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Review

Thermodynamic properties of an emerging chemical disinfectant, peracetic acid

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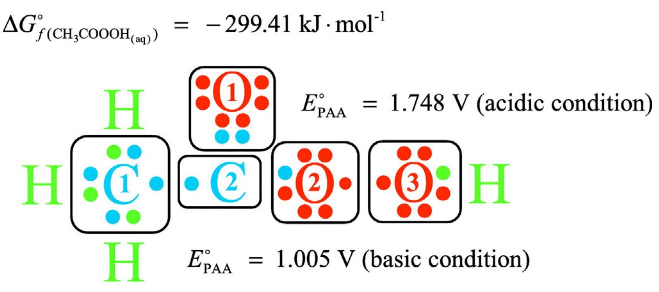
HIGHLIGHTS

- Peracetic acid (PAA or CH_3COOOH) is a promising disinfectant alternative to chlorine.
- This work for the first time summarized the thermodynamic properties of PAA.
- The standard Gibbs energy of formation of $CH_3COOOH_{(aq)}$ is $-299.41\ kJ \cdot mol^{-1}$.
- The standard Gibbs energy of formation of $CH_3COOO^-_{(aq)}$ is $-252.60\ kJ \cdot mol^{-1}$.
- The standard redox potential of PAA is 1.748 V vs. standard hydrogen electrode (pH 0).

GRAPHICAL ABSTRACT



The Lewis Structure of Peracetic Acid (CH_3COOOH)

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ABSTRACT

Peracetic acid (PAA or CH_3COOOH) is an emerging disinfectant with a low potential to form carcinogenic disinfection by-products (DBPs). Basic thermodynamic properties of PAA are, however, absent or inconsistently reported in the literature. This review aimed to summarize important thermodynamic properties of PAA, including standard Gibbs energy of formation and oxidation-reduction (redox) potential. The standard Gibbs energies of formation of $CH_3COOOH_{(aq)}$, $CH_3COOOH_{(g)}$, $CH_3COOOH_{(l)}$, and $CH_3COOO^-_{(aq)}$ are $-299.41\ kJ \cdot mol^{-1}$, $-283.02\ kJ \cdot mol^{-1}$, $-276.10\ kJ \cdot mol^{-1}$, and $-252.60\ kJ \cdot mol^{-1}$, respectively. The standard redox potentials of PAA are 1.748 V and 1.005 V vs. standard hydrogen electrode (SHE) at pH 0 and pH 14, respectively. Under biochemical standard state conditions (pH 7, 25 °C, 101,325 Pa), PAA has a redox potential of 1.385 V vs. SHE, higher than many disinfectants. Finally, the environmental implications of the thermodynamic properties of PAA were systematically discussed. Those properties can be used to predict the physicochemical and biological behavior of aquatic systems exposed to PAA.

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1. Introduction

Peracetic acid (PAA or CH_3COOOH) is a strong and broad-spectrum disinfectant (Chhetri et al., 2016; Kitis, 2004; Moor et al., 2016; Pechacek et al., 2015; Zanetti et al., 2007; Zhang et al., 2016c) with a high oxidation-reduction (redox) potential (Caretti and Lubello, 2003; Klenk et al., 2000). Like chlorine-based disinfectants, PAA shows strong biocidal effects on bacteria such as fecal coliforms, *Escherichia coli*, *Pseudomonas* spp., and *Salmonella* spp. (Veschetti et al., 2003). PAA treatment also exhibits a similar or even higher kill-rate against bacteria than ultraviolet (UV) light irradiation in secondary wastewater effluent (De Sanctis et al., 2016; Di Cesare et al., 2016). Coupled with other treatment options, a sunlight/PAA based advanced oxidation process (AOP) has a higher microbial kill-rate than a sunlight/hydrogen peroxide based AOP in treating secondary wastewater effluent (Formisano et al., 2016). It is worth noting that even though PAA might not absorb in the visible light range, it can generate hydroxyl radical (HO·) under the irradiation of UV light in the sunlight (Caretti and Lubello, 2003). Moreover, PAA disinfection can significantly inhibit bacterial regrowth in wastewater effluent even at very low PAA residual levels (Antonelli et al., 2006).

