Supporting Information

Tailoring the Acidity of Liquid Media with Ionizing Radiation: Rethinking the Acid-Base Correlation Beyond pH

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S1.1 RELATION OF π^* TO pH IN NON-IRRADIATED SOLUTIONS

For non-irradiated solutions, the concentrations of H^+ and OH^- are coupled and their ratio depends on pH. The following equation is designed to be applied in non-irradiated solutions only, therefore it is avoided to call it the decadic logarithm of this ratio π^* here.

$$\begin{aligned}\lg\left(\frac{c(\mathrm{H}^+)}{c(\mathrm{OH}^-)}\right) &= \lg\big(c(\mathrm{H}^+)\big) - \lg\big(c(\mathrm{OH}^-)\big)\\ &= 2\lg\big(c(\mathrm{H}^+)\big) - \lg\big(c(\mathrm{OH}^-)\big) - \lg\big(c(\mathrm{H}^+)\big)\\ &= -2\big[-\lg\big(c(\mathrm{H}^+)\big)\big] - \big[\lg\big(c(\mathrm{OH}^-)\big) + \lg\big(c(\mathrm{H}^+)\big)\big]\\ &= -2\big[-\lg\big(c(\mathrm{H}^+)\big)\big] - \lg\big(c(\mathrm{OH}^-)\cdot c(\mathrm{H}^+)\big) \qquad \text{(S1)}\end{aligned}$$

Inserting equations (3) and (4) into (S1) yields:

$$\lg\left(\frac{c(\mathrm{H}^+)}{c(\mathrm{OH}^-)}\right) = -2\mathrm{pH} - \lg(K_\mathrm{W}) \qquad \text{(S2)}$$

This linear relationship is depicted in Figure S1.

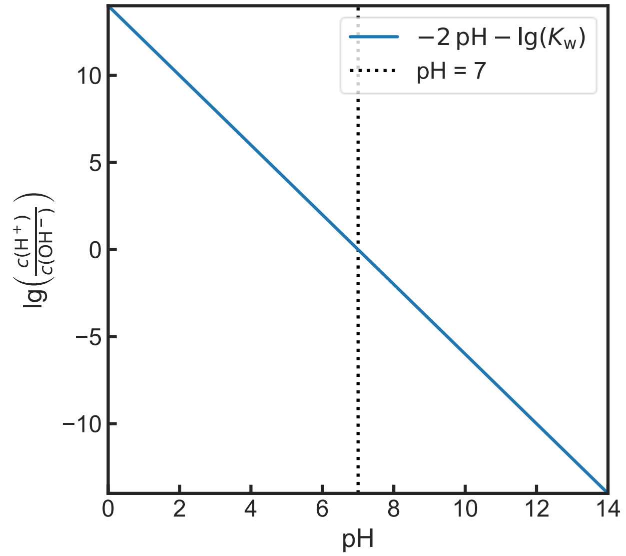

Figure S1:Linear relation of the decadic logarithm of the H^+ and OH^- concentrations at a given pH value for non-irradiated solutions after eq. (S2).

S1.2 RADIOLYTIC ACIDITY π^* AT pH 7.

The simulation for neat, aerated water under standard conditions (no radiation, 25 °C, pH 7) is shown in Figure S2. In this case, π^* remains at positive values between 0.25 and 2 for all dose rates considered. This can be compared to non-irradiated solutions with pH of 6 – 6.875. A π^* of 1 can be considered neutral condition (i.e. the ratio of $c(H^+)$ and $c(OH^-)$ of almost unity). A peak appears 1 $kGy\cdot s^{-1}$ with π^* of about 2, yielding an acidic environment that can be compared to pH 6 in a non-irradiated environment.

The temporal evolution of these steady state concentrations is depicted in Figure S3.

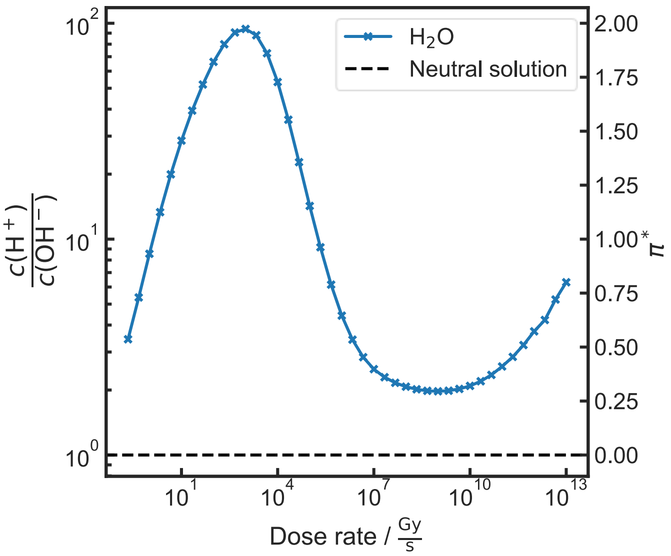

Figure S2:Dependence of the decadic logarithm of the H^+ and OH^- concentrations at pH 7 for irradiated solutions. The data shown here is a zoom of the data presented for pure water in Figure 3.

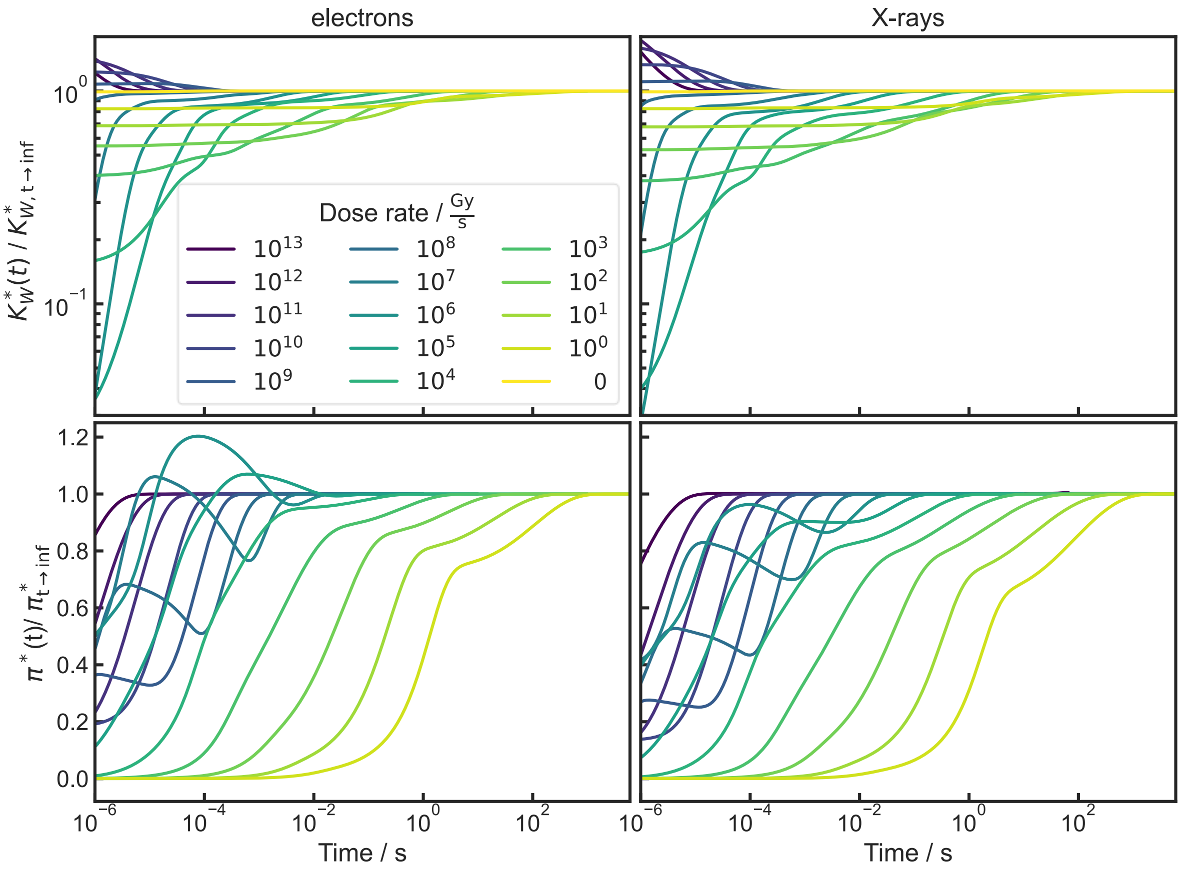

Figure S3: Time dependency of K_W^* (top) and π^* (bottom) for different dose rates (color coded) of electron (left) and X-ray (right) irradiation. Both measures are normalized to the steady state value. The simulation assumes neat, aerated water at an initial pH value of 7. Only values greater than 10^{-6} s are shown because the simulation only provides physically meaningful results after more than 1 μs.

S1.3 INELASTIC RADIATION-MATTER INTERACTIONS

Inelastic interactions between ionizing radiation and water trigger a relaxation cascade that is summarized in Figure S4 which is based on literature.[1,2]. First, the primary energy transfer and rapid electronic relaxation processes occur, causing excitation of high-energy molecular orbitals or molecule ionization in the temporal order of femtoseconds. This so-called 'physical stage' is highly irradiation dependent. The excited products now undergo further relaxation processes including dissociation and first ion-molecule interactions ('physico-chemical stage').

