REACTIVITY OF HYDROGEN ATOMS WITH LIQUID WATER*

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Summary

The reactivity of hydrogen atoms with liquid water was investigated by determination of the final products obtained by the photolysis ($\lambda = 184.9$ nm) of two systems in the range pH 10 - 13: (a) $OH^-/N_2O/H_2O$ and (b) OH^-/H_2O (air free). Based on the product yields of the two systems, non-linear fitting computations were performed including all possible reactions; a value of $k(H + H_2O) = 10 \pm 2$ dm^3 mol^{-1} s^{-1} was determined. The share of each individual reaction leading to the formation of H_2 was also deduced.

1. Introduction

From the abundant published data on aqueous solutions it is well known that the primary products of liquid water photolysis are H, OH and a small amount of e^-_{aq} (*e.g.* refs. 1 - 7). Their quantum yields are strongly dependent on the excitation energy [3, 6], and their initial distribution, particularly when UV sources of low intensity are used, can influence the reaction probability in the bulk of the solution markedly. In many respects the knowledge of the fate of the hydrogen atoms is of special interest, especially when the rate constant for the reactions of hydrogen atoms with a very diluted solute (less than 10^{-4} mol dm^{-3}) is less than 10^7 dm^3 mol^{-1} s^{-1}. Although the behaviour of hydrogen atoms in aqueous solutions in the pH range 0 - 14 is well understood, nothing is known about their reactivity towards water, with the exception of the corresponding rate constant $k(e^-_{aq} + H_2O)$ of e^-_{aq} (the second form of hydrogen atoms), which is 16 dm^3 mol^{-1} s^{-1} at pH 11 [8]. It rises to 27 dm^3 mol^{-1} s^{-1} at pH 13. The aim of this work was to determine the rate constant of reaction (1), which is effectively the back reaction of the well-known reaction (2):

$$H + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2 + OH \tag{1, 2}$$

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In addition it was of interest to estimate the share of each individual reaction leading to H_2 formation in the pH range 10 - 13.

2. Experimental details

2.1. Light source and actinometry

A low pressure mercury lamp (Osram, HNS 10 OZ) emitting at 184.9 and 253.7 nm was used in combination with a 4π-geometry irradiation vessel as previously described [5, 6]. The second line of the light was not absorbed by the solutions used. By measuring the hydrogen yield produced by the photolysis of pure methanol ($Q(H_2)$ = 0.83 [9]) the light intensity I_0 at 184.9 nm was determined as $4 \times 10^{16} h\nu$ ml^{-1} min^{-1} (25 °C). In addition, 5 mol dm^{-3} of aqueous ethanol solutions were applied as an actinometer with $Q(H_2)$ = 0.4 [10], and we obtained $I_0 = 4.1 \times 10^{16} h\nu$ ml^{-1} min^{-1}. The irradiation dose was varied from 2×10^{16} to $1 \times 10^{17} h\nu$ ml^{-1}.

2.2. Preparation of solutions

The alkaline solutions (10^{-4} - 10^{-1} (mol OH$^-$) dm^{-3}) were prepared by dissolving NaOH and Ba(OH)$_2 \cdot$8H$_2$O (p.A. Merck AG., Darmstadt) in at least four-times-distilled water, whereby the dissolved CO_2 was eliminated as barium carbonate. Special precautions were taken in order to avoid traces of O_2, CO_2 and organic compounds from the samples before irradiation, because they were found to interfere strongly with the observed reactions. For exact adjustment of the pH the solutions were measured with a glass electrode (Radiometer, Copenhagen) and also by conductometric titration with 0.1 (mol HCl) dm^{-3}. In order to obtain a more consistent value for $k(H + H_2O)$, two systems were investigated under illumination at 184.9 nm: (a) 10^{-4} - 10^{-1} (mol OH$^-$) dm^{-3} solutions saturated with high purity N_2O (Messer Griesheim, Vienna); (b) solutions of 10^{-4} - 10^{-1} (mol OH$^-$) dm^{-3} saturated with oxygen-free argon (Messer Griesheim, Vienna).

