Conductometric Pulse Radiolysis Study on the Reaction of the Solvated Electron with 5-Bromouracil in Aqueous Solutions at Different pH Values

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Conductometric pulse radiolysis, 5-bromouracil

To study the reaction of the solvated electron with 5-bromouracil an aqueous solution has been examined by conductometric pulse radiolysis at pH values between 4.68 and 8.74. Alcohol was added to scavenge the hydrogen atom and the hydroxyl radical. G(Br⁻) = (2.64 ± 0.08)/100 eV was found to be independent of the pH. The mobility of the bromouracil mono-anion was measured to be (2.7 ± 0.2) 10⁻⁴ cm² V⁻¹ s⁻¹ at 20 °C, and the rate constant of reaction (3b) was determined to be k(H⁺ + BrUr⁻) = (2.3 ± 0.2) 10⁹¹ mole⁻¹ s⁻¹*

We have re-examined the reaction of solvated electrons with 5-bromouracil by means of conductometric pulse radiolysis¹ in the pH range 4.68 to 8.74. By taking into account that an aqueous solution of bromouracil acts as a buffer, the analysis of the data leads to the conclusion that all solvated electrons react quantitatively with bromouracil to yield bromide ions.

The initial species produced on irradiation of water are: H₂O → H⁺ + e⁻ + OH⁻ + non ionic species (1). A solvated electron reduces bromouracil to the uracil radical and the bromide anion:

\[ \text{H₂O} \rightarrow \text{H}⁺ + \text{e}⁻ + \text{OH}⁻ + \text{non ionic species} (1) \]

\[ \text{e}⁻ + \text{BrUr} \rightarrow \text{H}⁺ + \text{Br}⁻ \quad (2) \]

Bromouracil is a weak acid (pKₐ ≈ 7.83 at 24 °C and pKₐ ≈ 13°C). WEMPEN and FOX³ have shown that the 5-bromouracil mono-anion is best represented by a mixture of 1 and 2 in the ratio 1:2.

The protons produced by the pulse react by the reverse reaction (3b) because of the buffer effect at pH values greater than five.

The experiments were carried out with a 2.8 MeV van de Graaff accelerator with a pulse duration of 1 μs. All solutions were de-aerated and either methanol, or ethanol, or tert-butanol was added to scavenge at least 98% of the hydroxyl radicals and the uracil radicals. The hydrogen atoms were scavenged 88% with 1 m methanol, 98% with 0.7 m ethanol at a substrate concentration of 10⁻³ M and 31% with 0.2 m tert-butanol at a substrate concentration of 2 · 10⁻³ M (k(H⁺ + BrUr⁻) = 2.2 · 10⁹¹ mole⁻¹ s⁻¹*). The alcohol radicals do not lead to a permanent conductivity with bromouracil as was indicated by an experiment with 10⁻³ M of bromouracil and 0.5 M of methanol saturated with N₂O. The alcohol radicals themselves do not lead to ionic species in the pH range studied, because their pKₐ values are all much higher: 10.7 (Methanol radical), 11.6 (ethanol radical), and 12.2 (iso-propanol radical)*. We would like to mention that the properties of the solvent water are changed on addition of alcohols. The dissociation constants² as well as the

* Note added in proof: In a recent paper G(Br⁻) = 2.8±100 eV has been reported in agreement with our results (K. BHATIA and R. H. SCHULER, J. physic. Chem. 77, 1888 [1973]).

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conductivity\textsuperscript{7,8} are affected. The volume percentage of alcohols in our experiments was between 2 and 4\%, and the mole fraction of water was of the order of 0.01. Since we measured a decrease in conductivity of 4\% for a 8.0 \cdot 10^{-3} \text{ mol} solution of HClO\textsubscript{4}, when methanol (0.9 \text{ m}) was added, the mobilities therefore decrease by the same amount. The extent of hydrolysis over several hours was of the order 0.5\%. The relative error in each measurement is estimated to be ± 10\%. All errors given are standard Gaussian deviations.

The experimental data and the results are summarized in Table I and Fig. 1\textsuperscript{a}.

The permanent change in conductivity $\Delta \kappa$ in D\textsuperscript{1} cm\textsuperscript{-1} after the pulse is caused by changes in concentrations:

$$\Delta \kappa = F \left( \Delta [\text{H}^+] \mu_{\text{H}^+} + \Delta [\text{Br}^{-}] \mu_{\text{Br}^{-}} + \Delta [\text{BrUr}^{-}] \mu_{\text{BrUr}^{-}} + \Delta [\text{OH}^-] \mu_{\text{OH}^-} \right). \quad (4)$$

($F$ = Faraday constant, $\mu$ = mobility in cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}, concentration in moles per liter). The mobilities of the proton and the bromide were taken from the literature\textsuperscript{9} and used without corrections, and that of the bromouracil anion was determined in alkaline solutions by measuring the conductivity: $(2.7 \pm 0.2) \cdot 10^{4}$ cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} at 20 \degree C.

