Direct optical observation of the formation of some aliphatic alcohol radicals. A pulse radiolysis study

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Abstract. The kinetics of the reactions of hydroxyl radicals and hydrogen atoms with some aliphatic alcohols in aqueous solutions were studied using pulse radiolysis. Based on the increase in optical absorption in the UV region, the rate constants for the reaction of hydroxyl radicals and hydrogen atoms with methanol, ethanol, 2-propanol or *t*-butyl alcohol were determined to be $9 \cdot 0 \times 10^8$, $2 \cdot 2 \times 10^9$, $2 \cdot 0 \times 10^9$, 62×10^8 and $1 \cdot 1 \times 10^6$, $1 \cdot 8 \times 10^7$, $5 \cdot 3 \times 10^7$, $2 \cdot 3 \times 10^5$ $dm^3 \, mol^{-1} \, s^{-1}$ respectively. The bimolecular decay rate constants for the alcohol radicals produced in methanol and ethanol were evaluated to be $2 \cdot 4 \times 10^9$ and $1 \cdot 5 \times 10^9$ $dm^3 \, mol^{-1} \, s^{-1}$. The values observed are in fairly good agreement with those reported earlier.

Keywords. Aliphatic alcohols; hydroxyl radical; hydrogen atom; rate constant; UV absorption.

1. Introduction

In aqueous solution, ionizing radiation generates hydrogen atoms and hydroxyl radicals along with other highly reactive species. Alcohols are used as scavengers for hydroxyl radicals and hydrogen atoms in order to simplify the redox system. Alternatively, the reaction of the subsequently formed secondary alcohol radicals with a variety of substrates can be investigated. The rate constants for the reaction of hydroxyl radicals with methanol, ethanol, 2-propanol and *t*-butyl alcohol were determined earlier by interpreting the kinetics of various competition reactions.[1–17] The rate constants for the reaction of hydrogen atoms with these alcohols were also previously determined either by monitoring the decay of the hydrogen atom using EPR techniques,[18–21] or by interpreting competition reactions in steady-state *g*-radiolysis.[22] It is striking, that so far no attempt has been reported to determine the rate constant by observing directly the optical absorption of the alcohol radical. One reason could be the low absorption exhibited by alcohol radicals in the UV region.[23] Recent developments in detection techniques now allow the absorption of these radicals to be studied directly.

In this communication, the recent evaluation of rate constants based on optical absorption measurements of alcohol radicals is revisited.[24,25] The alcohol radicals were generated in aqueous solutions containing methanol, ethanol, 2-propanol, or *t*-butyl alcohol when attacked by hydroxyl radicals or hydrogen atoms.

2. Experimental

The pulse radiolysis apparatus[26] and the computer software[27] 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 set to about ten nanosec.[28] The optical signals were derived from the average of several hundred individual experiments in order to improve the signal-to-noise ratio. The data of each individual experiment is first calculated in terms of the display units, in this case the molar absorbance, prior to averaging, in order to achieve greater accuracy. Furthermore, in all experiments described below, 8000 data points were recorded which were reduced to 1000 points for data handling by averaging eight points into one, a process we call 'horizontal averaging'. Throughout the experiment, the solution was flowing continuously through the cell; about twice the cell volume was exchanged during the period between two consecutive irradiating pulses. The optical absorption was calculated by dividing the optical absorbance (A) by the radical concentration generated in a pulse (c) times the length of the optical cell ($l = 1.5$ cm), and thus is expressed in units of ϵ[dm^3 mol^{-1} cm^{-1}]. The absorbed dose per pulse was calibrated by using a molar absorbance of 1.9×10^4 dm^3 mol^{-1} cm^{-1} for the absorption of the hydrated electron at 700 nm.[29] The yield of hydrated electrons 100 ns after the electron pulse was taken to be 2.6 species per 100 eV of absorbed energy (0.269 *m*mol J^{-1}).[30] For measurements in the UV region, high transmission band-pass filters (UV-R types, Schott) were inserted in front of the monochromator in order to avoid stray-light effects.