2.3. Analysis

The gaseous reaction products (N_2, H_2 and O_2) were pumped from the irradiated solutions into a high vacuum apparatus and were analysed by gas chromatography against standards (Perkin–Elmer Fraktometer 116E; 2 m; molecular sieve, 5 Å; argon at 40 N cm^{-2}; 40 °C; thermistor detector). For the quantitative determination of the hydrogen peroxide produced, the following methods were used and the results were compared: the oxidation of peroxide to O_2 by KMnO$_4$ in H_2SO_4 [11] and subsequent measurement by gas chromatography; spectrophotometric determinations of the Ti(IV)–sulphate complex (λ = 410 nm) [11 - 16]; oxidation of the leucobase of phenolphthalein with Cu^{2+} catalyst [17] followed by spectrophotometric measurement (λ = 535 nm). In each case, standard solutions were used. The pH after irradiation was determined as mentioned before.

3. Computer simulations

Although the systems studied are relatively simple, several reaction pathways may lead to the analytically determined final products. Hence, in order to obtain a more consistent reaction mechanism for the explanation of product formation, computer simulations were performed. These were founded on the applied irradiation dose and on the quantum yields of the primary photolytic products of H_2O and OH^- and also of N_2O in the first system. The effect of the ionic strength of the alkaline solutions on the k values used was taken into account. For the computations the WR 16 program by Schmidt [18, 19] was adapted for the CDC computer of Vienna University.

4. Results and discussion

For simplicity the two systems investigated will be presented and discussed separately.

4.1. Photolysis of the $OH^-/N_2O/H_2O$ system

The molar extinction coefficients ϵ for the three absorbing components (OH^-, H_2O, N_2O) at 184.9 nm were determined by direct spectrophotometry and are given in Table 1. They were found to be in good agreement with published data [20 - 23]. The yields of the final products (H_2, N_2 and H_2O_2) were first studied as a function of the UV dose. The initial values determined

TABLE 1

Individual absorption of H_2O and OH^- at various pH values for N_2O-saturated aqueous alkaline solutions

pH	Substance	Optical density (cm^{-1} (%))	
10	OH^-	0.37	(11.60)
	H_2O	1.65	(51.72)
	N_2O	1.17	(36.68)
11	OH^-	3.70	(65.75)
	H_2O	1.65	(25.31)
	N_2O	1.17	(17.94)
12	OH^-	37.0	(92.92)
	H_2O	1.65	(4.14)
	N_2O	1.17	(2.94)
13	OH^-	370.0	(99.24)
	H_2O	1.65	(0.44)
	N_2O	1.17	(0.31)

$\epsilon_{185}(H_2O) = 2.97 \times 10^{-3}$ m^2 mol^{-1}; $\epsilon_{185}(OH^-_{aq}) = 370$ m^2 mol^{-1}; $\epsilon_{185}(N_2O) = 5$ m^2 mol^{-1}.
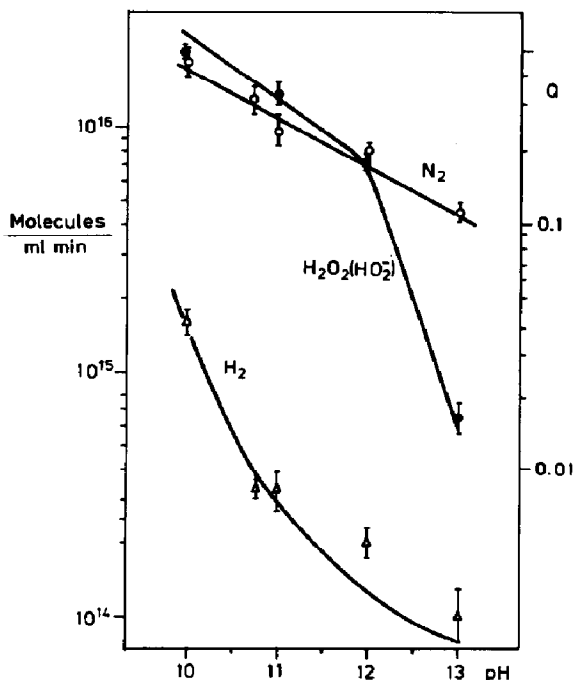
Fig. 1. Yields of H_2, N_2 and H_2O_2 (HO_2^-) in N_2O saturated solutions: O, ●, △, experimental data; ——, calculated values.

