JOURNAL OF CHEMICAL EDUCATION
Article
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Assigning Oxidation States to Organic Compounds via Predictions from X-ray Photoelectron Spectroscopy: A Discussion of Approaches and Recommended Improvements

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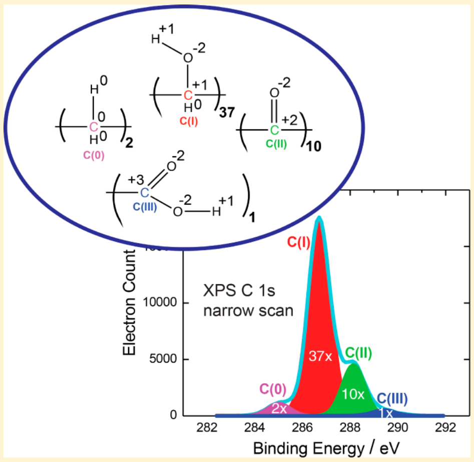
Supporting Information

ABSTRACT: The traditional assignment of oxidation states to organic molecules is problematic. Accordingly, in 1999, Calzaferri proposed a simple and elegant solution that is based on the similar electronegativities of carbon and hydrogen: hydrogen would be assigned an oxidation state of zero when bonded to carbon. Here, we show that X-ray photoelectron spectroscopy, a core electron spectroscopy that is sensitive to oxidation states of elements, generally agrees with his suggestion. We also list the typical (IUPAC) rules for assigning oxidation states, review recent suggestions of Loock and Steinborn that are based on Pauling's earlier approach, discuss the traditional (IUPAC and Pauling–Loock–Steinborn) assignments of oxidation states to organic molecules, review Calzaferri's suggestion, introduce X-ray photoelectron spectroscopy (XPS), show the general agreement of Calzaferri's suggestion with XPS results, provide supporting examples from the literature, and discuss the limitations of Calzaferri's recommendation vis-à-vis XPS results. We conclude by recommending that either (i) Calzaferri's suggestion be implemented into the current IUPAC rules or (ii) the Loock definition be explanded to deal specifically with atoms with similar electronegativities.



KEYWORDS: *First-Year Undergraduate/General, Second-Year Undergraduate, Upper-Division Undergraduate, Analytical Chemistry, Organic Chemistry, Physical Chemistry, Misconceptions/Discrepant Events, Textbooks/Reference Books, Oxidation State*

Oxidation states are almost universally taught in general chemistry. They are a useful bookkeeping tool for recognizing oxidation–reduction (redox) reactions and for identifying the species that are oxidized or reduced in them. Oxidation states are often applied in inorganic chemistry. For example, hydride (H^-), hydrogen (H_2), and the hydrogen ion (H^+) have oxidation states of −1, 0, and +1, respectively, where these numbers correlate and can be viewed as being consistent with the very different chemistries of these three types of hydrogen. A number of articles have been published in this *Journal* on the topic of oxidation states, including discussions of the rules for assigning them.[1−18] Clearly this is a topic with significant impact on chemical educators and students of the discipline. As noted by Steinborn:[11] "The concept of oxidation states is one of the most powerful heuristic concepts in chemistry."

Herein, we first list the traditional (IUPAC) rules for assigning oxidation states. We then note a recent suggestion by Loock to both generalize them and make them more chemically reasonable and acceptable to students, where his recommendation builds on the earlier approach by Pauling. For inorganic species, the IUPAC and Pauling–Loock approaches typically give oxidation states that are in reasonable agreement with observed chemistry. However, when applied to organic molecules, these rules often lead to unusual, and sometimes unchemical, predictions. A few years ago, Calzaferri recognized this problem and made a simple suggestion:[19] because of the similar electronegativities of carbon and hydrogen, hydrogen would be assigned an oxidation state of zero when bonded to carbon. Here, we show that results from X-ray photoelectron spectroscopy, a core electron spectroscopy that is sensitive to oxidation states of elements,[20,21] generally agree with Calzaferri's recommendation. We then provide supporting examples from the literature, discuss some of the limitations of the Calzaferri approach, and end with one of two recommendations to the community, which are to (i) incorporate the Calzaferri suggestion into the IUPAC rules or (ii) consider a modification of Loock's suggestion that encompasses and broadens Calzaferri's recommendation. We favor the latter of these two approaches.

Published: December 31, 2013