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The reduction of I_2 by 1-hydroxyalkyl radicals in aqueous solution. A pulse radiolysis study

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Abstract

The one electron reduction of iodine by various 1-hydroyalkyl radicals in aqueous solution is described, which leads first to the formation of I_2^- , and to I^- at longer times. Rate constants of 5×10^9 , 6.5×10^9 , or 8×10^9 dm³ mol⁻¹ s⁻¹ were obtained for the reaction between iodine and the radical of methanol, ethanol or 2-propanol, respectively. © 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

During the past several years, the interest in cells for harvesting solar energy has increased considerably. In aqueous solutions or organic solvents, the redox couple iodine/iodide is a favorable system in photo-electrochemical solar cells (PEC) [1]. An example would be the dye sensitized nanostructured TiO_2 PEC, where conversion efficiencies of more than 10% are observed [2–4]. A solar energy to electrical power conversion as efficient as this is only observed for a PEC containing the iodine/iodide redox couple.

Considerable effort, therefore, has been spent to understand the redox reactions in the iodine/iodide

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system [5,6] and the fundamental iodide equilibria [7,8]. Basic radiation chemistry experiments show that hydrogen atoms effectively reduce iodine with a high rate constant of 3.5×10^{10} dm³ mol⁻¹ s⁻¹ [9]. Furthermore, we report in the present Letter on the one electron reduction of iodine by 1-hydroxyalkyl radicals in aqueous solution utilizing pulse radiolysis. The reduction of iodine leads to the formation of I₂⁻ and demonstrates that 1-hydroxyalkyl radicals also have the power to reduce iodine with high rate constants.

2. Experimental

The pulse radiolysis apparatus [10] and the computer software [11] of the 4 MeV van de Graaff accelerator facility ELBENA at the Hahn–Meitner-Institut were described previously. The duration of the electron pulses was 50 ns [12]. The optical signals were derived from the average of 10

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individual experiments. The optical absorption was calculated by dividing the absorptivity (A) by the concentration of the radicals (c) generated in a pulse and by the length of the optical cell (l = 1.5)cm), and thus was expressed in units of molar absorptivity (ε). The absorbed dose per pulse was calibrated by using $\varepsilon = 1.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for the e_{aq}^{-} absorption at 700 nm [13]. The yield of electrons in water at pH 7 was taken to be 2.6 species per 100 eV of absorbed energy (0.269 μ mol J⁻¹) [14]. The software for the simulation of kinetic data was described elsewhere [15]. The solutions were prepared daily using triply distilled water and were deaerated with argon. All experiments were performed at room temperature, i.e., at around 22 °C.

3. Results and discussion

Aqueous solutions containing iodine and an alcohol, i.e., methanol, ethanol or 2-propanol, are irradiated. In a solution at pH 2 and purged with argon, hydrated electrons produced during the radiolysis of water are converted into hydrogen atoms according to

$$e_{\rm aq}^- + {\rm H}^+ \Rightarrow {\rm H}^- \quad k = 2.3 \times 10^{10} \ {\rm dm}^3 \ {\rm mol}^{-1} \ {\rm s}^{-1}$$
(1)

hydrogen atoms and hydroxyl radicals subsequently react with the alcohol (RH) to form 1hydroxyalkyl radicals (R[•])

$$\mathbf{H}^{\cdot} + \mathbf{R}\mathbf{H} \Rightarrow \mathbf{R}^{\cdot} + \mathbf{H}_2 \tag{2}$$

$$OH + RH \Rightarrow R' + H_2O \tag{3}$$

where RH is methanol, ethanol or 2-propanol, and R[•] is •CH₂OH, CH₃•CHOH or (CH₃)₂•COH, and $k_2 = 1.1 \times 10^6$, 1.8×10^7 or 5.3×10^7 dm³ mol⁻¹ s⁻¹, and, $k_3 = 9.0 \times 10^8$, 2.2×10^9 or 2.0×10^9 dm³ mol⁻¹ s⁻¹, respectively [14,16,17]. Thus, the main products of the water radiolysis are converted into 1-hydroxyalkyl radicals.

Optical absorption vs. time curves at 725 nm are depicted in Fig. 1 for solutions containing either methanol or two different concentrations of 2propanol. During the pulse, the absorption of hydrated electrons appears as a short spike as a



Fig. 1. Absorption vs. time curves at 725 nm for aqueous solutions of 5×10^{-5} mol dm⁻³ I₂ at pH 2 and containing 1×10^{-3} mol dm⁻³ 2-PrOH (curve a), 0.2 mol dm⁻³ 2-PrOH (curve b), or 2.4 mol dm⁻³ MeOH (curve c). Solutions were purged with Ar. Dose per pulse corresponds to 1.2×10^{-6} mol dm⁻³ of e_{aa}^{-} .

result of reaction (1). This is followed by the buildup of an absorption ascribed to I_2^- which exhibits absorption bands at 725 and 385 nm [13]. After the absorption of the hydrated electron vanishes, the I_2^- can be expected to be the only absorbing species at this wavelength. The absorption vs. time curves for two different concentrations of 2-propanol concentrations are also shown in Fig. 1. At first glance, it may be surprising that the build-up of the absorption is faster the lower the alcohol concentration. This can be attributed to the competition between the alcohol, reaction (2), and the iodine for hydrogen atoms according to

The 1-hydroxyalkyl radical, in turn, reacts with iodine according to

$$\mathbf{R}^{\cdot} + \mathbf{I}_2 \Rightarrow \mathbf{I}_2^- + \mathbf{X} + \mathbf{H}^+, \tag{5}$$

where X is an oxidation product of the alcohol radical: formaldehyde, acetaldehyde, or acetone, for methanol, ethanol, or 2-propanol, respectively. At low alcohol concentration, both reducing species, H^{\cdot} and R^{\cdot}, participate in the reduction of iodine, while at high alcohol concentration most of the hydrogen atoms are scavenged by the alcohol, and the 1-hydroxyalkyl radical is practically the only reducing agent. The reaction between hydrogen atoms and iodine, reaction (4), seems to be faster than the one between 2-propanol radicals and iodine, reaction (5). Similar results were obtained for solutions containing methanol or ethanol.

