



Calculated and measured transient product yields in pulse radiolysis of aqueous solutions: Concentration dependence

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ABSTRACT

Pulse radiolysis of aqueous solutions was modeled by using 54 equations for the reaction of water radiolysis intermediates with carefully selected rate coefficients. Yields of products formed in the hydrated electron+solute and hydroxyl radical+solute reactions were calculated and compared with the measured yields in wide concentration range. These reactions are in competition with the reactions of the water radiolysis intermediates with each other and with H_2O , H^+ and H_2O_2 . An empirical equation was developed for the calculation of scavenged product yields that can be used in cases when due to low rate coefficient, low solubility or very high absorbance, low solute concentrations are applied and a considerable fraction of the water radiolysis intermediates does not react with the solute.

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1. Introduction

It is generally accepted that applying a short pulse of electrons to pure water after 10^{-7} s the spur processes are over and the three reactive intermediates, hydrated electron, hydrogen atom, hydroxyl radical and the products hydrogen peroxide and molecular hydrogen are distributed in the solution practically homogeneously. Their yields are taken as: $G(e_{\text{aq}}^-)=0.27 \mu\text{mol J}^{-1}$, $G(\text{H}^\bullet)=0.07 \mu\text{mol J}^{-1}$, $G(\text{OH}^\bullet)=0.27 \mu\text{mol J}^{-1}$, $G(\text{H}_2\text{O}_2)=0.07 \mu\text{mol J}^{-1}$ and $G(\text{H}_2)=0.047 \mu\text{mol J}^{-1}$. When the reaction of a given intermediate with the S solute is studied generally appropriately high solute concentration is used to ensure practically complete scavenging of the investigated intermediate. This appropriate concentration is actually determined by the product of the rate coefficient (k) and the solute concentration ($[\text{S}]$). This quantity is called scavenging capacity: Scavenging capacity= $k[\text{S}]$.

With appropriately selected concentration the yield of transients formed from the solute is practically equal to the yield of the water radiolysis intermediates. In this case, for instance, for the hydrated electron reaction, we can say: $G(e_{\text{aq}}^-)=G(\text{S}^-)$. The G -value is used for the calculation of the molar absorption coefficient, which is often needed for the identification of the absorption spectra and for the calculation of the second order rate coefficient (Swallow, 1982; Buxton 1982, 1987, 2004). (When very high solute concentration is used the scavenging reaction competes with the spur processes. For such cases the scavenged

yield is proportional to the square root of the concentration (Schuler et al., 1981).)

With a k rate coefficient in the diffusion controlled range, $\sim 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, and with $10^{-3} \text{ mol dm}^{-3}$ solute concentration ($[\text{S}]$) the scavenging is close to completion (scavenging capacity, $k[\text{S}] \approx 10^7 \text{ s}^{-1}$). In practice, however, the scavenging capacities are often much smaller than 10^7 s^{-1} , due to, for instance, low reactivity (low k) or to low solubility (low $[\text{S}]$). Low solute concentrations should also be used in the case of molecules with very strong absorbance in the near UV-visible region (low light transparency). As an example we mention the organic dyes that have molar absorption coefficients up to $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ in the visible range. The spectra of these molecules strongly overlap with those of the transient products. So there is a decrease in absorbance due to the depletion (negative Δ absorbance) and an increase in absorbance (positive Δ absorbance) due to the transients. The net result may be either positive or negative. In the literature there are techniques to calculate the absorption spectra under these conditions (Sharma et al., 2002, 2003). Recently we developed a simple equation for this purpose (Wojnárovits et al., 2005; Wojnárovits and Takács, 2008); the equation contains the yield of water radiolysis intermediate (e_{aq}^- , H^\bullet or OH^\bullet) scavenged by the solute.

When scavenging capacity is much smaller than 10^7 s^{-1} , the water radiolysis intermediate+solute reaction is not complete and a considerable fraction (at lower solute concentrations may be the major fraction) of the water radiolysis intermediates is lost in their reactions with each other or in their reaction with H_2O , H^+ and H_2O_2 .

In this short publication we analyze these reactions, develop a simple empirical formula for the calculation of the scavenged

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fraction in the 10^{-3} – 10^{-6} mol dm $^{-3}$ concentration range and compare the calculated values with the experimental results.

2. Experimental

2.1. Chemicals and experimental setup

Thiocyanate (99%) and p-cresol (98%) were obtained from Sigma-Aldrich, and diethyl fumarate (98%) from Fluka, and they were used as received.

The transient intermediates were studied by pulse radiolysis. The setup is working with 800 ns pulses of 4 MeV electrons. The changes in the absorbance were followed with UV–vis kinetic spectrophotometry in 2 cm cells (Földiák et al., 1988). The dose/pulse values were generally between 5 and 30 Gy determined by thiocyanate dosimeter.

Deoxygenating of solutions was carried out by bubbling with appropriate gases for 25 min before irradiation and the bubbling was continued during the experiments.

2.2. Model used in calculations

There are numerous kinetic calculations on the complex reactions taking place in water radiolysis (e.g. Joseph et al., 2008; Ershov and Gordeev, 2008). These calculations are often connected to the practical application of water as a reactor coolant. Our calculations are based on carefully selected rate coefficients of 50 reactions collected in Table 1 ((R1)–(R50)). We show also in the table the reactions of water radiolysis intermediates with N $_2$ O, nitrous oxide applied to convert e_{aq}^- to \cdot OH in reaction (R51) followed by (R42). The (R53) reaction of tert-butanol eliminates the \cdot OH radical reactions in N $_2$ or Ar saturated solutions (Swallow, 1982). The reaction of H $^+$ atom with tert-butanol (R54) has a low weight due to the low rate coefficient.