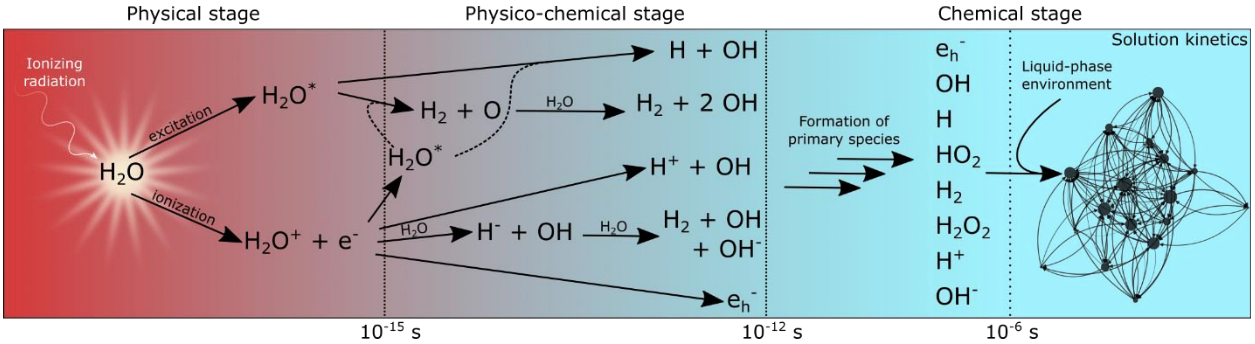

Figure S4: Illustration of inelastic radiation-matter interactions in water that is modeled using equations (5) and (6) in the main manuscript. According to literature.[1,2].

Afterwards, intermolecular interactions dominate the relaxation cascade, as excited energy states are mostly decayed. Hence, this is referred to as 'chemical stage'. A homogeneous distribution of primary species is achieved usually in the µs-range, which are now interacting with the surrounding liquid-phase environment based on the laws of solution kinetics. The ratio of these primary species is described by a set of *G*-values which are determined by the character of the ionizing radiation (Table S1).

Table S1: Generation values used in this work.

	G-value / (Molecules/100 eV)	
primary species	e-beam irrad.[3]	X-ray irrad.[4]
e_h^-	3.47	2.60
H^+	4.42	3.10
OH^-	0.95	0.50
H_2O_2	0.47	0.70
H	1.00	0.66
OH	3.63	2.70
HO_2	0.08	0.02
H_2	0.17	0.45
H_2O	-5.68	-4.64

S1.4 π^* FOR X-RAYS DEPENDENT ON INITIAL pH

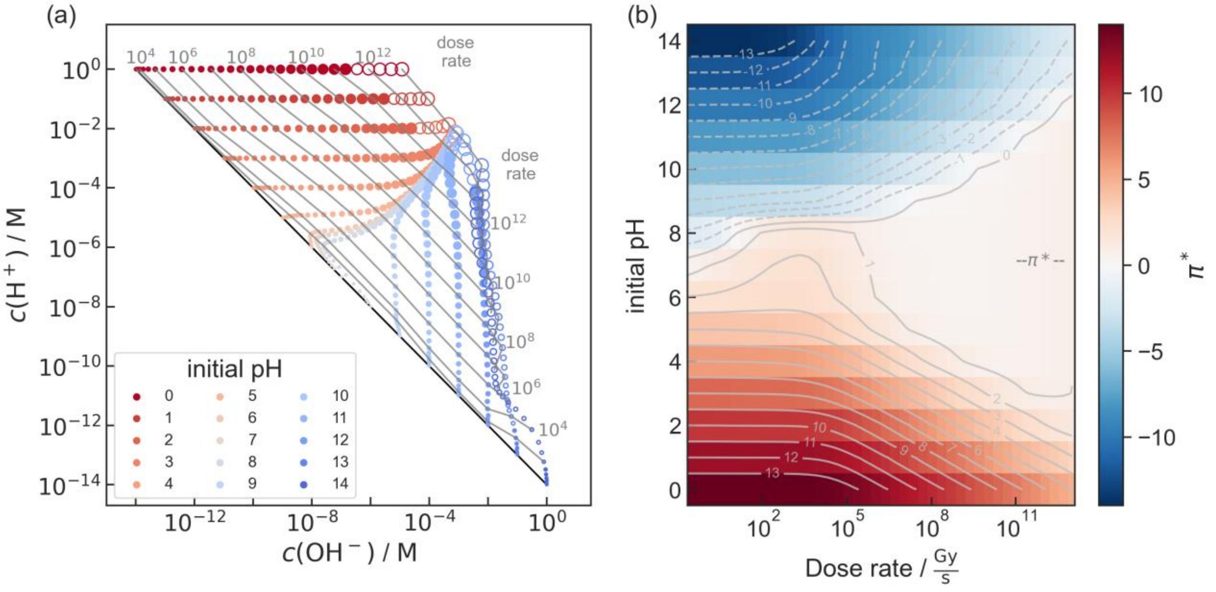

Figure S5: Acid-base chemistry of neat, aerated water as a function of dose rate of incident X-ray radiation and the initial pH value. (a) Concentrations of H^+ and OH^- in the steady state. Each dot represents the steady state concentration of a simulation, while its size is a measure of the dose rate. Dose rate (grey numbers) is given in $Gy \cdot s^{-1}$ and indicated by contour lines. The black diagonal line corresponds to water under equilibrium conditions ($K_W = 10^{-14}\ M^2$) without irradiation. Empty dots represent steady states, where the concentration of water is below 99% of the unirradiated solution. (b) π^* (color map and grey contour lines) as function of initial pH and dose rate. The equivalent plots for electron beam irradiation are shown in Figure 3.

S1.5 K_W^* FOR E-BEAM AND X-RAY IRRADIATION

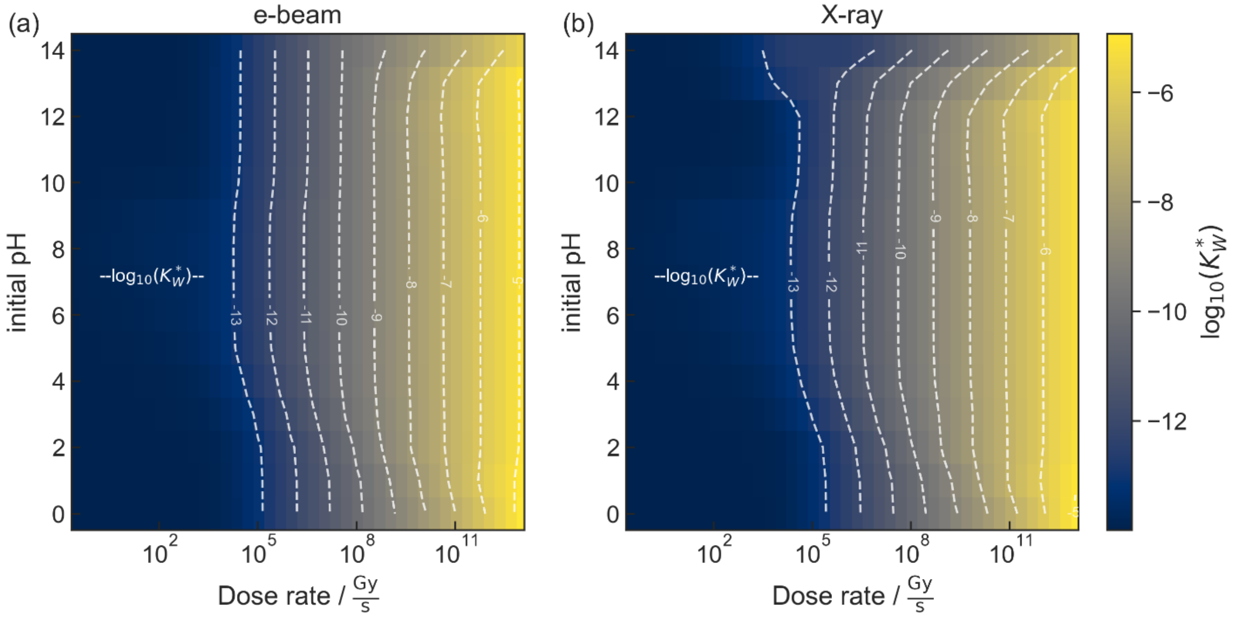

Figure S6: K_W^* depending on dose rate and initial pH for (a) electrons and (b) X-rays.

S1.6 DIFFERENT ADDITIVES

In Figure S7 the concentrations of H^+ and OH^- for initial concentrations of the anions Cl^-, Br^- and NO_3^- of 1 mM as well as 10 mM are compared against pure water (blue).

Figure S8 displays the evolution of the radiolytic ion product relative to the respective value of pure water.