Chemical reagents were of supra pure quality and used as received. Nitrous oxide was of ultra high purity. Solutions were prepared daily using triply distilled water. In some experiments, where no additives were used to adjust pH, the pH is referred to as 'natural', i.e. slightly below pH 7.

3. Results and discussion

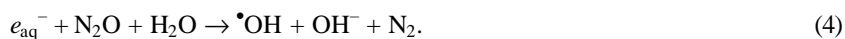Hydroxyl radicals react with the alcohol (RH) according to reaction 1.

$$^\bullet OH + RH \rightarrow R^\bullet + H_2O. \tag{1}$$

Hydrogen atoms also react with the alcohol by reaction 2.

$$H^\bullet + RH \rightarrow R^\bullet + H_2. \tag{2}$$

The alcohol radicals recombine via reaction 3.

$$R^\bullet + \quad R^\bullet \rightarrow products. \tag{3}$$

In solutions containing nitrous oxide, hydrated electrons are converted into hydroxyl radicals by reaction 4.

$$e_{aq}^- + N_2O + H_2O \rightarrow {}^\bullet OH + OH^- + N_2. \tag{4}$$

When solutions are saturated with nitrous oxide, this conversion occurs within a few nanoseconds, i.e. basically during the radiation pulse.[31] Thus, hydroxyl radicals are generated to a much larger extent than hydrogen atoms; G($^\bullet$OH) = 2.7 + 2.6 = 5.3 and G(H$^\bullet$) = 0.6 species per 100 eV (0.549 and 0.062 *m*mol J^{-1}) respectively.[30] In acidic solutions, pH 1 for example, all hydrated electrons are converted to hydrogen atoms according to reaction 5.
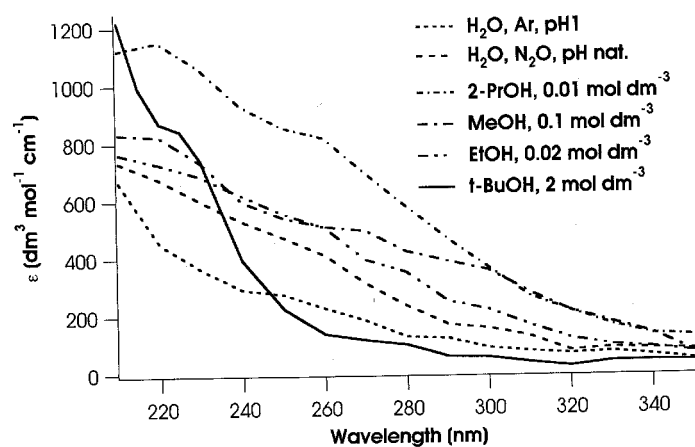
Figure 1. Optical spectra obtained in aqueous solutions of various aliphatic alcohols; solutions were purged with N_2O. Added are the spectra obtained in water of natural pH and saturated with N_2O and of pH 1 and purged with Ar. Dose per pulse corresponds to 3×10^{-6} mol dm^{-3} of $^\bullet OH$. Values were taken 1 *ms* after irradiation, taken from kinetic curves which represent the average of 50 individual experiments.
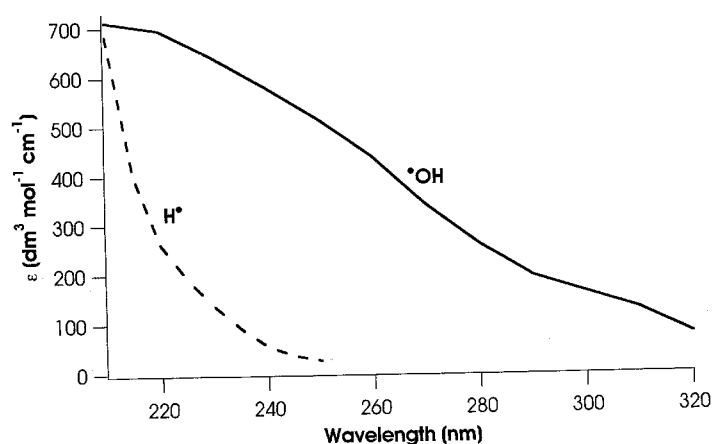
**Figure 2.** Spectra of H$^\bullet$ and $^\bullet OH$ as calculated from the experiments of figure 1.

