Spectroscopic and Kinetic Characteristics of $H\dot{O}_2$ and $\dot{O}_2^-$ Species Studied by Pulse Radiolysis

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The formation and decay of $H\dot{O}_2$ and $\dot{O}_2^-$ 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 $H\dot{O}_2$ $\lambda_{max} = 230$ nm ($\varepsilon_{230} = 130$ m^2 mol^{-1}), $2k\,(H\dot{O}_2 + H\dot{O}_2) = (3.7 \pm 0.2) \times 10^6$ dm^3 mol^{-1} s^{-1}, and for $\dot{O}_2^-$ $\lambda_{max} = 245$ nm ($\varepsilon_{245} = 215$ m^2 mol^{-1}), $2k\,(\dot{O}_2^- + \dot{O}_2^-) < 10$ dm^3 mol^{-1} s^{-1}.

The formation and reactivity of both forms of the superoxide radical ($H\dot{O}_2$ and $\dot{O}_2^-$) have been a subject of extensive studies in respect to its importance in radiation and physico chemistry [1–8], as well as in biochemistry and biology [9–17]. The reported molar extinction coefficients (ε) of $H\dot{O}_2$ and $\dot{O}_2^-$ are showing a large discrepancy. By means of pulse radiolysis and using an aqueous solution containing N_2O and H_2O_2 (pH = 7) a value of $\varepsilon_{260}(\dot{O}_2^-) = 100$ m^2 mol^{-1} was found, whereas for oxygenated solutions in absence of H_2O_2 (pH = 13) it was $\varepsilon_{260}(\dot{O}_2^-) = 200$ m^2 mol^{-1} [18]. Other authors reported $\varepsilon_{260}(\dot{O}_2^-) = 87$ m^2 mol^{-1}, which was not corrected for $\varepsilon_{260}(\dot{O}H)$ [2] and $\varepsilon_{260}(\dot{O}_2^-) = 180$ m^2 mol^{-1} [6], using formate as an $\dot{O}H$ scavenger. The last authors observed for $H\dot{O}_2$ $\lambda_{max} = 230$ nm ($\varepsilon_{230} = 125$ m^2 mol^{-1}) and for $\dot{O}_2^-$ $\lambda_{max} = 245$ nm ($\varepsilon_{245} = 197$ m^2 mol^{-1}). For the equilibrium: $H\dot{O}_2 \rightleftharpoons \dot{O}_2^- + H^+$ 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: $k\,(H\dot{O}_2 + H\dot{O}_2) = 8.5 \times 10^7$ dm^3 mol^{-1} s^{-1} [6] and $(8.6 \pm 0.6) \times 10^5$ dm^3 mol^{-1} s^{-1} [8], whereas for $k\,(\dot{O}_2^- + \dot{O}_2^-) < 100$ dm^3 mol^{-1} s^{-1} [6] and < 0.35 dm^3 mol^{-1} s^{-1} [8].

The scope of the present study was to reinvestigate the spectroscopic and kinetic characteristics of both species (HO_2 and O_2^-) by pulse radiolysis of oxygenated aqueous solutions (1.42×10^3 mol · dm^{-3} O_2), containing 10^{-2} mol · dm^{-3} t-butanol as an $\dot{O}H$ scavenger ($k\,(\dot{O}H + \text{t-}C_4H_9OH) = 5.5 \times 10^8$ dm^3 mol^{-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:

$$H_2O \rightsquigarrow e^-_{aq}\,(2.7),\; H\,(0.6),\; \dot{O}H\,(2.8),\; H_2\,(0.45),\; H_2O_2\,(0.74),\; H^+_{aq}\,(2.7)^{**} \qquad (1)$$

$$e^-_{aq} + H^+_{aq} \rightarrow H \qquad (k_2 = 2.3 \times 10^{10}\ \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}\ [22]), \qquad (2)$$

$$H + O_2 \rightarrow H\dot{O}_2 \qquad (k_3 = 2 \times 10^{10}\ \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}\ [23]), \qquad (3)$$

$$H + \text{t-}C_4H_9OH \rightarrow \text{t-}\dot{C}_4H_8OH \qquad (k_4 = 1.2 \times 10^5\ \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}\ [23]), \qquad (4)$$

$$OH + \text{t-}C_4H_9OH \rightarrow \text{t-}\dot{C}_4H_8OH + H_2O) \qquad (k_5 = 5.5 \times 10^8\ \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}\ [19]), \qquad (5)$$

$$H\dot{O}_2 + H\dot{O}_2 \rightarrow H_2O_2 + O_2 \qquad (2k_6\ \text{to be determined}). \qquad (6)$$

Under these conditions the obtained total absorption spectrum represents the absorption of $H\dot{O}_2$, H_2O_2 and t-$\dot{C}_4H_8OH$ 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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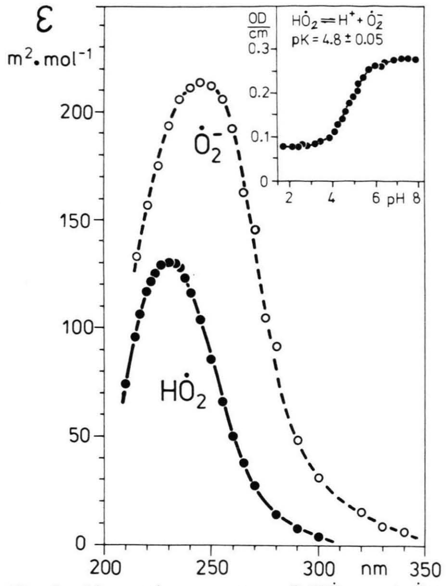