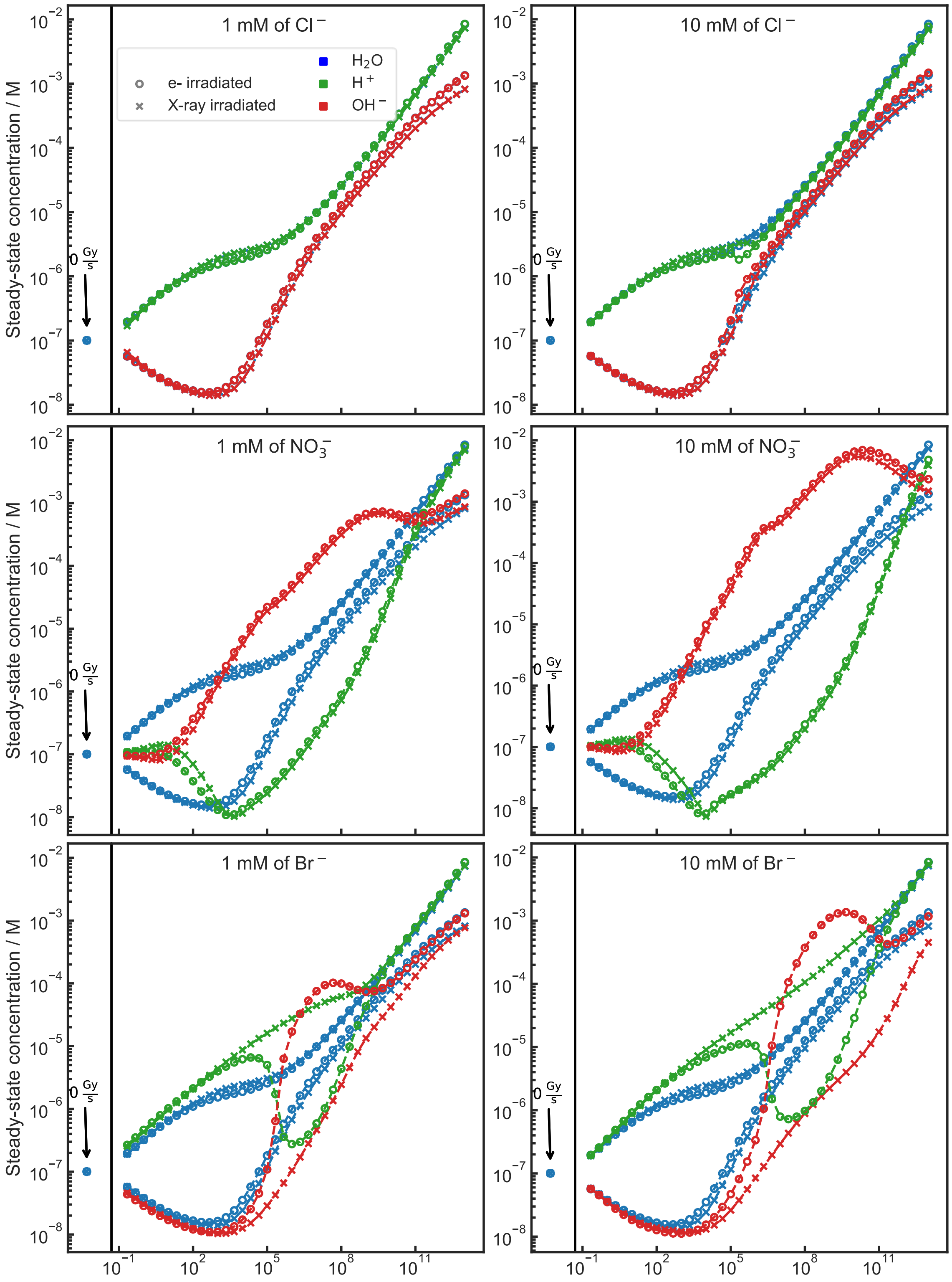

Figure S7: Steady-state concentrations of c(H^+) and c(OH^-) in both, pure, aerated water, and aqueous solutions containing either 1 mM (left) or 10 mM (right) Cl^-, Br^- or NO_3^- ions as functions of the dose rate.

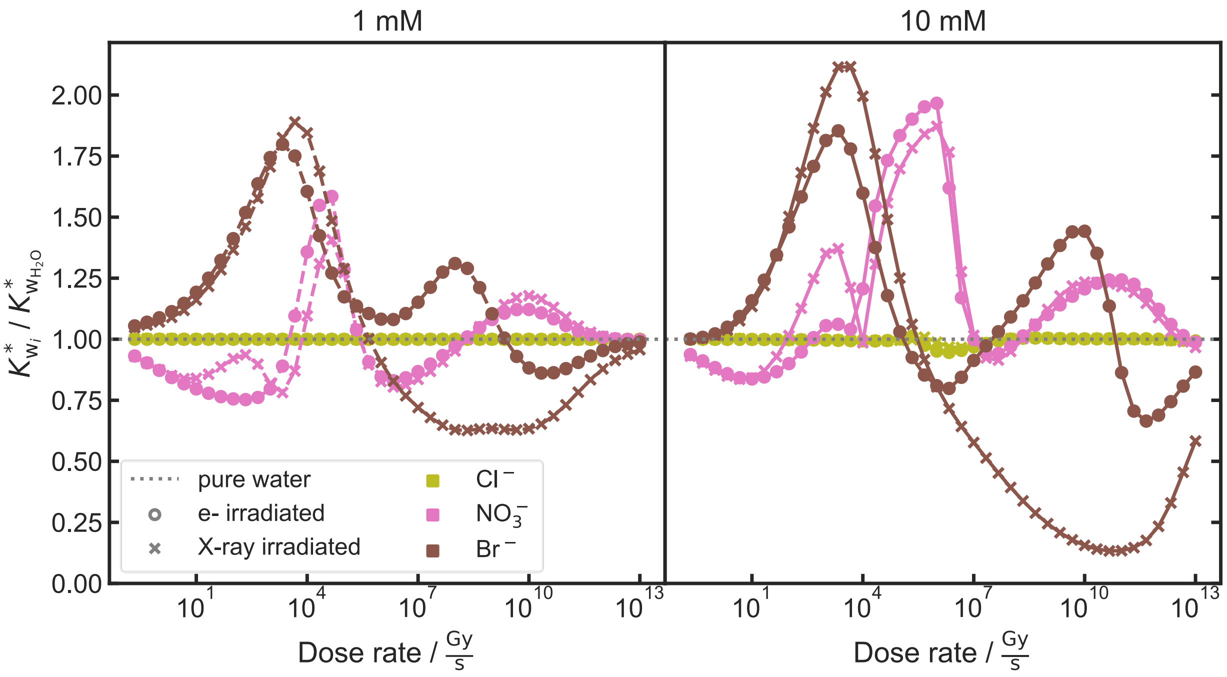

Figure S8: Relation of the ion product K_W^* to the radiolytic ion product of aerated water for aqueous solutions of 1 mM (left) and 10 mM (right). The colors denote the different ionic solutes, whereas the symbol relates to the used G-values.

S1.7 IMPACT OF ALKALI METALS ON THE ACIDITY UNDER IRRADIATION

Albeit the standard potentials of Li^+ is slightly higher than the reductive potential of solvated electrons (see main manuscript), the difference is close to thermal energy. To demonstrate that its impact is negligible for the discussion within this work, we simulated an extreme case scenario, in which we assume the reactivity of Li^+ to be similar to the one of Na^+. For the latter, Tesler and Schindewolf[5] measured a reduction by solvated electrons. They reported the reaction:

$Na^+ + e_h^- \rightarrow Na$ with a rate constant of $2 \cdot 10^4\,(Ms)^{-1}$

As decay, the reaction with H_2O was given within the same manuscript as:

$2\,Na + 2\,H_2O \rightarrow H_2 + 2\,Na^+ + 2\,OH^-$ with a rate constant of $1.5 \cdot 10^9\,(Ms)^{-1}$

Particularly the latter reaction has the potential to alter the acidity under irradiation. However, to simulate elementary steps only, the latter reaction was considered in the form of

$Na + H_2O \rightarrow H + Na^+ + OH^-$ with a rate constant of $1.5 \cdot 10^9\,(Ms)^{-1}$

because the recombination of $2\,H \rightarrow H_2$ (Reaction 34 in Table S2) is more than five times faster than the value given here, so that the oxidation of Na was assumed to be rate-determining.

By incorporating these proposed reactions (Table S6) we simulate the evolution of H^+ and OH^- steady state concentrations of 10 mM solutions of pure Na^+, NaBr, NaCl, and $NaNO_3$ under 300 keV electron irradiation (Figure S9). It is evident that Na^+ does not alter the obtained concentrations when considered as a hypothetical stand-alone reactant to pure water. This does not change notably when more realistic scenarios (NaBr, NaCl, $NaNO_3$) are regarded. Consequently, a change of Li^+ is likely to be negligible throughout all simulations within this manuscript.

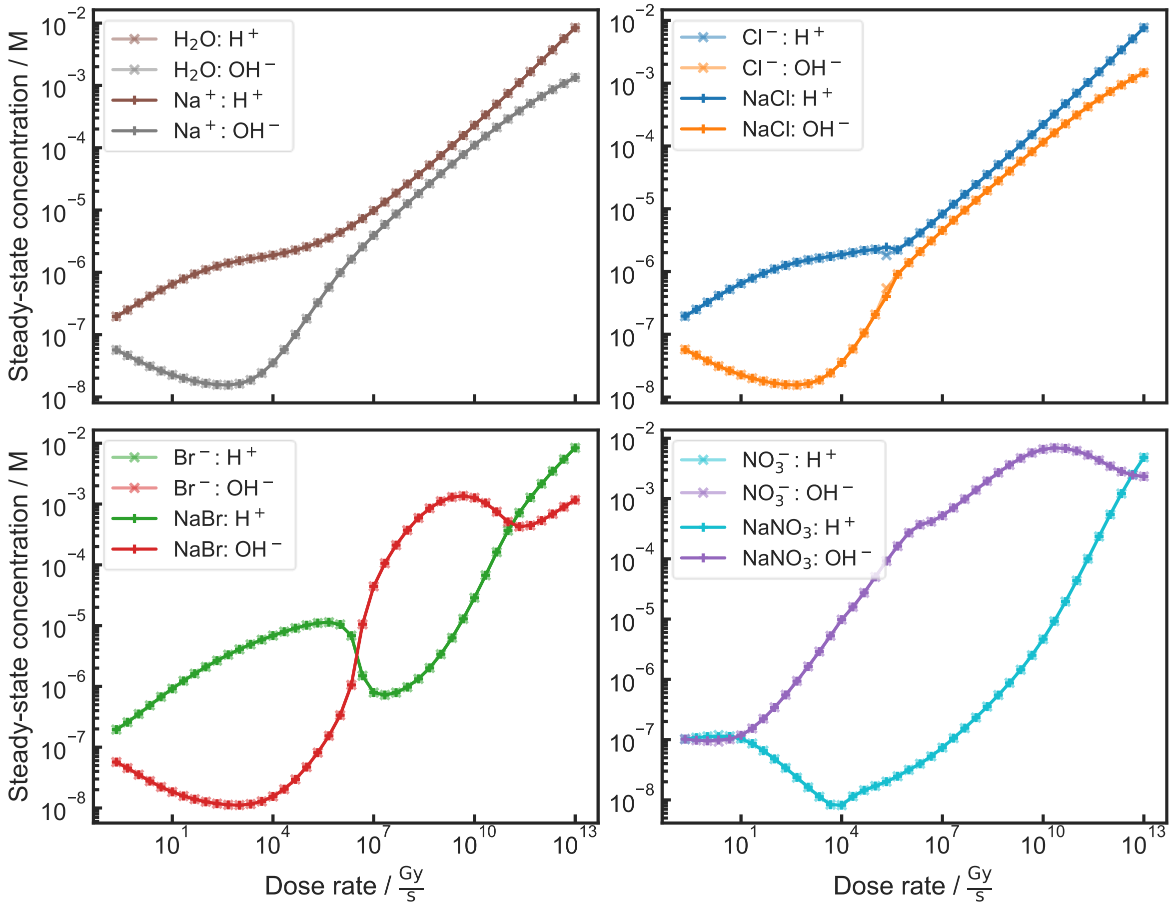

Figure S9: Steady-state evolutions of c(H^+) and c(OH^-) in pure water, and 10 mM Cl^-, Br^-, or NO_3^--containing solutions with and without additional 10 mM Na^+ present.