$$e_{aq}^{-} + H^{+} \rightarrow H^{\bullet}. \tag{5}$$

Here, hydrogen atoms and hydroxyl radicals are generated to a similar extent, $G(^\bullet OH) = 2 \cdot 7$ and $G(H^\bullet) = 2 \cdot 6 + 0 \cdot 6 = 3 \cdot 2$ ($0 \cdot 280$ and $0 \cdot 331$ *mm*ol J^{-1}).

Alcohol radicals absorb in the near-UV region where hydroxyl radicals and hydrogen atoms exhibit absorption as well. Figure 1 shows the spectra of the alcohol radicals under investigation as well as the absorption obtained in alcohol-free solutions. These spectra are in fair agreement with the ones published earlier.[32] Comparison of the measurements in water at pH 1 and purged with Ar and that at natural pH and saturated with nitrous oxide, allows the calculation of the spectra for hydrogen atoms and hydroxyl radicals, which are depicted in figure 2. The absorption in the region between 250 and 350 nm is

entirely due to hydroxyl radicals, whereas at shorter wavelengths hydrogen atoms also contribute. The spectrum of the hydrogen atom agrees well with the one reported earlier,[33] but the spectrum of the hydroxyl radical differs.[33]

Experiments, in which hydroxyl radicals react only with the alcohols, were carried out in solutions purged with nitrous oxide at natural *p*H. The region between 260 and 290 nm was selected because the difference in absorption between hydroxyl radicals and alcohol radicals is sufficiently large and there is no absorption from hydrogen atoms to distort the kinetic traces. The absorption vs time curve at 290 nm obtained in a solution containing ethanol is shown in figure 3. The curve shows a sharp initial increase followed by a more gradual one. The initial increase is due to the formation of hydroxyl radicals during the irradiation pulse. The subsequent slower increase is caused by the formation of alcohol radicals. Results from the computer simulation are also included in this figure showing the contribution of hydroxyl radicals and that of alcohol radicals. The ethanol concentration is low, therefore, the reaction of hydrogen atoms with ethanol does not contribute to the absorption on this time scale.
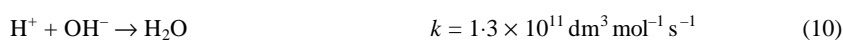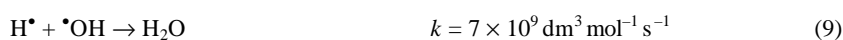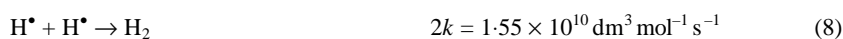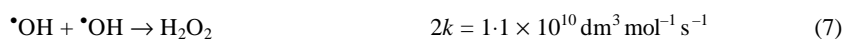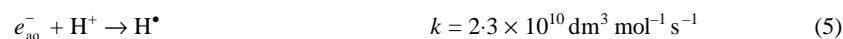