and the quantum yields Q are given in Fig. 1 as individual points. They represent mean values of several separate experiments. The yield of N_2 results from the direct photolysis of N_2O [2] and also from the scavenging of e_{aq}^- [24]. With increasing pH of the solution the absorption by N_2O decreases gradually and hence so does the role of direct N_2O photolysis. However, the amount of N_2 produced in the scavenging process rises correspondingly. Direct photolytic decomposition of H_2O_2 can be neglected because of the low concentration of H_2O_2: we found only $Q(O_2) = 2.5 \times 10^{-4}$. With long time irradiations, higher O_2 yields were observed.

The changes in concentration of the primary species (H, OH and O^-, e_{aq}^- as well as O, which results from N_2O photolysis) together with the final products were calculated as a function of time. The set of reactions given in Table 2 with the corresponding k values was used for this purpose. First, computations were carried out excluding reaction (1) and the result is shown as Fig. 2, curve 1. As can be seen, the curve is far below the experimental data. In the next step, it was assumed that reaction (1) takes place, and computations with various rate constants (100, 50 and 10) were performed. The best fit was obtained with $k(H + H_2O) = 10$ dm^3 mol^{-1} s^{-1}, as shown in Fig. 2, curve 3. Taking this k value for reaction (1) in combination with reactions (2) - (19) and the corresponding rate constants (Table 2), we computed the yields of the final products and these are presented as the full lines in Fig. 1. The very good agreement between the experimentally deter-

TABLE 2

Reactions and rate constants

Reaction	Rate constants k (dm^3 mol^{-1} s^{-1})	Number
$H + H_2O \rightarrow H_2 + OH$	10 ± 2 [a]	(1)
$OH + H_2 \rightarrow H + H_2O$	6.0×10^7	(2)
$H + H \rightarrow H_2$	1.5×10^{10}	(3)
$H + OH \rightarrow H_2O$	7.0×10^9	(4)
$H + OH^- \rightarrow e^-_{aq}$	1.2×10^7	(5)
$OH + OH \rightarrow H_2O_2$	6.0×10^9	(6)
$OH + OH^- \rightarrow O^- + H_2O$	3.6×10^8	(7)
$O^- + H_2O \rightarrow OH + OH^-$	4.6×10^4	(8)
$O^- + H_2 \rightarrow H + OH$	1.8×10^7	(9)
$O^- + OH \rightarrow HO_2$	2.6×10^{10}	(10)
$H^+ + HO_2^- \rightleftharpoons H_2O_2$	(pK 11.85)	(11)
$OH + H_2O_2 \rightarrow H_2O + H^+ + O_2^-$	4.5×10^7	(12)
$O^- + H_2O_2 \rightarrow H_2O + O_2^-$	5.0×10^7	(13)
$OH + HO_2^- \rightarrow H_2O + O_2^-$	7.0×10^8	(14)
$O^- + HO_2^- \rightarrow OH^- + O_2^-$	8.1×10^8	(15)
$H^+ + OH^- \rightleftharpoons H_2O$	($K_D = 1.832 \times 10^{16}$)	(16)
$e^-_{aq} + N_2O \rightarrow N_2 + OH + OH^-$	5.6×10^9 (pH $<$ 11)	(17)
$H + N_2O \rightarrow N_2 + OH$	1.2×10^4	(18)
$O + H_2O \rightarrow H_2O_2$	1.0×10^2	(19)
$e^-_{aq} + H_2O \rightarrow H_2 + OH^-$	16 (pH $<$ 11) 22 (pH 12) 27 (pH 13)	(20)
$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2OH^-$	4.5×10^9	(21)
$e^-_{aq} + H \rightarrow H_2 + OH^-$	2.5×10^{10}	(22)
$e^-_{aq} + H^+_{aq} \rightarrow H$	2.4×10^{10}	(23)
$e^-_{aq} + OH \rightarrow OH^-$ (homogeneous)	3.0×10^{10}	(24)
$e^-_{aq} + H_2O_2 \rightarrow OH + OH^-$	1.3×10^{10}	(25)
$e^-_{aq} + HO_2^- \rightarrow O^- + OH^-$	3.5×10^9	(26)