S1.8 KINETIC MODELS

The following section comprises the reaction sets utilized for simulations shown in this work in tabular and graph network[6,7] format. The latter emphasizes the fundamental difference between irradiated and non-irradiated solutions.

The equilibrium chemistry of pure water is fully described by Equation (1) and shown in Figure 1, the reaction interplay is fully described in (a), while the generation of reactive species by irradiation (Eq. (5)) triggers a reaction cascade comprising 83 reactions and 17 species (b). A tabular representation is shown in Table S2. In addition, the chlorine set comprises 89 reactions and 19 new species (Table S3, Figure S10). Both are a subset of the reaction set used for aqueous $HAuCl_4$ solutions introduced earlier[6].

Br^- containing solutions were described by 52 additional reactions and 10 additional species (Table S4, Figure S11)[8–15]. NO_3^--solutions were simulated using a reaction set of 18 additional species distributed over 73 reactions (Table S5, Figure S12)[12,16–24].

Table S2: Kinetic model for irradiation of neat, aerated water used in this work. k describes the kinetic constant in units of $mol^{-n+1}\,L^{3(n-1)}\,s^{-1}$, where n denotes the reaction order.

	Reaction			*k*	Source
1	H_2O	$\rightarrow$	$H^+ + OH^-$	$2.599 \cdot 10^{-5}$	25
2	$H^+ + OH^-$	$\rightarrow$	H_2O	$1.43 \cdot 10^{11}$	25
3	H_2O_2	$\rightarrow$	$H^+ + HO_2^-$	$1.119 \cdot 10^{-1}$	3
4	$H^+ + HO_2^-$	$\rightarrow$	H_2O_2	$5 \cdot 10^{10}$	3
5	$H_2O_2 + OH^-$	$\rightarrow$	$HO_2^- + H_2O$	$1.3 \cdot 10^{10}$	3
6	$HO_2^- + H_2O$	$\rightarrow$	$H_2O_2 + OH^-$	$5.82 \cdot 10^{7}$	3
7	$e_h^- + H_2O$	$\rightarrow$	$H + OH^-$	$1.9 \cdot 10^{1}$	3
8	$H + OH^-$	$\rightarrow$	$e_h^- + H_2O$	$2.2 \cdot 10^{7}$	3
9	H	$\rightarrow$	$e_h^- + H^+$	$3.9 \cdot 10^{0}$	3
10	$e_h^- + H^+$	$\rightarrow$	H	$2.3 \cdot 10^{10}$	3
11	$OH + OH^-$	$\rightarrow$	$O^- + H_2O$	$1.3 \cdot 10^{10}$	3
12	$O^- + H_2O$	$\rightarrow$	$OH + OH^-$	$1 \cdot 10^{8}$	3
13	OH	$\rightarrow$	$O^- + H^+$	$1.259 \cdot 10^{-1}$	3
14	$O^- + H^+$	$\rightarrow$	OH	$1 \cdot 10^{11}$	3
15	HO_2	$\rightarrow$	$O_2^- + H^+$	$1.346 \cdot 10^{6}$	3
16	$O_2^- + H^+$	$\rightarrow$	HO_2	$5 \cdot 10^{10}$	3
17	$HO_2 + OH^-$	$\rightarrow$	$O_2^- + H_2O$	$5 \cdot 10^{10}$	3
18	$O_2^- + H_2O$	$\rightarrow$	$HO_2 + OH^-$	$1.862 \cdot 10^{1}$	3
19	$e_h^- + OH$	$\rightarrow$	OH^-	$3 \cdot 10^{10}$	3
20	$e_h^- + H_2O_2$	$\rightarrow$	$OH + OH^-$	$1.1 \cdot 10^{10}$	3
21	$e_h^- + O_2^- + H_2O$	$\rightarrow$	$HO_2^- + OH^-$	$1.3 \cdot 10^{10}$	3
22	$e_h^- + HO_2$	$\rightarrow$	HO_2^-	$2 \cdot 10^{10}$	3
23	$e_h^- + O_2$	$\rightarrow$	O_2^-	$1.9 \cdot 10^{10}$	3
24	$2\ e_h^- + 2\ H_2O$	$\rightarrow$	$H_2 + 2\ OH^-$	$5.5 \cdot 10^{9}$	3
25	$e_h^- + H + H_2O$	$\rightarrow$	$H_2 + OH^-$	$2.5 \cdot 10^{10}$	3
26	$e_h^- + HO_2^-$	$\rightarrow$	$O^- + OH^-$	$3.5 \cdot 10^{9}$	3
27	$e_h^- + O^- + H_2O$	$\rightarrow$	$OH^- + OH^-$	$2.2 \cdot 10^{10}$	3
28	$e_h^- + O_3^- + H_2O$	$\rightarrow$	$O_2 + OH^- + OH^-$	$1.6 \cdot 10^{10}$	3
29	$e_h^- + O_3$	$\rightarrow$	O_3^-	$3.6 \cdot 10^{10}$	3
30	$H + H_2O$	$\rightarrow$	$H_2 + OH$	$1.1 \cdot 10^{1}$	3
31	$H + O^-$	$\rightarrow$	OH^-	$1 \cdot 10^{10}$	3
32	$H + HO_2^-$	$\rightarrow$	$OH + OH^-$	$9 \cdot 10^{7}$	3

	Reaction			*k*	Source
33	$H + O_3^-$	→	$OH^- + O_2$	$1 \cdot 10^{10}$	[3]
34	$2\ H$	→	H_2	$7.8 \cdot 10^{9}$	[3]
35	$H + OH$	→	H_2O	$7 \cdot 10^{9}$	[3]
36	$H + H_2O_2$	→	$OH + H_2O$	$9 \cdot 10^{7}$	[3]
37	$H + O_2$	→	HO_2	$2.1 \cdot 10^{10}$	[3]
38	$H + HO_2$	→	H_2O_2	$1.8 \cdot 10^{10}$	[3]
39	$H + O_2^-$	→	HO_2^-	$1.8 \cdot 10^{10}$	[3]
40	$H + O_3$	→	HO_3	$3.8 \cdot 10^{10}$	[3]
41	$2\ OH$	→	H_2O_2	$3.6 \cdot 10^{9}$	[3]
42	$OH + HO_2$	→	$H_2O + O_2$	$6 \cdot 10^{9}$	[3]
43	$OH + O_2^-$	→	$OH^- + O_2$	$8.2 \cdot 10^{9}$	[3]
44	$OH + H_2$	→	$H + H_2O$	$4.3 \cdot 10^{7}$	[3]
45	$OH + H_2O_2$	→	$HO_2 + H_2O$	$2.7 \cdot 10^{7}$	[3]
46	$OH + O^-$	→	HO_2^-	$2.5 \cdot 10^{10}$	[3]
47	$OH + HO_2^-$	→	$HO_2 + OH^-$	$7.5 \cdot 10^{9}$	[3]
48	$OH + O_3^-$	→	$O_3 + OH^-$	$2.6 \cdot 10^{9}$	[3]
49	$OH + O_3^-$	→	$2\ O_2^- + H^+$	$6 \cdot 10^{9}$	[3]
50	$OH + O_3$	→	$HO_2 + O_2$	$1.1 \cdot 10^{8}$	[3]
51	$HO_2 + O_2^-$	→	$HO_2^- + O_2$	$8 \cdot 10^{7}$	[3]
52	$HO_2 + HO_2$	→	$H_2O_2 + O_2$	$7 \cdot 10^{5}$	[3]
53	$HO_2 + O^-$	→	$O_2 + OH^-$	$6 \cdot 10^{9}$	[3]
54	$HO_2 + H_2O_2$	→	$OH + O_2 + H_2O$	$5 \cdot 10^{-1}$	[3]
55	$HO_2 + HO_2^-$	→	$OH + O_2 + OH^-$	$5 \cdot 10^{-1}$	[3]
56	$HO_2 + O_3^-$	→	$O_2 + O_2 + OH^-$	$6 \cdot 10^{9}$	[3]
57	$HO_2 + O_3$	→	$HO_3 + O_2$	$5 \cdot 10^{8}$	[3]
58	$2\ O_2^- + 2\ H_2O$	→	$H_2O_2 + O_2 + 2\ OH^-$	$1 \cdot 10^{2}$	[3]
59	$O_2^- + O^- + H_2O$	→	$O_2 + 2\ OH^-$	$6 \cdot 10^{8}$	[3]
60	$O_2^- + H_2O_2$	→	$OH + O_2 + OH^-$	$1.3 \cdot 10^{-1}$	[3]
61	$O_2^- + HO_2^-$	→	$O^- + O_2 + OH^-$	$1.3 \cdot 10^{-1}$	[3]
62	$O_2^- + O_3^- + H_2O$	→	$O_2 + O_2 + 2\ OH^-$	$1 \cdot 10^{4}$	[3]
63	$O_2^- + O_3$	→	$O_3^- + O_2$	$1.5 \cdot 10^{9}$	[3]
64	$2\ O^- + H_2O$	→	$HO_2^- + OH^-$	$1 \cdot 10^{9}$	[3]
65	$O^- + O_2$	→	O_3^-	$3.6 \cdot 10^{9}$	[3]
66	$O^- + H_2$	→	$H + OH^-$	$8 \cdot 10^{7}$	[3]