A second set of experiments was carried out at *p*H 1 with Ar purged solutions. Here, hydrogen atoms and hydroxyl radicals are generated to a similar extent. A typical absorption trace measured on the 6 *μs* time scale for a solution containing methanol $(0.02 \text{ mol dm}^{-3})$ is depicted in figure 4, curve (a). An initial fast increase is followed by a slow one eventually reaching a final plateau value. The magnitude of the initial growth during the pulse is about half of the final value. The fast initial increase is due to the generation of alcohol radicals by hydroxyl radicals whereas the slow increase is caused by an additional production of alcohol radicals due to the reaction of hydrogen atoms with methanol. In addition, an absorption vs time curve is shown in figure 4 which is obtained in a solution containing the same methanol concentration but at natural *p*H and
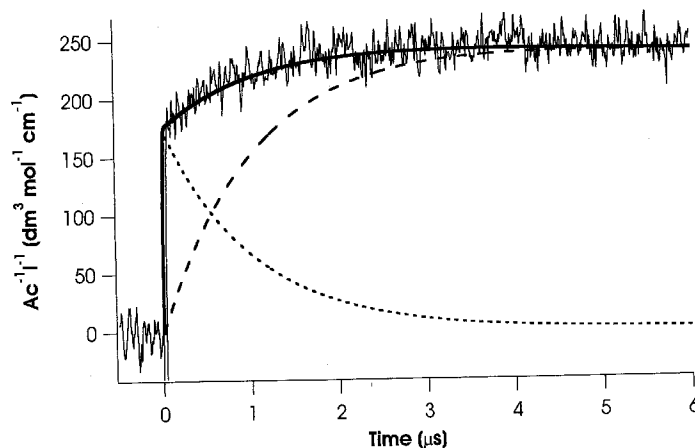
Figure 3. Absorption vs time curve at 290 nm for a solution containing 5 × $10^{-4} \text{ mol dm}^{-3}$ of ethanol purged with N_2O at natural *p*H. Dose per pulse corresponds to $4 \times 10^{-6} \text{ mol dm}^{-3}$ of •OH. The curve represents the average of 1000 individual experiments. Results of the computer simulation are included with the curves for the hydroxyl radical (dotted line) and the 1-hydroxyethyl radical (dashed line), and the sum of both curves (thick solid line).
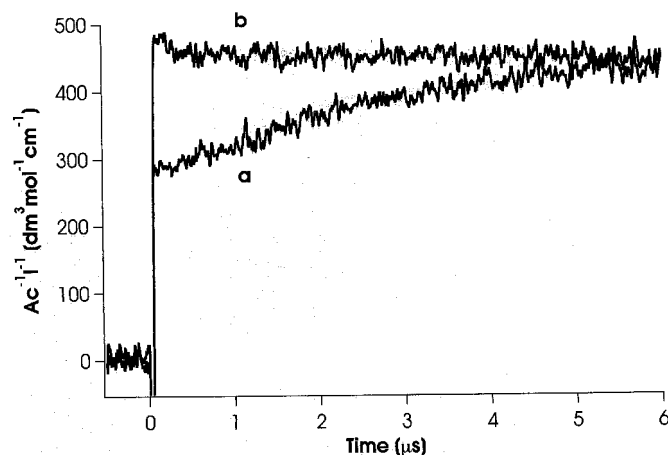
Figure 4. Absorption vs time curves at 270 nm for aqueous solutions containing 0.02 mol dm^{-3} methanol; curve (a) pH 1 and Ar purged; curve (b) natural pH and N$_2$O saturated. Dose per pulse corresponds to 2×10^{-6} mol dm^{-3} of $^{\bullet}$OH. The curve represents the average of several hundred individual experiments.

$$^{\bullet}\text{OH} + \text{RH} \rightarrow \text{R}^{\bullet} + \text{H}_2\text{O} \tag{1}$$

$$\text{H}^{\bullet} + \text{RH} \rightarrow \text{R}^{\bullet} + \text{H}_2 \tag{2}$$

$$\text{R}^{\bullet} + \text{R}^{\bullet} \rightarrow \text{product} \tag{3}$$

$$e_{aq}^{-} + \text{N}_2\text{O} \rightarrow {}^{\bullet}\text{OH} + \text{OH}^{-} + \text{N}_2 \qquad k = 9.1 \times 10^{9}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} \tag{4}$$

$$e_{aq}^{-} + \text{H}^{+} \rightarrow \text{H}^{\bullet} \qquad k = 2.3 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} \tag{5}$$

$$e_{aq}^{-} + e_{aq}^{-} \rightarrow \text{H}_2\text{O} + 2{}^{\bullet}\text{OH}^{-} \qquad 2k = 1.1 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} \tag{6}$$