The rate constants of the reactions used for the computer simulations are taken from refs. 25 and 26. Reactions (1) - (19) were considered for solutions saturated with N_2O. For solutions saturated with argon the computations were based on reactions (1) - (16) and (20) - (26).

[a]This work.

mined and the calculated product yields is further evidence for the consistence of the computed rate constant k_1.

4.2. Photolysis of the OH^-/H_2O system (air free)

In this case, only two components (OH^- and H_2O) are absorbing the incident light of 184.9 nm. Their absorption characteristics were redetermined and are presented in Table 3. The initial yields of the final products (H_2 and H_2O_2) are mean values of several determinations and the quantum yields at the applied pH are shown in Fig. 3, again as single points.

Computer simulations were performed to explain the formation of H_2 in solutions saturated with argon and were based on the same assumptions as
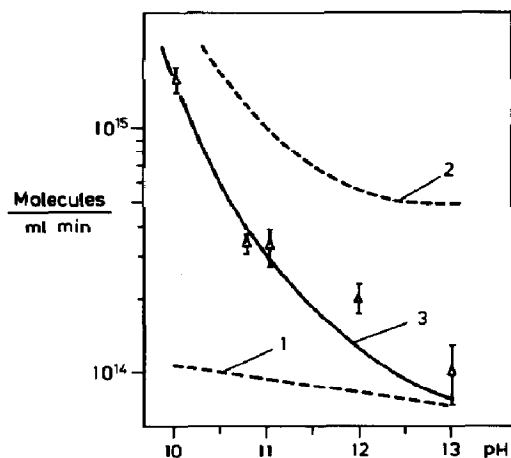
Fig. 2. Computed data for H_2 formation for different assumptions in solutions saturated with N_2O: △, experimental yields of H_2; curve 1, from the set of reactions in Table 2, reaction (1) was omitted; curve 2, from the set of reactions in Table 2, reaction (1) was considered with $k_1 = 100$ dm^3 mol^{-1} s^{-1}; curve 3, from the set of reactions in Table 2, reaction (1) was considered with $k_1 = 10$ dm^3 mol^{-1} s^{-1}.

TABLE 3

Individual absorption of OH^- and H_2O at various pH values for argon-saturated alkaline aqueous solutions

pH	Substance	Optical density $(cm^{-1}$ (%))	
10	OH^-	0.37	(18.32)
	H_2O	1.65	(81.68)
11	OH^-	3.70	(69.16)
	H_2O	1.65	(30.84)
12	OH^-	37.0	(95.73)
	H_2O	1.65	(4.27)
13	OH^-	370.0	(99.56)
	H_2O	1.65	(0.44)

$\epsilon_{185}(H_2O) = 2.97 \times 10^{-3}$ m^2 mol^{-1}; $\epsilon_{185}(OH^-) = 370$ m^2 mol^{-1}.

mentioned above. The best fits of the computed data with the experimental points were again obtained with $k(H + H_2O) = 10 \pm 2$ dm^3 mol^{-1} s^{-1}. The results are presented in Fig. 4. All assumptions made for the $OH^-/N_2O/H_2O$ system are also applicable in this case.