	Reaction			k	Source
67	$O^- + H_2O_2$	→	$O_2^- + H_2O$	$5 \cdot 10^8$	3
68	$O^- + HO_2^-$	→	$O_2^- + OH^-$	$4 \cdot 10^8$	3
69	$O^- + O_3^-$	→	$O_2^- + O_2^-$	$7 \cdot 10^8$	3
70	$O^- + O_3$	→	$O_2^- + O_2$	$5 \cdot 10^9$	3
71	O_3^-	→	$O_2 + O^-$	$3.3 \cdot 10^3$	3
72	$O_3^- + H^+$	→	$O_2 + OH$	$9 \cdot 10^{10}$	3
73	HO_3	→	$O_2 + OH$	$1.1 \cdot 10^5$	3
74	H_2O_2	→	$H_2O + O$	$1 \cdot 10^{-3}$	25
75	$2\ O$	→	O_2	$1 \cdot 10^9$	25
76	O_3	→	$O_2 + O$	$3 \cdot 10^{-6}$	26
77	$2\ O_3^- + H_2O$	→	$OH^- + HO_2^- + 2\ O_2$	$1 \cdot 10^4$	27
78	$2\ HO_3$	→	$H_2O_2 + 2\ O_2$	$5 \cdot 10^9$	27
79	$O_3 + OH^-$	→	$HO_2^- + O_2$	$1 \cdot 10^2$	27
80	$O_2 + O$	→	O_3	$4 \cdot 10^9$	28
81	$H_2O_2 + O$	→	$OH + HO_2$	$1.6 \cdot 10^9$	29
82	$O + HO_2^-$	→	$OH + O_2^-$	$5.3 \cdot 10^9$	29
83	$O + OH^-$	→	HO_2^-	$4.2 \cdot 10^8$	29

Table S3: Kinetic model used to describe the radiolysis of Cl^--containing aqueous solutions. Here, k denotes the respective kinetic constant in units of mol^{-n+1} $L^{3(n-1)}$ s^{-1}, where n denotes the reaction order. Please refer to Table S2 for the first 83 reactions.

	Reaction			k	Source
84	$OH + Cl^-$	→	$ClOH^-$	$4.3 \cdot 10^9$	25
85	$OH + HClO$	→	$ClO + H_2O$	$9 \cdot 10^9$	25
86	$OH + ClO_2^- + H^+$	→	$ClO_2 + H_2O$	$6.3 \cdot 10^9$	25
87	$e_h^- + Cl$	→	Cl^-	$1 \cdot 10^{10}$	25
88	$e_h^- + Cl_2^-$	→	$2\ Cl^-$	$1 \cdot 10^{10}$	25
89	$e_h^- + ClOH^-$	→	$Cl^- + OH^-$	$1 \cdot 10^{10}$	25
90	$e_h^- + HClO$	→	$ClOH^-$	$5.3 \cdot 10^{10}$	25
91	$e_h^- + Cl_2$	→	Cl_2^-	$1 \cdot 10^{10}$	25
92	$e_h^- + Cl_3^-$	→	$Cl_2^- + Cl^-$	$1 \cdot 10^{10}$	25
93	$e_h^- + ClO_2^- + H^+$	→	$ClO + OH^-$	$4.5 \cdot 10^{10}$	25
94	$e_h^- + ClO_3^- + H^+$	→	$ClO_2 + OH^-$	$1 \cdot 10^{10}$	30
95	$H + Cl$	→	$Cl^- + H^+$	$1 \cdot 10^{10}$	25
96	$H + Cl_2^-$	→	$2\ Cl^- + H^+$	$8 \cdot 10^9$	25

	Reaction			***k***	**Source**
97	$H + ClOH^-$	→	$Cl^- + H_2O$	$1 \cdot 10^{10}$	[25]
98	$H + Cl_2$	→	$Cl_2^- + H^+$	$7 \cdot 10^{9}$	[25]
99	$H + HClO$	→	$ClOH^- + H^+$	$1 \cdot 10^{10}$	[25]
100	$H + Cl_3^-$	→	$Cl_2^- + Cl^- + H^+$	$1 \cdot 10^{10}$	[25]
101	$HO_2 + Cl_2^-$	→	$Cl^- + HCl + O_2$	$4 \cdot 10^{9}$	[25]
102	HCl	→	$Cl^- + H^+$	$5 \cdot 10^{5}$	[25]
103	$Cl^- + H^+$	→	HCl	$6.29 \cdot 10^{-1}$	[25,31]
104	$HO_2 + Cl_2$	→	$Cl_2^- + O_2 + H^+$	$1 \cdot 10^{9}$	[25]
105	$HO_2 + Cl_3^-$	→	$Cl_2^- + HCl + O_2$	$1 \cdot 10^{9}$	[25]
106	$O_2^- + Cl_2^-$	→	$2\ Cl^- + O_2$	$1.2 \cdot 10^{10}$	[25]
107	$O_2^- + HClO$	→	$ClOH^- + O_2$	$7.5 \cdot 10^{6}$	[25]
108	$H_2O_2 + Cl_2^-$	→	$2\ HCl + O_2^-$	$1.4 \cdot 10^{5}$	[25]
109	$H_2O_2 + Cl_2$	→	$HO_2 + Cl_2^- + H^+$	$1.9 \cdot 10^{2}$	[25]
110	$H_2O_2 + HClO$	→	$HCl + H_2O + O_2$	$1.7 \cdot 10^{5}$	[25]
111	$OH^- + Cl_2^-$	→	$ClOH^- + Cl^-$	$7.3 \cdot 10^{6}$	[25]
112	$OH^- + Cl_2$	→	$HClO + Cl^-$	$6 \cdot 10^{8}$	[25]
113	$H^+ + ClOH^-$	→	$Cl + H_2O$	$2.1 \cdot 10^{10}$	[25]
114	$H_2O + Cl_2O_2$	→	$HClO + ClO_2^- + H^+$	$1 \cdot 10^{4}$	[27]
115	$H_2O + Cl_2O$	→	$2\ HClO$	$1 \cdot 10^{2}$	[25]
116	$H_2O + Cl_2O_4$	→	$ClO_2^- + ClO_3^- + 2\ H^+$	$1 \cdot 10^{2}$	[25]
117	$H_2O + Cl_2O_4$	→	$HClO + HCl + O_4$	$1 \cdot 10^{2}$	[25]
118	O_4	→	$2\ O_2$	$1 \cdot 10^{5}$	[25]
119	$Cl^- + Cl$	→	Cl_2^-	$2.1 \cdot 10^{10}$	[25]
120	$Cl^- + ClOH^-$	→	$Cl_2^- + OH^-$	$9 \cdot 10^{4}$	[25]
121	$Cl^- + HClO$	→	$Cl_2 + OH^-$	$1 \cdot 10^{1}$	[30]
122	$Cl^- + Cl_2$	→	Cl_3^-	$1 \cdot 10^{4}$	[25]
123	$ClOH^-$	→	$OH + Cl^-$	$6.1 \cdot 10^{9}$	[25]
124	Cl_2^-	→	$Cl + Cl^-$	$1.1 \cdot 10^{5}$	[25]
125	$2\ Cl_2^-$	→	$Cl_3^- + Cl^-$	$7 \cdot 10^{9}$	[25]
126	Cl_3^-	→	$Cl_2 + Cl^-$	$5 \cdot 10^{4}$	[25]
127	$2\ ClO$	→	Cl_2O_2	$1.5 \cdot 10^{10}$	[25]
128	$2\ ClO_2$	→	Cl_2O_4	$1 \cdot 10^{2}$	[25]

		Reaction		***k***	**Source**
129	Cl_2O_2 + ClO_2^-	→	ClO_3^- + Cl_2O	$1 \cdot 10^{2}$	25
130	2 HClO	→	Cl^- + ClO_2^- + 2 H^+	$6 \cdot 10^{-9}$	25
131	ClO_2^- + HClO	→	Cl^- + ClO_3^- + H^+	$9 \cdot 10^{-7}$	25
132	2 HClO	→	O_2 + 2 HCl	$3 \cdot 10^{-10}$	25
133	HClO + Cl^- + H^+	→	Cl_2 + H_2O	$9 \cdot 10^{3}$	25
134	Cl_2 + H_2O	→	HClO + Cl^- + H^+	$1.5 \cdot 10^{1}$	25
135	Cl_2^- + H_2	→	H + HCl + Cl^-	$4.3 \cdot 10^{5}$	25
136	2 Cl	→	Cl_2	$8.8 \cdot 10^{7}$	32
137	ClO_2 + O_3	→	O_2 + ClO_3	$1.1 \cdot 10^{3}$	33
138	ClO_2 + OH	→	ClO_3^- + H^+	$4 \cdot 10^{9}$	33
139	ClO_2 + O^-	→	ClO_3^-	$2.7 \cdot 10^{9}$	33
140	ClO_2 + O_3^-	→	O_2 + ClO_3^-	$1.8 \cdot 10^{5}$	33
141	ClO_2 + O_3^-	→	O_3 + ClO_2^-	$1.8 \cdot 10^{5}$	33
142	ClO_2^- + O_3	→	O_3^- + ClO_2	$4 \cdot 10^{6}$	33
143	ClO_2	→	O_2 + Cl	$6.7 \cdot 10^{9}$	34
144	HClO	→	H^+ + ClO^-	$2 \cdot 10^{3}$	27
145	H^+ + ClO^-	→	HClO	$5 \cdot 10^{10}$	27
146	$HClO_2$	→	H^+ + ClO_2^-	$9.53 \cdot 10^{8}$	27
147	H^+ + ClO_2^-	→	$HClO_2$	$5 \cdot 10^{10}$	27
148	Cl + O_3^-	→	Cl^- + O_3	$1 \cdot 10^{9}$	27
149	ClO + O_3^-	→	ClO^- + O_3	$1 \cdot 10^{9}$	27
150	Cl_2^- + ClO_2	→	Cl_2O_2 + Cl^-	$1 \cdot 10^{9}$	27
151	Cl + ClO_2	→	Cl_2O_2	$1 \cdot 10^{9}$	27
152	ClO + ClO_2^-	→	ClO^- + ClO_2	$9.4 \cdot 10^{8}$	27
153	ClO^- + O^- + H^+	→	ClO + OH^-	$2.3 \cdot 10^{8}$	27
154	Cl^- + H_2O_2	→	ClO^- + H_2O	$1.8 \cdot 10^{-9}$	27
155	Cl^- + H_2O_2 + H^+	→	HClO + H_2O	$8.3 \cdot 10^{-7}$	27
156	ClO^- + H_2O_2	→	Cl^- + O_2 + H_2O	$3.4 \cdot 10^{3}$	27
157	HClO + HO_2^-	→	Cl^- + O_2 + H_2O	$4.4 \cdot 10^{7}$	27
158	Cl_2 + HO_2^-	→	2 Cl^- + O_2 + H^+	$1.1 \cdot 10^{8}$	27
159	Cl + H_2O_2	→	Cl^- + H^+ + HO_2	$2 \cdot 10^{9}$	27
160	Cl + HO_2	→	Cl^- + H^+ + O_2	$3.1 \cdot 10^{9}$	27
161	Cl + OH^-	→	$ClOH^-$	$1.8 \cdot 10^{10}$	27

