

# A resurrection of the Haber–Weiss reaction

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 ARISING FROM Zhao et al. *Nature Communications* <https://doi.org/10.1038/s41467-020-20071-w> (2020)

As Elimelech et al.<sup>1</sup> point out, there is a legitimate need for a method that produces singlet dioxygen ( $^1\Delta_g\text{O}_2$ ) efficiently, because this species plays a role in a research fields like environmental science and biochemistry. They<sup>1</sup> describe a flow-through filtration process whereby singlet dioxygen is generated electrochemically. The mechanism proposed by Elimelech et al.<sup>1</sup> for its production is based on the reduction of hydrogen peroxide by superoxide, the infamous Haber–Weiss reaction, and is therefore incorrect. Furthermore, the evidence for formation of singlet dioxygen is questionable.

The mechanism, shown in Fig. 4 of that publication<sup>1</sup>, starts with reduction of  $\text{O}_2$  at the cathode to  $\text{O}_2^{\bullet-}$  and  $\text{H}_2\text{O}_2$ .  $\text{H}_2\text{O}_2$  is, of course, also formed by the spontaneous disproportionation of  $\text{O}_2^{\bullet-}$ . Subsequently,  $^1\Delta_g\text{O}_2$  is proposed to be produced via reaction 1:



This reaction became known as the Haber–Weiss reaction (with  $^1\Delta_g\text{O}_2$  or  $^3\Sigma_g^-\text{O}_2$ ) and was proposed in 1931<sup>2</sup>. It proceeds with a rate constant of at best  $1 \text{ M}^{-1}\text{s}^{-1}$ <sup>3</sup>, and cannot compete<sup>4</sup> with the rapid and spontaneous<sup>5</sup> disproportionation of  $\text{O}_2^{\bullet-}$ .

Elimelech et al. cite my 1976 publication<sup>6</sup> in support for formation of  $^1\Delta_g\text{O}_2$ . Indeed, I wrote that reaction (1) is thermodynamically possible. However, the standard Gibbs energies of formation of  $\text{HO}^\bullet$  and  $\text{O}_2^{\bullet-}$  have been determined more accurately since then<sup>7</sup>, with the result that reaction 1 with  $\text{O}_2$  in the singlet state is thermodynamically not possible<sup>3,8</sup>.

Elimelech et al. report that insignificant amounts of  $\text{HO}^\bullet$  were detected. This should have led them to reject Reaction 1, because for every  $^1\Delta_g\text{O}_2$  also one  $\text{HO}^\bullet$  is formed. Could it be that the terephthalate concentration these authors used to detect  $\text{HO}^\bullet$  was insufficient? If  $^1\Delta_g\text{O}_2$  was detected with micromolar concentrations of furfuryl alcohol, then  $\text{HO}^\bullet$  should also have been seen, given that the rate constants of  $^1\Delta_g\text{O}_2$  and  $\text{HO}^\bullet$  with furfuryl alcohol and terephthalate are similar, that terephthalate was present in millimolar concentrations, and that unlike  $\text{HO}^\bullet$ ,  $^1\Delta_g\text{O}_2$  is quenched in water at a rate of  $2.7 \cdot 10^5 \text{ s}^{-1}$ <sup>9</sup>. Although irrelevant at this stage, the notion that  $\text{HO}^\bullet$  reacts with terephthalate to yield hydroxyterephthalate is incorrect. Instead, an adduct is formed that needs to be oxidised to yield hydroxyterephthalate.

The authors base their conclusion that  $^1\Delta_g\text{O}_2$  is formed also on the reaction of the latter with 2,2,6,6-tetramethylpiperidine, but do not discuss the possibility that this compound may be oxidised at the anode and then yields 2,2,6,6-tetramethyl-4-piperidinol-*N*-oxyl after reaction with  $\text{O}_2$ <sup>10</sup>. Formation of any products from  $^1\Delta_g\text{O}_2$  would have been enhanced in  $\text{D}_2\text{O}$  where  $^1\Delta_g\text{O}_2$  lives much longer, or decreased by addition of a quencher, such as 1,4-diazobicyclo[2.2.2]octane.

Thermodynamically, a simpler route to  $^1\Delta_g\text{O}_2$  could be the oxidation of  $\text{O}_2^{\bullet-}$  to  $^1\Delta_g\text{O}_2$  at the anode, because the electrode potential of the couple  $^1\Delta_g\text{O}_2(\text{aq})/\text{O}_2^{\bullet-}$  is  $+0.81 \text{ V}$ <sup>11</sup>. In contrast, the spontaneous disproportionation of  $\text{O}_2^{\bullet-}$  is not an alternative, as the yield of  $^1\Delta_g\text{O}_2$  varies from not detectable to extremely low, as recently reviewed<sup>8</sup>.

If we assume that is  $^1\Delta_g\text{O}_2$  formed, we may ask: how much? Given the consumption of furfuryl alcohol, the rate constant of the reaction of this compound with  $^1\Delta_g\text{O}_2$ , the quenching rate constant for  $^1\Delta_g\text{O}_2$  in water<sup>9</sup>, and the flow rate, one arrives at a low nanomolar steady-state concentration of  $^1\Delta_g\text{O}_2$ . This calculation also shows that only 1.8% of all  $^1\Delta_g\text{O}_2$  reacts with furfuryl alcohol.

Experimental conditions and nomenclature need to be discussed too. Elimelech et al.<sup>1</sup> use scavengers at a single concentration, with the exception of terephthalate which was used at two concentrations. These experiments do not prove that  $^1\Delta_g\text{O}_2$ ,  $\text{O}_2^{\bullet-}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HO}^\bullet$  are formed, because such a non-dose-dependent approach only gives an indication. The authors refer to these scavengers as specific for a particular species. Since  $\text{HO}^\bullet$  reacts with nearly everything at high rates, such terminology is inappropriate. Indeed,  $\text{N}_3^-$  quenches  $^1\Delta_g\text{O}_2$ , but it also reacts with  $\text{HO}^\bullet$ , as do *p*-benzoquinone and catalase. It would have been beneficial if the authors had consulted the Solution Kinetics Database of the National Institute of Standards and Technology<sup>12</sup> for the relevant rate constants. The description of  $^1\Delta_g\text{O}_2$  as “possessing an empty  $\pi^*$  orbital”<sup>1</sup> is simplistic<sup>13</sup>. When electro-filtration was carried out to remove substances, temperature and pH were not mentioned. The word “quenching” is used as a synonym of “scavenging”, which is incorrect<sup>14</sup>. The term ROS for Reactive Oxygen Species, although widespread, is misleading as neither  $\text{O}_2^{\bullet-}$  nor  $\text{H}_2\text{O}_2$  are reactive, as argued before<sup>15</sup>. A study of the thermodynamics and kinetics of reactions of small, short-lived, oxygen-containing species will illustrate this.

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In summary, it is not impossible that Elimelech et al. produced singlet dioxygen, but certainly not via the oxidation of  $O_2^{\bullet-}$  by  $H_2O_2$ .

Received: 22 March 2021; Accepted: 18 November 2021;

Published online: 19 January 2022

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## Author contributions

This is a paper was conceived and written by a single author.

## Competing interests

The author declares no competing interests.

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