The strong bactericidal activity of PAA is accompanied with a low potential to form harmful disinfection by-products (DBPs) (Crebelli et al., 2005; Kitis, 2004; Veschetti et al., 2003). PAA for drinking water disinfection only generates a low level of *N*-Nitrosodi-*n*-propylamine out of eight monitored *N*-nitrosamines, whereas free chlorine and especially monochloramine produce a significant amount of *N*-nitrosamines (West et al., 2016). For lake water disinfection, PAA generates fewer clastogenic/aneugenic substances than chlorine dioxide or sodium hypochlorite (Monarca et al., 2003). In addition, no halogenated DBPs were detected other than carboxylic acids in PAA treated surface water (Monarca et al., 2002). Also, no halogenated phenols were formed following PAA disinfection of a secondary wastewater effluent (Dell'Erba et al., 2007). Furthermore, PAA has a low toxicity against aquatic organisms. For instance, the toxicities of PAA, UV light, ozone, and sodium hypochlorite against *Ceriodaphnia silvestrii*, *Daphnia similis*, *Chironomus xanthus*, and *Danio rerio* are in the order of free chlorine > ozone > UV > PAA (da Costa et al., 2014). In light of these findings, PAA is viewed as a promising alternative to chlorine-based disinfectants for water and wastewater disinfection (Guzzella et al., 2004; Monarca et al., 2002; Rossi et al., 2007; Stampi et al., 2002; Wagner et al., 2002).

The United States Environmental Protection Agency (US EPA) first registered PAA as an antimicrobial agent in 1985. Since then, the disinfection process of PAA has been intensively examined (Baldry, 1983; Baldry et al., 1991, 1995; Baldry and French, 1989; Dunkin et al., 2017; Formisano et al., 2016; Gehr et al., 2003; Koivunen and Heinonen-Tanski, 2005; Lefevre et al., 1992; Liu et al., 2016; Mbithi et al., 1990; Rajala-Mustonen et al., 1997; Santoro et al., 2015; Stampi et al., 2001; Veschetti et al., 2003), and scientists have gained a significant understanding of its properties in aquatic environments. However, the basic thermodynamic characteristics of PAA, such as its redox potential, are not well investigated and summarized. As an example, the literature has a large discrepancy in the values of its redox potential (i.e., ranging from 1.06 V to 1.96 V) (Table 1). It is unclear how these values were obtained and whether they are reliable. It is possible that those redox potentials were determined at different pHs so that they have a large difference. At comparable pHs, the potential values should be comparable. Nonetheless, to the best of our knowledge, no literature is dedicated to summarizing the redox potential of PAA and clarifying the large discrepancy in its reported values. Without knowing the exact redox potential of PAA, it is almost impossible to predict the spontaneity of a reaction where PAA is a reactant or product in an aquatic environment. In addition, to correctly predict the equilibrium residual concentration of PAA in water and wastewater disinfection processes, we also need to know its redox potential. Therefore, this review was focused on summarizing the redox potential of PAA as well as its other important thermodynamic properties.

In the following sections, we summarized and reported important thermodynamic quantities of PAA, including Gibbs energy of formation and redox potential. We also discussed the environmental implications of the thermodynamic properties of PAA; for instance, utilizing the redox potential of PAA to predict its antimicrobial activity and DBP formation potential.

Table 1
Redox potential of PAA as reported in the literature.

Redox potential (V)	Reference
1.06	Anderson et al. (1995), Bajpai (2012, 2015), Biermann and Kronis (1997), Brasileiro et al. (2001), Kunigk et al. (2012), Zhao et al. (2007, 2008a)
1.70	Bhasarkar et al. (2015)
1.78	Semenza (2004)
1.80	Coyle et al. (2014), Merenyi et al. (1994)
1.81	Appels et al. (2012), Chaenko et al. (2011), Coyle and Ormsbee (2009), Finnegan et al. (2010), Flores et al. (2016), Ho et al. (2011), Hicks et al. (2015a, b), Hua et al. (2011), Jacks (2004), Joshi et al. (2013), Kornienko et al. (2014), Liu et al. (2014), Mishra and Gamage (2007), Mjalli et al. (2014), Monlau et al. (2013), Pechacek et al. (2015), Preša and Tavčer (2009), Santoro et al. (2015), Tashkhourian et al. (2013), Thi et al. (2015), Tumula et al. (2012), Valtchev et al. (2013), van den Broek et al. (2010), Virkutyte and Varma (2014), Wintner et al. (2005)
1.96	Luukkonen and Pehkonen (2017), Zhao and Hao (2014), Zhao et al. (2014)

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