	Reaction			*k*	Source
162	$ClO_2 + H_2O_2$	→	$ClO_2^- + H^+ + HO_2$	$4 \cdot 10^0$	[27]
163	$ClO_2 + HO_2^-$	→	$ClO_2^- + HO_2$	$1.3 \cdot 10^5$	[27]
164	$ClO_2 + HO_2$	→	$ClO_2^- + H^+ + O_2$	$1 \cdot 10^6$	[27]
165	$ClO_2 + O_2^-$	→	$ClO_2^- + O_2$	$3 \cdot 10^9$	[27]
166	$ClO_2^- + O_2^-$	→	$ClO^- + O^- + O_2$	$4 \cdot 10^1$	[27]
167	$ClO + ClO_2$	→	Cl_2O_3	$7.4 \cdot 10^9$	[27]
168	$ClO + ClO_3$	→	Cl_2O_4	$7.4 \cdot 10^9$	[27]
169	$Cl_2O_2 + OH^-$	→	$Cl^- + ClO_3^- + H^+$	$1 \cdot 10^{10}$	[27]
170	$Cl_2O_3 + H_2O$	→	$HClO + ClO_3^- + H^+$	$1 \cdot 10^4$	[27]
171	$ClOH^-$	→	$Cl + OH^-$	$2.3 \cdot 10^1$	[27]
172	$Cl + H_2O$	→	$ClOH^- + H^+$	$1.8 \cdot 10^5$	[27]
173	$Cl_2^- + O_3$	→	$ClO + Cl^- + O_2$	$9 \cdot 10^7$	[27]

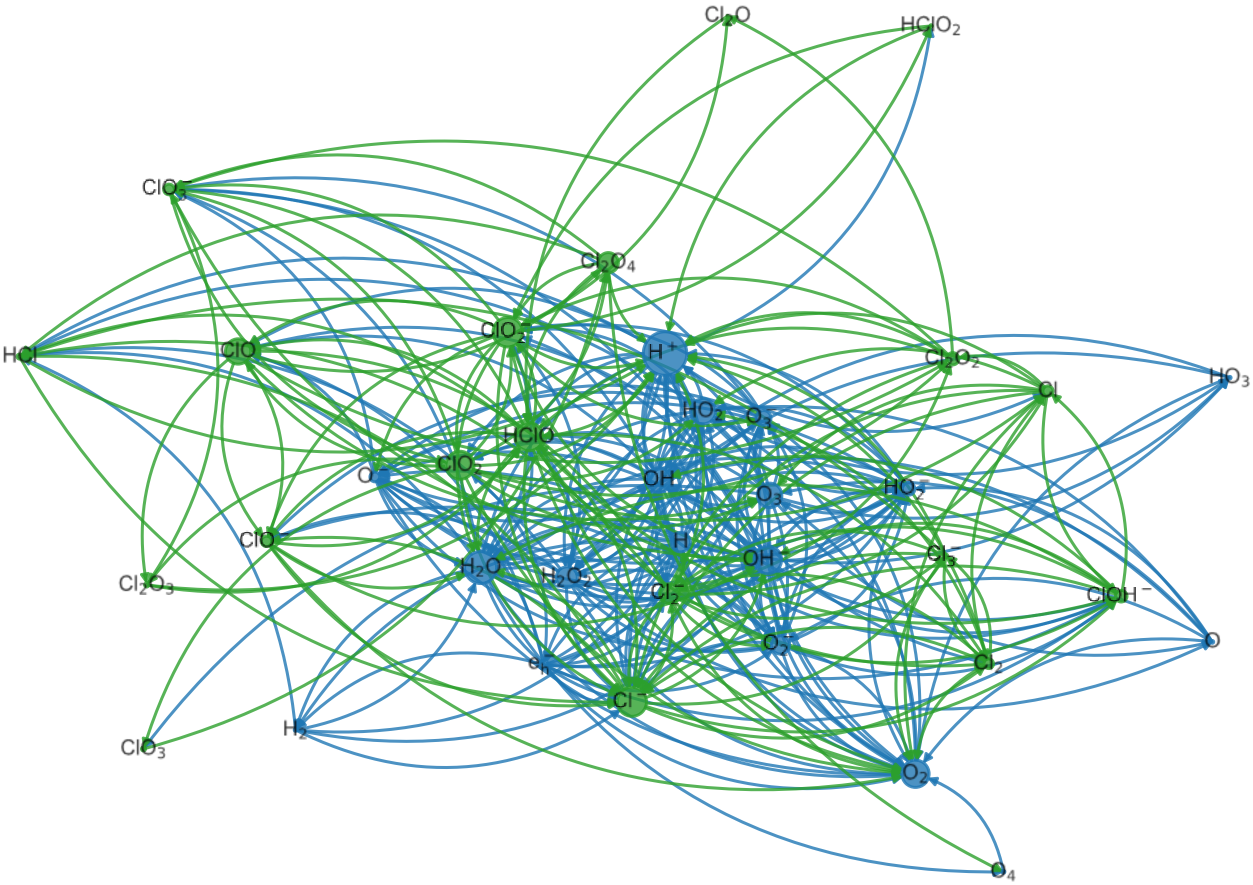

Figure S10: Graph representation of the kinetic model of Cl⁻-containing aqueous solutions. Tabular representation is found in Table S3.

Table S4: Kinetic model used to describe the radiolysis of Br^--containing aqueous solutions. Here, k denotes the respective kinetic constant in units of $mol^{-n+1}\,L^{3(n-1)}\,s^{-1}$, where n denotes the reaction order. Please refer to Table S2 for the first 83 reactions.

	Reaction			**k**	**Source**
84	$Br^- + OH$	→	$BrOH^-$	$1.1 \cdot 10^{10}$	8
85	$BrOH^-$	→	$Br^- + OH$	$3.3 \cdot 10^{7}$	8
86	$BrOH^- + H^+$	→	$Br + H_2O$	$4.4 \cdot 10^{10}$	8
87	$BrOH^-$	→	$Br + OH^-$	$4.2 \cdot 10^{6}$	8
88	$Br + OH^-$	→	$BrOH^-$	$1.3 \cdot 10^{10}$	8
89	$Br + Br^-$	→	Br_2^-	$1.2 \cdot 10^{10}$	8
90	Br_2^-	→	$Br + Br^-$	$1.9 \cdot 10^{4}$	8
91	$2\ Br_2^-$	→	$Br_3^- + Br^-$	$2.4 \cdot 10^{9}$	8
92	$Br + Br_2^-$	→	Br_3^-	$5 \cdot 10^{9}$	8
93	$Br_2 + Br^-$	→	Br_3^-	$1.6 \cdot 10^{8}$	8
94	Br_3^-	→	$Br_2 + Br^-$	$1 \cdot 10^{7}$	8
95	$2\ Br$	→	Br_2	$5 \cdot 10^{9}$	8
96	$Br + e_h^-$	→	Br^-	$1 \cdot 10^{10}$	8
97	$Br_2^- + e_h^-$	→	$2\ Br^-$	$1.3 \cdot 10^{10}$	8
98	$Br_3^- + e_h^-$	→	$Br_2^- + Br^-$	$2.7 \cdot 10^{10}$	8
99	$H + Br$	→	$H^+ + Br^-$	$1 \cdot 10^{10}$	8
100	$Br_2^- + H$	→	$2\ Br^- + H^+$	$1.4 \cdot 10^{10}$	8
101	$Br_3^- + H$	→	$Br_2^- + Br^- + H^+$	$1.2 \cdot 10^{10}$	8
102	$Br_2^- + HO_2$	→	$O_2 + H^+ + 2\ Br^-$	$1 \cdot 10^{8}$	8
103	$Br_3^- + HO_2$	→	$Br_2^- + HBr + O_2$	$1 \cdot 10^{7}$	8
104	$BrOH^- + Br^-$	→	$Br_2^- + OH^-$	$1.9 \cdot 10^{8}$	8
105	$Br_2^- + OH^-$	→	$BrOH^- + Br^-$	$2.7 \cdot 10^{6}$	8
106	$Br^- + H$	→	HBr^-	$1.7 \cdot 10^{6}$	8
107	$HBr^- + H^+$	→	$H_2 + Br$	$1.1 \cdot 10^{10}$	8
108	$H^+ + Br^-$	→	HBr	$1 \cdot 10^{4}$	9
109	HBr	→	$H^+ + Br^-$	$1 \cdot 10^{13}$	9
110	$2\ Br_2^-$	→	$Br_2 + 2\ Br^-$	$1.9 \cdot 10^{9}$	10
111	$Br + Br_2^-$	→	$Br_2 + Br^-$	$2 \cdot 10^{9}$	10
112	$Br_2 + e_h^-$	→	Br_2^-	$5.3 \cdot 10^{10}$	11
113	$Br_2 + H$	→	$Br_2^- + H^+$	$1 \cdot 10^{10}$	12
114	$Br^- + O_3$	→	$BrO^- + O_2$	$1.6 \cdot 10^{2}$	13
115	$Br + H_2O$	→	$BrOH^- + H^+$	$1.36 \cdot 10^{0}$	14