Again, using $k_1 = 10$ dm^3 mol^{-1} s^{-1} in the set of reactions (1) - (16) and (20) - (26) in Table 2 the yield of H_2O_2 (HO_2^-) was calculated and is presented in Fig. 3. In this case also a very good correspondence with the experimental data is observed, which confirms the k_1 value.

In the course of studying the photoreduction of H_2O_2 by hydrogen atoms Field *et al.* [27] observed an additional consumption of hydrogen by
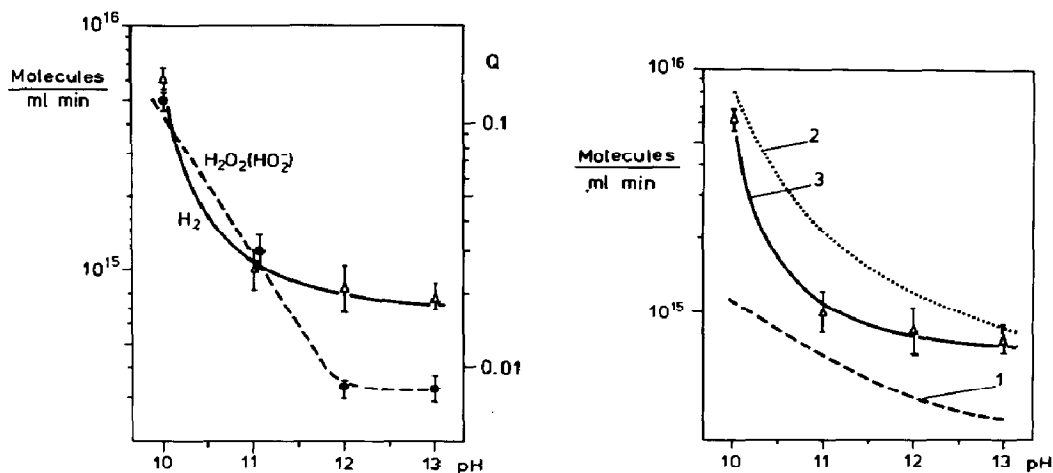
Fig. 3. Yields of H_2 and H_2O_2 (HO_2^-) produced in argon-saturated alkaline aqueous solutions: O, ●, △, experimental data; ———, – – –, calculated values.

Fig. 4. Computed data for H_2 formation for different assumptions in solutions saturated with argon: △, experimental yields of H_2; curve 1, from the set of reactions in Table 2, reaction (1) was omitted; curve 2, from the set of reactions in Table 2, reaction (1) was considered with $k_1 = 100$ dm^3 mol^{-1} s^{-1}; curve 3, from the set of reactions in Table 2, reaction (1) was considered with $k_1 = 10$ dm^3 mol^{-1} s^{-1}.

an unknown pseudo-first-order reaction with a rate constant k'(H + X) of 600 s^{-1}. Assuming that this process is identical with reaction (1), we can calculate its rate constant by dividing k' by the molarity of water (55.6); a value of k(H + H_2O) = 10.8 dm^3 mol^{-1} s^{-1} was obtained. This is in accordance with the value determined for our system and is further evidence for our postulation.

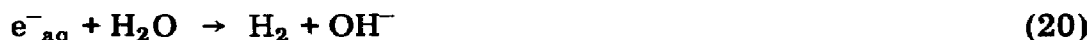Considering the kinetics of reaction (2), which is the back reaction of hydrogen attack on water, namely

