Spectroscopic and Kinetic Characteristics of HO_2 and O_2^- Species Studied by Pulse Radiolysis

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The formation and decay of HO_2 and 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 HO_2 $\lambda_{\text{max}} = 230 \text{ nm}$ ($\epsilon_{230} = 130 \text{ m}^2 \text{ mol}^{-1}$), $2k(\text{HO}_2 + \text{HO}_2) = (3.7 \pm 0.2) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and for O_2^- $\lambda_{\text{max}} = 245 \text{ nm}$ ($\epsilon_{245} = 215 \text{ m}^2 \text{ mol}^{-1}$), $2k(\text{O}_2^- + \text{O}_2^-) < 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The formation and reactivity of both forms of the superoxide radical (HO_2 and 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 HO_2 and 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 $\epsilon_{260}(\text{O}_2^-) = 100 \text{ m}^2 \text{ mol}^{-1}$ was found, whereas for oxygenated solutions in absence of H_2O_2 (pH = 13) it was $\epsilon_{260}(\text{O}_2^-) = 200 \text{ m}^2 \text{ mol}^{-1}$ [18]. Other authors reported $\epsilon_{260}(\text{O}_2^-) = 87 \text{ m}^2 \text{ mol}^{-1}$, which was not corrected for $\epsilon_{260}(\text{OH})$ [2] and $\epsilon_{260}(\text{O}_2^-) = 180 \text{ m}^2 \text{ mol}^{-1}$ [6], using formate as an OH scavenger. The last authors observed for HO_2 $\lambda_{\text{max}} = 230 \text{ nm}$ ($\epsilon_{230} = 125 \text{ m}^2 \text{ mol}^{-1}$) and for O_2^- $\lambda_{\text{max}} = 245 \text{ nm}$ ($\epsilon_{245} = 197 \text{ m}^2 \text{ mol}^{-1}$). For the equilibrium: $\text{HO}_2 \rightleftharpoons \text{O}_2^- + \text{H}^+$ 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 peroxy radical were found to be: $k(\text{HO}_2 + \text{HO}_2) = 8.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [6] and $(8.6 \pm 0.6) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [8], whereas for $k(\text{O}_2^- + \text{O}_2^-) < 100 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [6] and $< 0.35 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [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 ($1.42 \times 10^3 \text{ mol} \cdot \text{dm}^{-3}$ O_2), containing $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ t-butanol as an OH scavenger ($k(\text{OH} + \text{t-C}_4\text{H}_9\text{OH}) = 5.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [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 $15 \text{ J} \cdot \text{kg}^{-1}$ (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 $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ t-butanol (pH = 1.5–2) the following reactions are taking place:

Under these conditions the obtained total absorption spectrum represents the absorption of HO_2 , H_2O_2 and $\text{t-C}_4\text{H}_8\text{OH}$ 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 HO_2 and 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 $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ t- $\text{C}_4\text{H}_9\text{OH}$ solution, taking also into account the contribution of t- $\text{C}_4\text{H}_8\text{OH}$ radicals produced by H-atoms). The resulting absorption spectrum for HO_2 is shown in Figure 1. The obtained absorption maximum, $\lambda_{\text{max}} = 230 \text{ nm}$ and $\varepsilon_{230} = 130 \text{ m}^2 \text{ mol}^{-1}$, agree very well with one of the earlier reported data [6].

The formation of O_2^- species was studied in the pH range of 7.5 to 8.3, using oxygenated 10^{-2} t-bu-

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

The absorption spectrum of O_2^- species obtained after matrix-correction is presented likewise in Figure 1. A maximum of $\lambda = 245 \text{ nm}$ with $\varepsilon_{245} = 215 \text{ m}^2 \text{ mol}^{-1}$ as a spectroscopic characteristics of 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: $2k_6(\text{HO}_2 + \text{HO}_2) = (3.7 \pm 0.2) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $2k_8(\text{O}_2^- + \text{O}_2^-) < 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Although t- $\text{C}_4\text{H}_8\text{OH}$ radicals are known to be rather unreactive, their reactivity with the HO_2 and O_2^- transients cannot be excluded completely. Hence, the obtained rate constants (k_6 to k_8) are somewhat higher.

The dissociation constant of HO_2 , $\text{pK} = 4.8 \pm 0.05$ 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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- [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. Fridovich, *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. Fildes, 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. Fildes, *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).