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The Solvated Proton is NOT H_3O^+ !

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ABSTRACT: In a recent article in this *Journal*, Ault stressed the importance of writing organic structures that show the correct predominant ionization form in aqueous solution at the given pH. For example, aqueous carboxylic acids at $\text{pH} > 6$ are predominantly deprotonated (RCOO^- , not RCOOH) and amines at $\text{pH} < 8$ are protonated (RNH_3^+ , not RNH_2) and so forth. Ault also argues in favor of the use of H_3O^+ in place of $\text{H}^+(\text{aq})$. Moore et al., in the same issue of this *Journal*, argue the very opposite: Because the specific polyatomic cation H_3O^+ does NOT actually exist in aqueous solution, it is both simpler and more realistic to use $\text{H}^+(\text{aq})$. There are a number of reasons to agree with Moore et al. and favor the use of $\text{H}^+(\text{aq})$.

KEYWORDS: High School/Introductory Chemistry, First-Year Undergraduate/General, Inorganic Chemistry, Misconceptions/Discrepant Events, Textbooks/Reference Books, Acids/Bases, Amino Acids, Aqueous Solution Chemistry, Bronsted-Lowry Acids/Bases, Carboxylic Acids

In his recent article in this *Journal*, “Telling It Like It Is: Teaching Mechanism in Organic Chemistry”¹ Ault stressed the importance of writing organic structures that show the correct predominant ionization form in aqueous solution at the given pH. I wish to thank him for this; I cannot tell you how many times colleagues and students alike have rolled their eyes when I insist that aqueous carboxylic acids at $\text{pH} > 6$ be written as RCOO^- and not RCOOH , amines at $\text{pH} < 8$ be written as RNH_3^+ and not RNH_2 , and so forth. We might be tempted to write the neutral form because it is easier and also because that is the form that predominates in nonpolar solvent solutions. However, as Ault makes clear in his article, you cannot get the mechanism right if you are starting with the incorrect molecular structure.

It is therefore ironic that in the same issue of this *Journal* that includes Ault’s article, Moore et al. in their “Historical Development of the Hydrogen Ion Concept”² argue AGAINST the use of H_3O^+ in balanced equations. I understand why Ault and so many others adopt this system—they wish to show that H^+ does not simply fall off of a protonated acid, it must be pulled off by a base, and in water that base is often H_2O . However, Ault wrote that “Because the bare proton is not present in a condensed phase... H^+ should not appear in either the balanced equation or the mechanism.” By this reasoning, H_3O^+ should also not be used, because it also “is not present” in aqueous solution.

Moore et al. give an excellent summary of the history of $\text{H}^+(\text{aq})$ nomenclature in the literature. Experimentally supported models for the hydrated proton have specified hydration shells of two waters,³ four waters,⁴ and large clusters of up to 20 waters!^{5,6} There is no experimental evidence supporting the existence of H_3O^+ in aqueous solution.

Another argument to consider is that we do not specify the number of waters in the hydration shell of any other ion, so why should H^+ be treated differently? For $\text{Cu}^{2+}(\text{aq})$, we do not write $\text{CuH}_8\text{O}_4^{2+}$, and for $\text{Co}^{2+}(\text{aq})$, we do not write $\text{CoH}_{12}\text{O}_6^{2+}$, so why should we write H_3O^+ (or H_5O_2^+ , etc.) for $\text{H}^+(\text{aq})$?

Ault and others argue that when an acid ionizes in water, we need to identify a single water molecule as the base, giving the product H_3O^+ . However, Moore et al. point out that the actual base is a cluster containing an indeterminate number of water

molecules. Moore et al. argue, I think quite convincingly, that this protonated water-cluster base should be indicated as $\text{H}^+(\text{aq})$, rather than H_3O^+ . In the acid ionization reaction, then



the H_2O over the arrow, signifying a water cluster, is understood as the base, and $\text{H}^+(\text{aq})$ as the hydrated proton product. This system has the double advantage of being both simpler and truer than the $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ system. Moore et al. argue from experimental, pedagogical, and philosophical perspectives that we should jettison H_3O^+ in favor of $\text{H}^+(\text{aq})$: “the simple unencumbered proton concept used by the early workers retains its practical usefulness... ‘if it works, don’t [try to] fix it!’” Hear, hear!

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REFERENCES

- (1) Ault, A. J. *Chem. Educ.* **2010**, 87 (9), 937–941.
- (2) Moore, C. E.; Jaselskis, B.; Florian, J. J. *Chem. Educ.* **2010**, 87 (9), 922–923.
- (3) *The Hydrogen Bond: Recent Developments and Experiments. II, Structure and Spectroscopy*; Schuster, P.; Zundel, G.; Sandorfy, C., Eds.; North Holland: Amsterdam, 1976; pp 683–766.
- (4) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, 3, 1–19.
- (5) Saykally, R. J.; Blake, G. A. *Science* **1993**, 259, 1570–1575.
- (6) Castleman, A. W.; Wei, S.; Shi, Z. J. *Chem. Phys.* **1991**, 94, 3268–3270.

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