim,§ Fook S. Tham,§ and Christopher A. Reed*§

Department of Chemistry, University of California, Riverside, California 92521, and Boreskov Institute of Catalysis, Prospekt Lavrentieva, 5, Novosibirsk 630090, Russia

Received January 20, 2005; E-mail: chris.reed@ucr.edu

Writing H$^+$ or H$_{hydr}^+$ frequently suffices for the description of the active protonating species in an acid-catalyzed reaction, reflecting how little attention is paid to the exact nature of strong acids in organic solvents. In O-atom donor solvents, such as ethers, alcohols, and ketones, proton disolvates prevail because of the stability of short, strong, low-barrier (SSLB) H-bonds in linear two-coordinate [solv−H$^+$−solv]$^+$ cations. Much less is known about the ionization of acids in weak donor solvents, such as arenes or halocarbons, and there is the additional problem of the role of trace water. Its ubiquitous presence in organic solvents means that hydronium ions (H$_3$O$^+$, H$_2$O$_2^+$, etc.) are likely candidates for the active protonating agents in many acid-catalyzed reactions.

In this communication, we show how newly developed carborane acids provide insight into the solvation environment of the H$_3$O$^+$ ion in benzene. Carborane acids are chosen because they are the strongest (yet gentlest) pure Brønsted acids presently known, and their large, charge-delocalized conjugate bases allow the isolation of salts whose cations are more discrete than previously accessible.

The very weak attraction of carborane anions to cations minimizes ion pairing, better allowing a cation to reveal its response to the solvent environment.

In benzene, the carborane acid H(CHB$_{11}$Cl$_{11}$)$_3$ protonates water at the 1 equiv level to give relatively concentrated solutions (~10$^{-2}$ M) of the H$_3$O$^+$ ion. Single crystals of a tetrabenzenesolvate [H$_3$O][CHB$_{11}$Cl$_{11}$]•4C$_6$H$_6$, I, are deposited upon standing at 6 °C. A novel feature of the X-ray structure is π-complexation of H$_3$O$^+$ by three of the benzene solvate molecules (Figure 1). Cation/anion interactions, typical of previous structural analyses of H$_3$O$^+$ salts, are absent. The π-interactions of O−H bonds with aromatic acceptors are recognized in H$_2$O solvates$^3$ and in benzenewater gas-phase clusters,$^6$ but the only precedent with H$_3$O$^+$ is an ion-paired structure having a benzyl group as part of an anion.$^7$

The H-atoms of the pyramidal H$_3$O$^+$ ion in I lie inside the C−C bond framework of benzene, but do not point directly at the center of the ring. The O⋯C distances lie in the range of 3.06−3.74 Å. The H⋯C plane normal distances are 2.13, 2.16, and 2.26 Å (black dots in insert a, Figure 1). The vectors of the O−H bonds point somewhat closer to the C−C bonds (black dots in insert b, Figure 1). The DFT-calculated structure of H$_3$O(benzene)$_3$$^*$ shows a nearly C$_{6v}$ symmetry structure with the O−H vectors pointing close to a carbon atom of benzene (red dots in Figure 1 inserts; H ⋯ C = 2.005 Å, ZO−H ⋯ C = 173.3°).

Tribenzene solvation of the H$_3$O$^+$ ion is conceptually related to tritwater solvation in the familiar “Eigen-type” H$_2$O$_2^+$ ion of aqueous acid solution, which was isolated as a discrete carbonate salt some time ago.$^8$ Tribenzene solvation of H$_3$O$^+$ also rationalizes the solubility of a small cation in a nonpolar solvent. It is reminiscent of Ag$^+$ salts which are soluble in arene solvents because of conceptually analogous π-complexation.

† University of California.
§ Boreskov Institute of Catalysis.

Figure 1. X-ray structure of [H$_3$O•3C$_6$H$_6$][CHB$_{11}$Cl$_{11}$]•C$_6$H$_6$, I, showing tribenzene solvation of H$_3$O$^+$. Two lattice benzene solvate molecules sit on symmetry sites so only half of each is contained in the asymmetric unit. ZH−O−H$_{hydr}$ = 105.6° (calcd 112.1°). Insert a: Experimental (black) and calculated (red) positions of the H-atoms normal to the benzene planes. Insert b: Points where the experimental (black) and calculated (red) O−H vectors intersect the benzene planes.
In benzene solution, the IR spectrum of the $H_3O^+$ ion interacts with benzene in a manner related to that of the $K^+$ ion. Arene-rich membrane channels have been implicated in $K^+$ transport, and it is not unreasonable to speculate that arene rings could participate in the biological transport of protons via $\pi$-complexed hydronium ions.

Acknowledgment. This work was supported by NIH Grant GM 23851 and NSF Grant CHE-0095206.

Supporting Information Available: Experimental details of sample preparation, IR spectra, X-ray crystallography, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

References


\( \text{JA050401K} \)