In numerical integrations we used the KINTECUS program package (Ianni, 2003), which is based on the Bader–Deuflhard algorithm. This technique in case of a large number of reactions is faster than the often applied Cash–Karp Runge–Kutta method. In sensitivity analysis calculations we modified the rate coefficients by 10% and determined which of the reactions influence basically the final result.

3. Model calculations

3.1. pH dependence of intermediate yields at 10^{-7} s

As a first step we calculated the concentrations of e_{aq}^- , H $^+$, \cdot OH, O $^-$, HO $_2^-$ intermediates and that of the product H $_2$ O $_2$ at 10^{-7} s in pure deoxygenated water based on the G-values as shown before (Fig. 1). Our results in the low pH region slightly differ from the results published in the literature (Draganic et al., 1969): at the low pH edge a slight increase in the e_{aq}^- +H $^+$ yield was observed. It was explained by the different diffusivities of e_{aq}^- and H $^+$ (Buxton, 2004). The analysis reported here is based on measurements in the medium pH range.

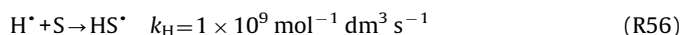
At 10^{-7} s most of the protolytic equilibria are already established. The concentration of e_{aq}^- , at a constant dose/pulse value, is constant in the pH range 5–10. At pH < 5, however, the e_{aq}^- concentration decreases with decrease in pH and that of the \cdot H atom increases due to H/ e_{aq}^- conversion in (R11). At pH > 13 the yield of e_{aq}^- increases due to H $^+$ +OH $^-$ reaction (R19). The latter reaction has a relatively low rate coefficient, 2.5×10^7 mol $^{-1}$ dm 3 s $^{-1}$, and becomes an important reaction at high OH $^-$ concentration only. The \cdot OH concentration clearly

reflects the \cdot OH/O $^-$ conversion (reaction (R41)) with pK $_a$ of 11.9 and the H $_2$ O $_2$ concentration reflects the H $_2$ O $_2$ /HO $_2^-$ conversion (reaction (R44)) with pK $_a$ of 11.6 (Buxton, 2004; Joseph et al., 2008).

According to the sensitivity analysis in pure water only 10–20 reactions out of 50 influence considerably the intermediate concentrations in neutral solutions. Hydrated electron concentration strongly depends on the self-reaction (R1). Reactions (R2), (R3) and (R5), the e_{aq}^- reactions with H $^+$, \cdot OH and H $_2$ O $_2$ contribute less significantly to the decay. The hydrogen atom concentration is influenced mostly by the H $^+$ atom reaction with hydrated electron (R2), with another hydrogen atom (R12) and to a smaller extent by the reaction with hydroxyl radical (R13). In the case of the hydroxyl radical the self-reaction (R20) and the reaction with hydrated electron (R3) have special importance.

3.2. Reactions of hydrated electron

The model calculations were carried out on 5 v/v% tert-butanol containing solutions. We chose dose/pulse values of 1, 10 and 100 Gy. For the rate coefficient of the solute with the hydrogen atom (R56) we applied 1×10^9 mol $^{-1}$ dm 3 s $^{-1}$.



With dose/pulse of 1–100 Gy the hydrated electron concentration at 10^{-7} s is in the 10^{-5} – 10^{-7} mol dm $^{-3}$ range. In Fig. 2a with the continuous line we show the scavenged fraction (SF), as a function of the logarithm of scavenging capacity (s^{-1}) divided by the dose (Gy) ($k[S]/D$). The numerical calculations were started at 10^{-9} s and continued until a nearly complete disappearance of the intermediate. When we plot the scavenged fraction values as a function of $\log(k[S]/D)$ the calculated points for D 1, 10 and 100 Gy determine practically the same S-type curve. According to our calculations also, as expected, at high scavenging capacities, $k[S] = 10^7$ s $^{-1}$ (e.g. when $k \approx 1 \times 10^{10}$ mol $^{-1}$ dm 3 s $^{-1}$ and $[S] \approx 10^{-3}$ mol dm $^{-3}$) practically all hydrated electrons that escape spur react with the solute. With 10 Gy/pulse dose at 10^{-6} mol dm $^{-3}$ solute concentration only 10% of the e_{aq}^- disappears in reaction with S. Reaction (R55) competes mainly with the diffusion controlled (R1), (R2) and (R3) reactions. When $k = 1 + 10^{10}$ mol $^{-1}$ dm 3 s $^{-1}$, in order to obtain SF=0.5, $[S] = 3.4 \times 10^{-6}$, 3.4×10^{-5} and 3.4×10^{-4} mol dm $^{-3}$ is needed at 1, 10 and 100 Gy dose/pulse, respectively.

The solute concentration obviously influences also the rate of product formation: the formation rate decreases with decrease in concentration. This may cause some problem, e.g. the molar absorption coefficient should be calculated based on longer time elapsed between the pulse and observation. At longer timescale in practical systems the decay of S $^-$ may also be not negligible.

In pulse radiolysis measurements the rate coefficient of the e_{aq}^- +S reaction is usually determined by assuming pseudo-first order conditions. At low solute concentrations there are some problems with this approach. There is a considerable depletion, transformation of S to S $^-$. On the other hand, e_{aq}^- decays not in a single reaction, i.e. in reaction with the solute, but reacting with several species disappears in complex reaction system. Therefore, a simple pseudo-first-order fit to hydrated electron decay in the pulse radiolysis curve may give false result. We have to mention, however, that according to our model calculations, under the usual condition the problem associated with the complex reaction system causes only a few percent uncertainty in the rate coefficient.

The calculations discussed are based on $k_H = 1 \times 10^9$ mol $^{-1}$ dm 3 s $^{-1}$ rate coefficient for hydrogen atom reaction with S (R56).

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