$$H + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2 + OH \qquad (1, 2)$$

and taking $k_1 = 10$ dm^3 mol^{-1} s^{-1} and $k_2 = 6 \times 10^7$ dm^3 mol^{-1} s^{-1}, we deduced a free energy ΔG of approximately 10 kcal mol^{-1} (approximately 42 kJ mol^{-1}) for reaction (1). It is difficult to elaborate precisely, from possible rearrangements of the solvation shell, the difference between the ΔG value based on the k_1 and k_2 values and the ΔG value calculated from the heat of formation and solvation. The interpretations by Henglein [28] for e^-_{aq}, H^+_{aq} and H_{aq}, based on such rearrangements, may be suggestive in some way, but the thermodynamics of that reaction are far from clear at the moment. In addition, it should be mentioned again that e^-_{aq} and H are only alkaline and acid forms of each other. Reaction (1) is further justified by the similarity of the electron spin resonance spectra of H and e^-_{aq} in water and in other solvents. This can be interpreted as comparable structures of both species in the potential field of the solvent [23]. As e^-_{aq} reacts with H_2O

with a reaction rate of about 16 dm^3 mol^{-1} s^{-1} (pH $\leqslant$ 11), a similar process for the hydrogen atoms can be expected with a rate of about the same order of magnitude. Hence, earlier experiments to try to find a pseudo-first-order reaction for H$_2$ formation by reactions involving H$_3$O* or H$_2$O* [29 - 31] can be considered as problematic [23].

If we compare the results of Figs. 2 and 4 an increase in H$_2$ formation in solutions saturated with argon is observed. This effect is assigned to the reactions of the solvated electrons, which are scavenged by N$_2$O in the first system:

$$e^-_{aq} + H_2O \rightarrow H_2 + OH^- \tag{20}$$

$$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2OH^- \tag{21}$$

$$e^-_{aq} + H \rightarrow H_2 + OH^- \tag{22}$$

These reactions influence the steady state concentration of hydrogen atoms and e$^-_{aq}$ and finally lead to H$_2$ formation. Beyond that, the rate of reaction (20) shows an increase from 16 to 27 l mol^{-1} s^{-1} if the pH increases from 10 to 13 (see Table 2), because of the ionic strength [32, 33]. In our case the influence of the ionic strength of the solutions was taken into consideration. If we further take into account the results of Grossweiner and Baugher [34] for the geminate recombination of e$^-_{aq}$, and with a quantum yield of unity for the excitation of OH$^-$, only 27% of the initially excited OH$^-$ leads to the formation of free solvated electrons e$^-_{aq}$. Instead of geminate recombination this can also be interpreted as an energy transfer from the initially Rydberg antecedents to the longer-lived charge transfer to solvent (CTTS) state and subsequent deactivation as the main pathway [35 - 37]. This also shows the postulated interference of the electron scavenger N$_2$O in the CTTS state.

On the basis of these conclusions it was further possible to calculate the percentage which each reaction (1), (3), (21) and (22) contributes to H$_2$ formation. The hydrogen formed (in percentage) in the investigated pH range 10 - 13 is presented in Table 4. The changes in the relative absorption and in the e$^-_{aq}$–H equilibrium are found to be responsible for the observed H$_2$ yields. It should be mentioned that of the various known k_4 values only the value given in Table 2 seems to be reasonable [38], since it was specially checked by our computation procedure.

TABLE 4

The share of each reaction in forming H$_2$ at different pH values

pH	H$_2$ from H + H$_2$O (%)	H$_2$ from H + H (%)	H$_2$ from e$^-_{aq}$ + e$^-_{aq}$ (%)	H$_2$ from e$^-_{aq}$ + H (%)
10	97.59	0.8	0.24	1.37
11	88.27	0.2	8.0	3.53
12	41.5	0.01	56.0	2.49
13	8.1	—	90.70	1.20

Finally it should be pointed out that the $k(H + H_2O)$ value determined has to be considered for all photolytic ($\lambda < 200$ nm) and radiolytic processes of aqueous solutions where the solute concentration is low (less than 10^{-4} mol dm^{-3}) and its reactivity with hydrogen atoms is relatively small ($k \leqslant 10^7$ dm^3 mol^{-1} s^{-1}).

Acknowledgments

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