116	$Br + H_2O_2$	→	$O_2^- + Br^- + 2\,H^+$	$4 \cdot 10^9$	10
117	$Br + HO_2$	→	$H^+ + O_2 + Br^-$	$1 \cdot 10^9$	10
118	$Br_2^- + Br$	→	$Br_2 + Br^-$	$2 \cdot 10^9$	10
119	$Br_2^- + H_2O_2$	→	$HO_2 + 2\,Br^- + H^+$	$5 \cdot 10^2$	10
120	$Br_2^- + O_2^-$	→	$O_2 + 2\,Br^-$	$1.7 \cdot 10^8$	10
121	$Br_2 + HO_2$	→	$Br_2^- + O_2 + H^+$	$1.1 \cdot 10^8$	10
122	$Br_2 + O_2^-$	→	$Br_2^- + O_2$	$5.6 \cdot 10^9$	10
123	$Br_2 + H_2O_2$	→	$2\,HBr + O_2$	$1.3 \cdot 10^3$	10
124	$Br_2 + H_2O$	→	$HOBr + Br^- + H^+$	$9.7 \cdot 10^1$	10
125	$Br_3^- + O_2^-$	→	$Br_2^- + Br^- + O_2$	$3.8 \cdot 10^9$	10
126	$BrO^- + H^+$	→	$HOBr$	$1 \cdot 10^{10}$	9
127	$HOBr$	→	$H^+ + BrO^-$	$2.3 \cdot 10^1$	9
128	$Br_2^- + OH$	→	$HOBr + Br^-$	$1 \cdot 10^9$	10
129	$HOBr + Br^- + H^+$	→	$Br_2 + H_2O$	$5 \cdot 10^9$	10
130	$HOBr + HO_2^-$	→	$Br^- + H_2O + O_2$	$7.6 \cdot 10^8$	10
131	$HOBr + H_2O_2$	→	$HBr + H_2O + O_2$	$1.5 \cdot 10^4$	10
132	$HOBr + O_2^-$	→	$BrOH^- + O_2$	$3.5 \cdot 10^9$	10
133	$BrO^- + H_2O_2$	→	$Br^- + H_2O + O_2$	$1.2 \cdot 10^6$	10
134	$BrO^- + O_2^- + H_2O$	→	$Br + 2\,OH^- + O_2$	$1 \cdot 10^2$	10
135	$BrO^- + e_h^-$	→	$Br^- + O^-$	$1.5 \cdot 10^{10}$	12,15

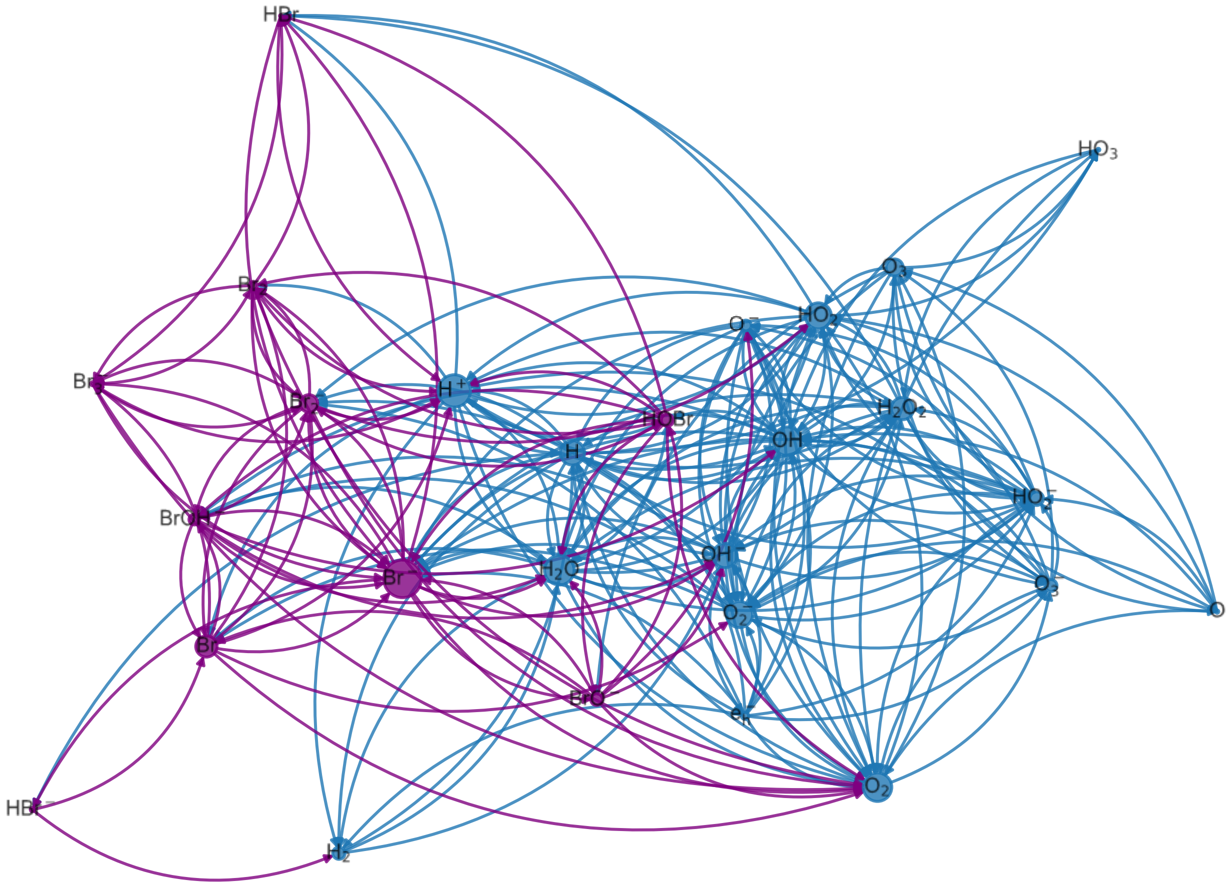

Figure S11: Graph representation of the kinetic model of Br⁻ -containing aqueous solutions. Tabular representation is found in Table S4.

Table S5: Kinetic model used to describe the radiolysis of NO_3^--containing aqueous solutions. Here, k denotes the respective kinetic constant in units of mol^{-n+1} $L^{3(n-1)}$ s^{-1}, where n denotes the reaction order. Please refer to Table S2 for the first 83 reactions.

	Reaction			k	Source
84	$NO_3^- + e_h^-$	$\rightarrow$	NO_3^{2-}	$9.7 \cdot 10^9$	[16]
85	$NO_3^- + H$	$\rightarrow$	HNO_3^-	$5.6 \cdot 10^6$	[17]
86	$NO_3^- + H^+$	$\rightarrow$	HNO_3	$6 \cdot 10^8$	[17]
87	HNO_3	$\rightarrow$	$H^+ + NO_3^-$	$1.46 \cdot 10^{10}$	[17]
88	$HNO_3 + OH$	$\rightarrow$	$NO_3 + H_2O$	$1.9 \cdot 10^7$	[17]
89	$NO_3^{2-} + OH$	$\rightarrow$	$NO_3^- + OH^-$	$3 \cdot 10^9$	[17]
90	$NO_3^{2-} + H_2O_2$	$\rightarrow$	$NO_3^- + OH$ $+ OH^-$	$1.6 \cdot 10^8$	[17]
91	$NO_3^{2-} + O_2$	$\rightarrow$	$NO_3^- + O_2^-$	$2.4 \cdot 10^8$	[17]
92	$NO_3^{2-} + H_2O$	$\rightarrow$	$NO_2 + 2\,OH^-$	$1 \cdot 10^3$	[17]
93	HNO_3^-	$\rightarrow$	$NO_3^{2-} + H^+$	$1.6 \cdot 10^3$	[17]