At pH 4.68 the last two terms are negligible, so that the change in conductivity (Fig. 1a), which was observed up to 2 ms to be constant, can be analysed as hydrobromic acid $[\text{H}^+] = [\text{Br}^-] = [\text{HBr}]$:

$$\Delta \kappa = F \Delta [\text{Br}^{-}] (\mu_{\text{H}^+} + \mu_{\text{Br}^-}). \quad (4a)$$

The $G$-values for $G(\text{Br}^-)$ given in Table I agree with a quantitative reaction via (2). With ethanol 98\% of the hydrogen atoms were scavenged. $G(\text{Br}^-)$ in this case was the same as in experiments in which the hydrogen atoms were not quantitatively scavenged. Therefore we conclude that the hydrogen atoms do not liberate bromide ions. This was also found recently by Adams and Wilson\textsuperscript{10}. Single pulse experiments with subsequent analysis of bromide by a bromide selective electrode gave $G(\text{Br}^-) = (2.7 \pm 0.1)/100$ eV in agreement with the result from the pulse conductivity method.

At pH 8.74 the simplification of Eqn (4) is also straightforward. The terms with $\Delta [\text{H}^+]$ and $\Delta [\text{OH}^-]$ are considered to be zero, because of the buffer effect. The permanent change in the conductivity signal therefore results in the substitution of the bromouracil anion by the bromide anion:

$$\Delta [\text{Br}^-] = -\Delta [\text{BrUr}^{-}],$$

and it follows

$$\Delta \kappa = F \Delta [\text{Br}^-] (\mu_{\text{Br}^-} - \mu_{\text{BrUr}^{-}}). \quad (4b)$$

At neutral pH about 11\% of the substrate is ionized. If the absolute concentration of the organic anion is at least five times higher than the concen-

Table I. Experimental data and calculated concentrations of 5-bromouracil anion in aqueous solutions at different pH values.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Alcohol added</th>
<th>pH</th>
<th>Additive</th>
<th>BrUr\textsuperscript{a}</th>
<th>BrUr\textsuperscript{b}</th>
<th>%\textsuperscript{b} ionized</th>
<th>$G(\text{Br}^-)$\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[mole l\textsuperscript{-1}]</td>
<td></td>
<td>[mole l\textsuperscript{-1}]</td>
<td>exper.</td>
<td>calcd.</td>
<td>[mole l\textsuperscript{-1}]</td>
<td>exper.</td>
</tr>
<tr>
<td>1a.</td>
<td>0.5 MeOH</td>
<td>4.68</td>
<td></td>
<td>2.0 \cdot 10\textsuperscript{-3}</td>
<td>HClO\textsubscript{4}</td>
<td>10\textsuperscript{-3}</td>
<td>7.08 \cdot 10\textsuperscript{-7}</td>
</tr>
<tr>
<td></td>
<td>1.0 MeOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.66 \pm 0.10\textsuperscript{g}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.7 EtOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.59 \pm 0.15\textsuperscript{g}</td>
<td></td>
</tr>
<tr>
<td>1b.</td>
<td>0.2 tert-BuOH</td>
<td>5.78</td>
<td></td>
<td>2.0 \cdot 10\textsuperscript{-4}</td>
<td>NaOH</td>
<td>2 \cdot 10\textsuperscript{-4}</td>
<td>1.77 \cdot 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>1c.</td>
<td>0.2 tert-BuOH</td>
<td>6.92</td>
<td></td>
<td>2.0 \cdot 10\textsuperscript{-5}</td>
<td>NaOH</td>
<td>2 \cdot 10\textsuperscript{-4}</td>
<td>2.18 \cdot 10\textsuperscript{-5}</td>
</tr>
<tr>
<td>1d.</td>
<td>0.2 tert-BuOH</td>
<td>8.74</td>
<td></td>
<td>1.8 \cdot 10\textsuperscript{4}</td>
<td>NaOH</td>
<td>2 \cdot 10\textsuperscript{-4}</td>
<td>1.78 \cdot 10\textsuperscript{-4}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Total concentration BrUr = Co.
\textsuperscript{b} Caled. from Eqn. (6).
\textsuperscript{c} Measured within a dose range from 5 \cdot 10\textsuperscript{-5} to 2 \cdot 10\textsuperscript{17} eV g\textsuperscript{-1}.
\textsuperscript{d} pH = -log[HClO\textsubscript{4}].
\textsuperscript{e} Caled. by interactive solution of cubic Eqn.: [H\textsuperscript{+}]\textsuperscript{3} + K\textsubscript{a}[H\textsuperscript{+}]\textsuperscript{2} - (K\textsubscript{w} + K\textsubscript{a} \cdot Co)[H\textsuperscript{+}] - K\textsubscript{a} \cdot K\textsubscript{w} = 0. K\textsubscript{w} = ion product of water.
\textsuperscript{f} Caled. from Eqn. (6) with [BrUr\textsuperscript{-}] = [Na\textsuperscript{+}].
\textsuperscript{g} 3\% of the electrons are scavenged by protons.
\textsuperscript{h} See text.