$$^{\bullet}\text{OH} + {}^{\bullet}\text{OH} \rightarrow \text{H}_2\text{O}_2 \qquad 2k = 1.1 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} \tag{7}$$

$$\text{H}^{\bullet} + \text{H}^{\bullet} \rightarrow \text{H}_2 \qquad 2k = 1.55 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} \tag{8}$$

$$\text{H}^{\bullet} + {}^{\bullet}\text{OH} \rightarrow \text{H}_2\text{O} \qquad k = 7 \times 10^{9}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} \tag{9}$$

$$\text{H}^{+} + \text{OH}^{-} \rightarrow \text{H}_2\text{O} \qquad k = 1.3 \times 10^{11}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} \tag{10}$$
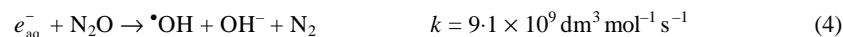
Rate constants of reactions (5)–(10) according to Buxton *et al*[11] and the original works cited therein.

Scheme 1. Reaction mechanism used in the computer simulation.

saturated with nitrous oxide (curve b). Here, the fast initial increase predominates. Both curves apparently reach the same final value, but a small droop can be seen in curve (b) due to the recombination of the alcohol radicals. The different values for the fast initial increase are consistent with the different yields of hydrogen atoms and hydroxyl radicals in acidic and in natural solutions. The rate of the reactions for hydrogen atoms and for

Table 1. Rate constants for the reaction of hydroxyl radicals and hydrogen atoms with various alcohols and for the recombination of the respective alcohol radicals.

Alcohol	$k_{OH + RH}$ [dm^3 mol^{-1} s^{-1}]		$k_{H + RH}$ [dm^3 mol^{-1} s^{-1}]		$2k_{R + R}$ [dm^3 mol^{-1} s^{-1}]	
	This work	Ref. [30]*	This work	Ref. [30]*	This work	Ref. [32]
Methanol	9.0×10^8	9.7×10^8	1.1×10^6	2.6×10^6	2.4×10^9	2.4×10^9
Ethanol	2.2×10^9	1.9×10^9	1.8×10^7	1.7×10^7	1.5×10^9	2.3×10^9
2-Propanol	2.0×10^9	1.9×10^9	5.3×10^7	7.4×10^7	1.1×10^9	1.4×10^9
t-Butyl alcohol	6.2×10^8	6.0×10^8	2.3×10^5	1.7×10^5	8.0×10^8	1.4×10^9

*Also taken from original work cited in ref. [30]

hydroxyl radicals with alcohol increased linearly with the alcohol concentration, and can be described by a pseudo-first order law. Measurements of the recombination of the respective alcohol radicals were carried out on a longer time scale. It should be mentioned that the final values for the absorption are different for solutions containing 2-propanol and, especially so, for those containing *t*-butyl alcohol, depending on the *p*H and the type of radical, which attacks the alcohol.

In order to derive accurately the rate constants for the reactions of hydroxyl radicals and hydrogen atoms with the various alcohols from the experimental data, computer simulations[34] were carried out using the reaction mechanism given in scheme 1, which contains all relevant reactions. The yields of the initial radiolysis products were used as mentioned above. The rate constants for reactions (4) to (10) were taken from the literature. The values for the best fit are shown in table 1, where the selected values are also included. Although the molar absorbance of these alcohol radicals is quite low (about $500 \, \text{dm}^3 \, \text{mol}^{-1} \, \text{cm}^{-1}$), the accuracy with which kinetic curves repeat was about 5%. The values of the rate constants obtained by computer simulation are accurate to 5%.

4. Conclusions

Data on the rate constants of the reaction of hydroxyl radicals and hydrogen atoms with methanol, ethanol, 2-propanol and *t*-butyl alcohol is presented (table 1), which was derived by directly observing the optical absorption of these radicals. The values thus obtained basically confirm the values already published and selected.

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