	Reaction			k	Source
94	$NO_2 + e_h^-$	→	NO_2^-	$1 \cdot 10^{10}$	[17]
95	$NO_2 + OH$	→	$HOONO$	$4.5 \cdot 10^{9}$	[17]
96	$NO_2 + HO_2$	→	$HOONO_2$	$1.8 \cdot 10^{9}$	[17]
97	$NO_2 + H$	→	HNO_2	$1 \cdot 10^{10}$	[17]
98	$NO_2 + O_2^-$	→	O_2NOO^-	$4.5 \cdot 10^{9}$	[17]
99	$2\ NO_2$	→	N_2O_4	$4.5 \cdot 10^{9}$	[17]
100	$NO_2 + NO_3$	→	$NO + NO_2 + O_2$	$2.41 \cdot 10^{5}$	[17]
101	$NO_2 + NO$	→	N_2O_3	$1.1 \cdot 10^{9}$	[17]
102	$NO_2 + O^-$	→	$ONOO^-$	$3.5 \cdot 10^{9}$	[17]
103	N_2O_4	→	$2\ NO_2$	$6 \cdot 10^{3}$	[17]
104	$N_2O_4 + H_2O$	→	$HNO_2 + HNO_3$	$1.8 \cdot 10^{1}$	[17]
105	$HNO_2 + OH$	→	$NO_2 + H_2O$	$2 \cdot 10^{9}$	[17]
106	HNO_2	→	$NO_2^- + H^+$	$3 \cdot 10^{7}$	[17]
107	$2\ HNO_2$	→	$NO_2 + NO + H_2O$	$1.34 \cdot 10^{1}$	[17]
108	$HNO_2 + e_h^-$	→	HNO_2^-	$4 \cdot 10^{9}$	[17]
109	$HNO_2 + H$	→	H_2NO_2	$3.88 \cdot 10^{8}$	[18]
110	$HNO_2 + NO_3$	→	$NO_2 + HNO_3$	$2 \cdot 10^{8}$	[17]
111	$HNO_2 + HNO_3$	→	$2\ NO_2 + H_2O$	$6.62 \cdot 10^{3}$	[17]
112	$NO_2^- + H^+$	→	HNO_2	$5 \cdot 10^{10}$	[17]
113	$NO_2^- + OH$	→	$NO_2 + OH^-$	$1 \cdot 10^{10}$	[17]
114	$NO_2^- + H$	→	HNO_2^-	$1.64 \cdot 10^{9}$	[18]
115	$NO_2^- + O^- + H_2O$	→	$NO_2 + 2\ OH^-$	$3.1 \cdot 10^{8}$	[17]
116	$NO_2^- + e_h^-$	→	NO_2^{2-}	$4.1 \cdot 10^{9}$	[17]
117	$NO_2^- + NO_3$	→	$NO_2 + NO_3^-$	$4.4 \cdot 10^{9}$	[17]
118	$2\ NO_3$	→	$2\ NO_2 + O_2$	$1.3 \cdot 10^{5}$	[19]
119	$NO_3 + H_2O_2$	→	$HNO_3 + HO_2$	$7.1 \cdot 10^{6}$	[17]
120	$NO_3 + OH$	→	$NO_2 + HO_2$	$1 \cdot 10^{10}$	[17]
121	$NO_3 + HO_2$	→	$HNO_3 + O_2$	$3 \cdot 10^{9}$	[17]
122	$NO_3 + H_2O$	→	$HNO_3 + OH$	$3 \cdot 10^{2}$	[17]
123	$NO_3 + OH^-$	→	$NO_3^- + OH$	$8.2 \cdot 10^{7}$	[17]
124	$HOONO$	→	$NO_3^- + H^+$	$9 \cdot 10^{-1}$	[17]
125	$HOONO$	→	$NO_2 + OH$	$3.5 \cdot 10^{-1}$	[17]
126	$HOONO_2$	→	$NO_2 + HO_2$	$2.6 \cdot 10^{-2}$	[17]

	Reaction			***k***	**Source**
127	$HOONO_2$	→	$HNO_2 + O_2$	$7 \cdot 10^{-4}$	[17]
128	$HOONO + H_2O$	→	$HNO_2 + H_2O_2$	$3 \cdot 10^{2}$	[17]
129	$HOONO_2$	→	$O_2NOO^- + H^+$	$7.1 \cdot 10^{4}$	[17]
130	$HOONO_2 + HNO_2$	→	$2\ HNO_3$	$1.2 \cdot 10^{1}$	[17]
131	O_2NOO^-	→	$NO_2^- + O_2$	$1.35 \cdot 10^{0}$	[17]
132	O_2NOO^-	→	$NO_2 + O_2^-$	$1 \cdot 10^{0}$	[17]
133	$O_2NOO^- + H^+$	→	$HOONO_2$	$5 \cdot 10^{10}$	[17]
134	HNO_2^-	→	$NO + OH^-$	$5 \cdot 10^{3}$	[17]
135	$NO_2^{2-} + H_2O$	→	$NO + 2\ OH^-$	$1.6 \cdot 10^{6}$	[17]
136	$2\ NO + O_2$	→	$2\ NO_2$	$5.9 \cdot 10^{6}$	[17]
137	$NO + OH$	→	$NO_2^- + H^+$	$1 \cdot 10^{10}$	[17]
138	$NO + HO_2$	→	$HOONO$	$3.2 \cdot 10^{9}$	[17]
139	$NO + O_2^-$	→	$ONOO^-$	$5 \cdot 10^{9}$	[17]
140	$ONOO^-$	→	$NO + O_2^-$	$2 \cdot 10^{-2}$	[17]
141	$HOONO + H^+$	→	$HNO_3 + H^+$	$4.3 \cdot 10^{0}$	[17]
142	$ONOO^- + OH$	→	$NO + O_2 + OH^-$	$4.8 \cdot 10^{9}$	[17]
143	N_2O_3	→	$NO + NO_2$	$8.4 \cdot 10^{4}$	[17]
144	$ONOO^- + N_2O_3$	→	$2\ NO_2 + NO_2^-$	$3.1 \cdot 10^{8}$	[17]
145	$N_2O_3 + H_2O$	→	$2\ NO_2^- + 2\ H^+$	$2 \cdot 10^{3}$	[17]
146	$ONOO^- + H^+$	→	$HOONO$	$5 \cdot 10^{10}$	[17]
147	$ONOO^- + NO_2$	→	$NO_2^- + NO_3$	$2.4 \cdot 10^{4}$	[17]
148	$H_2NO_2 + O_2^-$	→	$ONOO^- + H_2O$	$2.3 \cdot 10^{7}$	[12,20]
149	$NO_3^{2-} + H^+$	→	$NO_2 + OH^-$	$2 \cdot 10^{10}$	[12]
150	HNO_3^-	→	$NO_2 + OH^-$	$2 \cdot 10^{5}$	[12]
151	$HNO_2 + H$	→	$H_2O + NO$	$4.5 \cdot 10^{8}$	[21]
152	$HNO_2 + H_2O_2$	→	$NO_3^- + H^+ + H_2O$	$4.6 \cdot 10^{3}$	[22]
153	$NO + NO_2 + H_2O$	→	$2\ HNO_2$	$1.58 \cdot 10^{8}$	[19]
154	$2\ NO_2 + H_2O$	→	$HNO_2 + HNO_3$	$4.8 \cdot 10^{7}$	[19]
155	$HOONO$	→	$ONOO^- + H^+$	$5 \cdot 10^{4}$	[23]
156	$NO_2^- + O_3$	→	$O_2 + NO_3^-$	$3.7 \cdot 10^{5}$	[24]

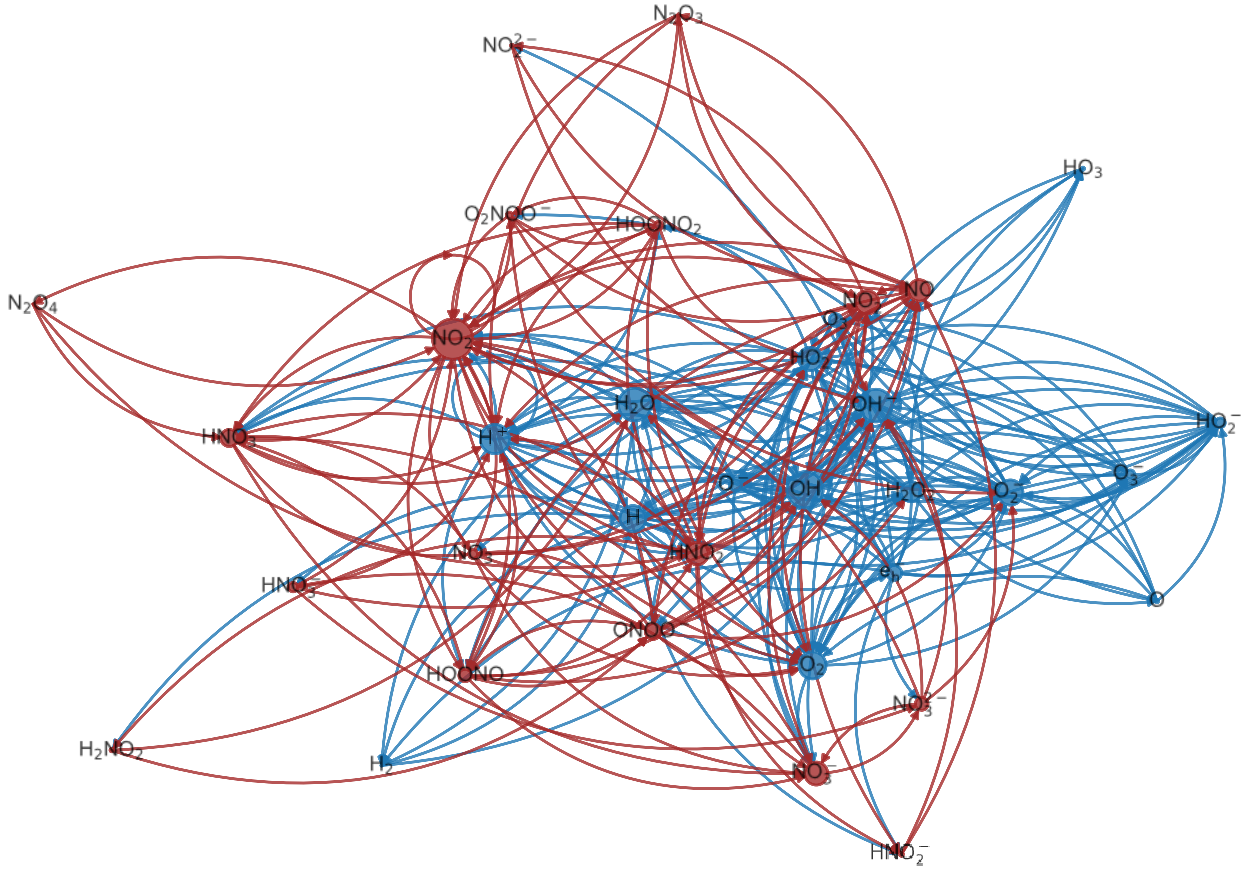

Figure S12: Graph representation of the kinetic model of NO_3^- -containing aqueous solutions. Tabular representation is found in Table S5.

Table S6: Kinetic model used to describe the radiolysis of Na^+-containing aqueous solutions. Here, k denotes the respective kinetic constant in units of $mol^{-n+1}\,L^{3(n-1)}\,s^{-1}$, where n denotes the reaction order. Please refer to Table S2 for the first 83 reactions.

	Reaction			***k***	**Source**
84	$Na^+ + e_h^-$	→	Na	$2 \cdot 10^4$	[5]
85	$Na + H_2O$	→	$H + Na^+ + OH^-$	$1.5 \cdot 10^9$	Assumed as rate-determining elementary step, after ref.[5]

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