\textsuperscript{*} Fig. 1 see Table on pp. 88 a, b.
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tration of the protons produced by the pulse, a solution of bromouracil even at this pH should act as a buffer and Eqn (4 b) should hold. This was indeed the case: \( G(\text{Br}^-) = (2.64 \pm 0.05)/100 \text{ eV} \).

At pH 5.78 the buffer capacity of the solution still is effective, but not quantitatively. For evaluation of the permanent conductivity signal at this pH only the term with \( \Delta[\text{OH}^-] \) can be neglected. All other terms have to be calculated explicitly. However for electroneutrality the following Equation holds:

\[
\Delta[\text{H}^+] = \Delta[\text{Br}^-] - \Delta[\text{BrUr}^-]. \tag{5}
\]

Assuming a \( G \)-value of \( G(\text{H}^+) = G(\text{Br}^-) = 2.65/100 \text{ eV} \) \( \Delta[\text{BrUr}^-] \) can be calculated from Eqn (6):

\[
\frac{[\text{BrUr}^-]}{C_0} = \frac{1}{1 + 10^{(pK_a - p\text{H})}} \tag{6}
\]

\( C_0 = \) total concentration of bromouracil). Considering that 5% of the electrons are scavenged by protons the calculated change equalled the experimental change in conductivity verifying the assumption.

Kinetic evaluation of the decay curve shown in Fig. 1c gives the rate constant for the overall reverse reaction (3b). After subtracting the net conductivity change caused by the substitution of the organic anion by the bromide ion the curve was treated assuming first order kinetics. The overall rate constant for reaction (3b) was calculated to be

\[
k_{\text{H}^+ \text{BrUr}^-} = (2.3 \pm 0.2) \times 10^{10} \text{ mol}^{-1} \text{s}^{-1}
\]

at an ionic strength 2.3 \( \times 10^{-3} \) mole l\(^{-1}\). The plot \( \ln(\Delta \kappa - \Delta \kappa_r) \) vs time was a straight line over four half lives with a least square deviation of 1%. From this we conclude though there are other ionic reactions

\[
\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \\
\text{BrUr} + \text{OH}^- \rightarrow \text{BrUr}^- + \text{H}_2\text{O} \tag{7}
\]

that reaction (3b) is predominant in this time interval.

We would like to express our appreciation to Fritz Schwörer, who was responsible for setting-up the van de Graaff accelerator.

3 I. Wempen and J. J. Fox, J. Amer. chem. Soc. 86, 2474 [1964].
5 B. O. Wagner, unpublished result.

8 G. Kortüm and A. Weller, Z. Naturforsch. 5a, 590 [1950].

Fig. 1a. \(10^{-3}\) mole l\(^{-1}\) 5-bromouracil, 0.5 mole l\(^{-1}\) methanol, time scale above 5 \(\mu\)s/cm, below 2 \(\mu\)s/cm dose \(1.25 \times 10^{17}\) eV g\(^{-1}\) (pH = 4.68).

Fig. 1b. \(2 \times 10^{-4}\) mole l\(^{-1}\) 5-bromouracil, 0.2 mole l\(^{-1}\) tert-butanol, time scale above 5 \(\mu\)s/cm, below 2 \(\mu\)s/cm dose \(9.17 \times 10^{16}\) eV g\(^{-1}\) (pH = 5.78).

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Fig. 1c. $2 \times 10^{-4}$ mole l$^{-1}$ 5-bromouracil, 0.2 mole l$^{-1}$ tert-butanol, time scale above 2 $\mu$s/cm, below 1 $\mu$s/cm
dose $1.02 \times 10^{17}$ eV g$^{-1}$ (pH = 6.92).

Fig. 1d. $2 \times 10^{-4}$ mole l$^{-1}$ 5-bromouracil, 0.2 mole l$^{-1}$ tert-butanol, time scale above 5 $\mu$s/cm, below 2 $\mu$s/cm
dose $1.12 \times 10^{17}$ eV g$^{-1}$ (pH = 8.74).