Fig. 1. Absorption spectra of $H\dot{O}_2$ and $\dot{O}_2^-$ radicals produced by pulse radiolysis of oxygenated aqueous solutions. *Insert:* OD/cm at 260 nm as a function of pH-value of the solution.

two species, obtained by pulse radiolysis of deoxygenated 10^{-2} mol · dm^{-3} t-C_4H_9OH solution, taking also into account the contribution of t-$\dot{C}_4H_8OH$ radicals produced by H-atoms). The resulting absorption spectrum for $H\dot{O}_2$ is shown in Figure 1. The obtained absorption maximum, $\lambda_{\max} = 230$ nm and $\varepsilon_{230} = 130$ m^2 mol^{-1}, agree very well with one of the earlier reported data [6].

The formation of $\dot{O}_2^-$ species was studied in the pH range of 7.5 to 8.3, using oxygenated 10^{-2} t-butanol solutions. In this case some additional reactions run of, namely:

$$e_{aq}^- + O_2 \rightarrow \dot{O}_2^- \qquad (k_7 = 1.9 \times 10^{10}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [22], \quad (7)$$

$$\dot{O}_2^- + \dot{O}_2^- \rightarrow O_2^{2-} + O_2 \quad (2k_8 \text{ to be determined}). \quad (8)$$

The absorption spectrum of $\dot{O}_2^-$ species obtained after matrix-correction is presented likewise in Figure 1. A maximum of $\lambda = 245$ nm with $\varepsilon_{245} = 215$ m^2 mol^{-1} as a spectroscopic characteristics of $\dot{O}_2^-$ 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: $2k_6\,(H\dot{O}_2 + H\dot{O}_2) = (3.7 \pm 0.2) \times 10^6$ dm^3 mol^{-1} s^{-1} and $2k_8\,(\dot{O}_2^- + \dot{O}_2^-) < 10$ dm^3 mol^{-1} s^{-1}. Although t-$\dot{C}_4H_8OH$ radicals are known to be rather unreactive, their reactivity with the $H\dot{O}_2$ and $\dot{O}_2^-$ transients cannot be excluded completely. Hence, the obtained rate constants (k_6 to k_8) are somewhat higher.

The dissociation constant of $H\dot{O}_2$, pK = 4.8 ± 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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[1] G. Czapski and B. H. J. Bielski, J. Phys. Chem. **67,** 2180 (1963).
[2] G. Czapski and L. M. Dorfman, J. Phys. Chem. **68,** 1169 (1964).
[3] J. Rabani, W. A. Mulac, and M. S. Matheson, J. Phys. Chem. **69,** 53 (1965).
[4] K. Sehested, O. L. Rasmussen, and H. Fricke, J. Phys. Chem. **72,** 626 (1968).
[5] J. Rabani and S. O. Nielson, J. Phys. Chem. **73,** 3736 (1969).
[6] D. Behar, G. Czapski, J. Rabani, L. M. Dorfman, and H. A. Schwarz, J. Phys. Chem. **74,** 3209 (1970).
[7] B. H. J. Bielski and H. W. Richter, J. Amer. Chem. Soc. **99,** 3019 (1977).
[8] J. Weinstein and B. H. J. Bielski, J. Amer. Chem. Soc. **101,** 58 (1979).
[9] W. Bors, M. Saran, E. Lengfelder, R. Spöttl, and C. Michel, Curr. Top. Radiat. Res. Quat. **9,** 247 (1974).
[10] I. Fridorich, Ann. Rev. Biochem. **44,** 147 (1975).
[11] J. S. Klebanoff, Semin. Hematol. **12,** 117 (1975).
[12] M. B. Babior, J. T. Curnutte, and B. J. Murrich, J. Clin. Invest. **58,** 989 (1976).
[13] F. Lavelle, M. E. McAdam, E. M. Filden, P. B. Roberts, K. Puget, and A. M. Michelson, Biochem. J. **161,** 3 (1977).
[14] M. E. McAdam, F. Lavelle, R. A. Fox, and E. M. Fielden, Biochem. J. **165,** 71; 81 (1977).
[15] D. Ross, Trends Biochem. Sci. **2,** 61 (1977).
[16] W. Bors, M. Saran, E. Lengfelder, C. Michel, C. Fuchs, and C. Frenzel, Photochem. Photobiol. **28,** 629 (1978).
[17] A. Samuni, A. Kalkstein, and G. Czapski, Radiat. Res. **82,** 65 (1980).
[18] J. Rabani, Advan. Radiat. Chem. Ser. **81,** 131 (1968).
[19] M. Gohn and N. Getoff, J. Chem. Soc., Faraday Trans. I **73,** 1207 (1977).
[20] N. Getoff and F. Schwörer, Radiat. Res. **41,** 1 (1970).
[21] N. Getoff and F. Schwörer, Int. J. Radiat. Phys. Chem. **5,** 101 (1973).
[22] M. Anbar, M. Bambenek, and A. B. Ross, Natl. Stand. Ref. Data Ser. (U.S. Nat. Bur. Stand.) No. 43 (1973).
[23] M. Anbar, Farhataziz, and A. B. Ross, Natl. Stand. Ref. Data Ser. (U.S. Nat. Bur. Stand.) No. 51 (1975).