Fig. 2 shows the spectra at various times after the impingement of the irradiation pulse. After the pulse the I_2^- absorption at 725 and 385 nm can be observed. As this absorption decreases, another band at around 230 nm grows in intensity and a bleaching at 480 nm occurs. The 230 nm band is ascribed to the I⁻ ion [7], while the bleaching is due to the consumption of iodine.

The transient absorption curves were analyzed using computer simulation for a reaction mechanism which, in addition to reactions (1)–(5), also consists of the following reactions

$$\mathbf{R}^{\cdot} + \mathbf{R}^{\cdot} \Rightarrow \text{prod}$$
 (6)

$$H^{\cdot} + H^{\cdot} \Rightarrow H_2$$

 $2k = 1.55 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (7)

$$I_{2}^{-} + I_{2}^{-} \Rightarrow I_{3}^{-} + I^{-}$$

2k = 4.6 × 10⁹ dm³ mol⁻¹ s⁻¹ (8)

$$I + I^{-} \iff I_{2}^{-}$$

$$k_{f} = 8.8 \times 10^{9} \text{ dm}^{3} \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_{h} = 7 \times 10^{4} \text{ s}^{-1}$$
(9)



Fig. 2. Spectra of a solution containing 5×10^{-5} mol dm⁻³ I₂ and 1×10^{-3} mol dm⁻³ 2-PrOH at 3 µs (solid line), 10 µs (dotted line), and 50 µs (dashed line) after irradiation. Solution at pH 2 was purged with Ar. Dose per pulse corresponds to 1.2×10^{-6} mol dm⁻³ of e_{aa}^{-3} .

$$I_2 + I^- \iff I_3^-$$

$$k_f = 5.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_b = 7.5 \times 10^6 \text{ s}^{-1}$$
(10)

$$I + I \Rightarrow I_2$$
 $2k = 3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (11)

The rate constants for the recombination of the alcohol radicals are: $k_6 = 2.4 \times 10^9$, 1.5×10^9 or 1.1×10^9 dm³ mol⁻¹ s⁻¹ for methanol, ethanol, or 2-propanol, respectively [16]. The computer simulation of this reaction mechanism can be carried out unambiguously, since, with the exception of the unknown rate constant of reaction (5), all other rate constants and the molar absorption coefficients are well known [9,14,16-18]. Fig. 3 depicts the experimental trace of the I⁻ absorption at 230 nm as well as the simulated curves for the overall absorption and for the contributions of I^- , I_2^- and I_3^- . The reaction of the 1-hydroxyalkyl radical with iodine results in the formation of I_2^- ions, which only contribute to the overall absorption during the initial phase. Also included in Fig. 3 are the overall absorption curves for a lower and a higher value for k_5 in order to show the extend to which the overall absorption depends on this reaction.



Fig. 3. Absorption vs. time curve at 230 nm for an aqueous solution of 5×10^{-5} mol dm⁻³ I₂ and 1×10^{-3} mol dm⁻³ 2-PrOH at pH 2 (thin solid line). Solution was purged with Ar. Dose per pulse corresponds to 1.1×10^{-6} mol dm⁻³ of e_{aq}^- . The result of the computer simulation (thick solid line) and the contributions of I⁻ (thick dashed line), I₂⁻ (thick dotted line), and I₃⁻ (dash-dotted line) are also shown for $k_5 = 8 \times 10^9$ dm³ mol⁻¹ s⁻¹. The results of computer simulation using 50% and 200% of k_5 are also included (thin dashed lines). Computer simulation used $\varepsilon(I^-) = 12000$ dm³ mol⁻¹ cm⁻¹, $\varepsilon(I_2^-) = 3800$ dm³ mol⁻¹ cm⁻¹ and $\varepsilon(I_3^-) = 5000$ dm³ mol⁻¹ cm⁻¹.

The simulation also indicates that at the end of the measurement I^- is the main product while the contributions of I_2^- or I_3^- are almost negligible. This is also demonstrated in Fig. 2 where at longer times there is no absorption of I_2^- or I_3^- , the latter with its characteristic absorption bands at 280 nm and 350 nm [7]. The lack of I_2^- and I_3^- indicates that equilibria (9) and (10) have shifted to the left.

From the computer simulation of the kinetic curves at 725 nm and 230 nm, rate constants for the reaction between iodine and the radical of methanol, ethanol or 2-propanol were obtained to be 5×10^9 , 6.5×10^9 , or 8×10^9 dm³ mol⁻¹ s⁻¹, respectively.

4. Conclusions

The extremely high rate constants for the reactions of some 1-hydroxyalkyl radicals with iodine show that they are diffusion controlled. These values are higher the larger the reduction potential of the 1-hydroxyalkyl radicals, -1.18, -1.25, or -1.39 V for radicals from methanol, ethanol, or 2-propanol, respectively. It can be concluded that the efficiency with which an electron is transferred from the 1-hydroxyalkyl radical to iodine is determined by the reducing power of the radical.

Photo-generated holes in nanostructured crystalline titanium dioxide can be reduced efficiently by organic solvents [19,20]. As demonstrated above, alcohol radicals can reduce iodine and can therefore influence the stability of the iodide/iodine system.

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