Spectroscopic and Kinetic Characteristics of HO₂ and O₂ Species Studied by Pulse Radiolysis

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The formation and decay of HO₂ and O₂ transients was reinvestigated using oxygenated aqueous t-butanol solutions in the pH range from 1.5 to about 8. The obtained spectroscopic and kinetic characteristics of both superoxide radical forms are: for HO₂, λ \text{max} = 230 nm (ε_{230} = 130 m² mol⁻¹⁻¹), 2k (HO₂ + HO₂) = (3.7 ± 0.2) x 10⁶ dm³ mol⁻¹⁻¹ s⁻¹, and for O₂, λ \text{max} = 245 nm (ε_{245} = 215 m² mol⁻¹⁻¹), 2k (O₂ + O₂) < 10 dm³ mol⁻¹⁻¹ s⁻¹.

The formation and reactivity of both forms of the superoxide radical (HO₂ and O₂) have been a subject of extensive studies in respect to its importance in radiation and physicochemistry [1–8], as well as in biochemistry and biology [9–17]. The reported molar extinction coefficients (ε) of HO₂ and O₂ are showing a large discrepancy. By means of pulse radiolysis and using an aqueous solution containing N₂O and H₂O₂ (pH = 7) a value of ε_{260}(O₂) = 100 m² mol⁻¹ was found, whereas for oxygenated solutions in absence of H₂O₂ (pH = 13) it was ε_{260}(O₂) = 200 m² mol⁻¹ [18]. Other authors reported ε_{260}(O₂) = 87 m² mol⁻¹, which was not corrected for ε_{260}(OH) [2] and ε_{260}(O₂) = 180 m² mol⁻¹ [6], using formate as an OH scavenger. The last authors observed for HO₂, λ \text{max} = 230 nm (ε_{230} = 125 m² mol⁻¹⁻¹) and for O₂, λ \text{max} = 245 nm (ε_{245} = 197 m² mol⁻¹⁻¹). For the equilibrium: HO₂ ↔ O₂ + H⁺ the reported pK-values ranged from 4.45 ± 0.1 [4], 4.5 ± 0.15 [1–3], 4.8 [5] to 4.88 ± 0.1 [6]. The decay constants for both forms of the peroxyde radical were found to be: k (HO₂ + HO₂) = 8.5 x 10⁵ dm³ mol⁻¹⁻¹ s⁻¹ [6] and (8.6 ± 0.6) x 10⁶ dm³ mol⁻¹⁻¹ s⁻¹ [8], whereas for k (O₂ + O₂) < 100 dm³ mol⁻¹⁻¹ s⁻¹ [6] and < 0.35 dm³ mol⁻¹⁻¹ s⁻¹ [8].

The scope of the present study was to reinvestigate the spectroscopic and kinetic characteristics of both species (HO₂ and O₂) by pulse radiolysis of oxygenated aqueous solutions (1.42 x 10⁵ mol · dm⁻³ O₂), containing 10⁻² mol · dm⁻³ t-butanol as an OH scavenger (k (OH + t-C₄H₉OH) = 5.5 x 10⁸ dm³ mol⁻¹⁻¹ s⁻¹ [19]) in the pH-range from 1.5 to about 8.

The pulse radiolysis facility* (3 MeV Van de Graaff accelerator) and the performance of the dosimetry have been previously described [20, 21]. The analysing light source (XBO 450 Watt Xenon lamp “Osram”) provides an up to 70-fold increase of the light intensity in the u. v. region by flashing. By means of a minicomputer (PDP-11/10, DEC) the stored data were reduced in number and transferred to another computer (PDP-10, DEC) on which the data collection program was run. The traces, normalized for dose, were averaged in order to improve the signal to noise ratio. The applied dose per 1 μs electron pulse was varied from 6 to 15 J · kg⁻¹ (0.6 to 1.5 krad). The solutions were prepared with R. G. chemicals (E. Merck) using at least four times distilled water.

In the oxygenated acid aqueous solutions of 10⁻² mol · dm⁻³ t-butanol (pH = 1.5 – 2) the following reactions are taking place:

H₂O → e_aq (2.7), H (0.6), OH (2.8), H₂ (0.45),
H₂O₂ (0.74), H₂O (2.7)** (1)
e_aq + H⁺ → H (k₂ = 2.3 x 10⁴ dm³ mol⁻¹⁻¹ s⁻¹ [22]), (2)
H + O₂ → HO₂ (k₃ = 2 x 10⁶ dm³ mol⁻¹⁻¹ s⁻¹ [23]), (3)
H + t-C₄H₉OH → t-C₄H₉OH (k₄ = 1.2 x 10⁵ dm³ mol⁻¹⁻¹ s⁻¹ [23]), (4)
OH + t-C₄H₉OH → t-C₄H₉OH + H₂O (k₅ = 5.5 x 10⁸ dm³ mol⁻¹⁻¹ s⁻¹ [19]), (5)
H₂O₂ + HO₂ → H₂O + O₂ (2k₆ to be determined). (6)

Under these conditions the obtained total absorption spectrum represents the absorption of HO₂, H₂O₂ and t-C₄H₉OH species. Hence it was corrected for matrix (subtraction of the absorption of the last

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** The G-values (number of species formed per 100 eV absorbed energy) of the primary products are given in parantheses.

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two species, obtained by pulse radiolysis of deoxygenated \( 10^{-2}\text{ mol} \cdot \text{dm}^{-3} \) \( \text{t-C}_6\text{H}_5\text{OH} \) solution, taking also into account the contribution of \( \text{t-C}_6\text{H}_5\text{OH} \) radicals produced by H-atoms. The resulting absorption spectrum for \( \text{HO}_2 \) is shown in Figure 1. The obtained absorption maximum, \( \lambda_{\text{max}} = 230 \text{ nm} \) and \( \varepsilon_{230} = 130 \text{ m}^2 \text{ mol}^{-1} \cdot \text{cm}^{-1} \), agree very well with one of the earlier reported data [6].

The formation of \( \text{O}_3^2 \) species was studied in the pH range of 7.5 to 8.3, using oxygenated \( 10^{-2} \) \( \text{t-bu-} \)

tanol solutions. In this case some additional reactions run of, namely:

\[
e_{\text{aq}} + \text{O}_2 \rightarrow \text{O}_3^2 \quad (k_7 = 1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) [22],
\]

\[
\text{O}_3^2 + \text{O}_2 \rightarrow \text{O}_3^2^- + \text{O}_2 \quad (2k_8 \text{ to be determined}).
\]

The absorption spectrum of \( \text{O}_3^2 \) species obtained after matrix-correction is presented likewise in Figure 1. A maximum at \( \lambda = 245 \text{ nm} \) with \( \varepsilon_{245} = 215 \text{ m}^2 \text{ mol}^{-1} \) as a spectroscopic characteristics of \( \text{O}_3^2 \) were obtained. These data are in fair agreement with previous ones [6].

The mean values of the determined rate constants for the decay of both forms of the superoxide radical are: \( 2k_6 (\text{HO}_2 + \text{HO}_2) = (3.7 \pm 0.2) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) and \( 2k_8 (\text{O}_3^2 + \text{O}_3^2) < 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \).

Although \( \text{t-C}_6\text{H}_5\text{OH} \) radicals are known to be rather unreactive, their reactivity with the \( \text{HO}_2 \) and \( \text{O}_3^2 \) transients cannot be excluded completely. Hence, the obtained rate constants \( (k_6 \text{ to } k_8) \) are somewhat higher.

The dissociation constant of \( \text{HO}_2^- \), \( pK = 4.8 \pm 0.05 \) was determined by plotting OD/cm-values at 260 nm as a function of pH (Fig. 1, insert). The obtained pK-value is in full agreement with an earlier reported one [5].

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