

Supplementary Information

On the Role of Hydrogen and Peroxyl Radicals in the Degradation of Aromatic Hydrocarbon-Based Proton Exchange Membranes

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1. Reactions of Radicals

Table S1. Relevant reactions of radicals (rate constants are room temperature values)^a and yields.

Radical	Reaction	k (M ⁻¹ s ⁻¹)	c (mM)	k' (s ⁻¹)	pH 2	pH 0	pH 2	pH 0
					N ₂		O ₂	
HO•	HO• + Ar → •Ar-OH	5·10 ⁹	1	5·10 ⁶	1%			
	HO• + tBuOH → ...	6·10 ⁸	1'000	6·10 ⁸	99%			
	HO• + Ar → •Ar-OH	5·10 ⁹	1	5·10 ⁶	8%			
	HO• + DMSO → ...	6·10 ⁹	10	6·10 ⁷	92%			
e ⁻ (aq)	e ⁻ (aq) + H ⁺ → H•	2.3·10 ¹⁰	10 1'000	2.3·10 ⁸ 2.3·10 ¹⁰	100% 100%		95%	100%
	e ⁻ (aq) + O ₂ → O ₂ • ⁻	1.9·10 ¹⁰	0.7 ^b 0.7 ^b	1.3·10 ⁷ 1.3·10 ⁷	– –		5%	0%
	e ⁻ (aq) + Ar → ...	1·10 ⁹	1	1·10 ⁶	0%		0%	
H•	H• + Ar → •Ar-H	1·10 ⁹	1	1·10 ⁶	100%		6%	
	H• + O ₂ → HO ₂ •	2.1·10 ¹⁰	0.7 ^b	1.5·10 ⁷	–		94%	
	H• + Ar → •Ar-H	1·10 ⁹	1	1·10 ⁶	91%			
	H• + DMSO → ...	1·10 ⁷	10	1·10 ⁵	9%			
•CH ₃	•CH ₃ + Ar → ...	1·10 ⁹	1	1·10 ⁶	100%		26%	
	•CH ₃ + O ₂ → •OO-CH ₃	4·10 ⁹	0.7 ^b	2.8·10 ⁶	–		74%	
•tBuOH ^c	•tBuOH + Ar → ...	1·10 ⁹	1	1·10 ⁶	100%		44%	
	•tBuOH + O ₂ → •OO-tBuOH	1.8·10 ⁹	0.7 ^b	1.3·10 ⁶	–		56%	

^a values are taken from Buxton et al., *J. Phys. Chem. Ref. Data* 17, 513–886 (1988) ; Reuvers et al., *Int. J. Radiat. Biol. Relat. Stud. Phys. Chem. Med.* 24, 533–536 (1973); Nemeth et al., *J. Phys. Chem. C* 126, 15606–15616 (2022); Koulkes-Pujo et al., *FEBS Letters* 129, 52–54 (1981); Marchaj et al., *J. Phys. Chem.* 95, 4440–4441 (1991); Nauser and Carreras, *Chem. Commun.* 50, 14349–14351 (2014); Mark et al., *J. Photochem. Photobiol. A: Chem.* 55, 157–168 (1990).

^b saturated in air with enriched O₂ content of ~60%.

^c •tBuOH = •CH₂C(CH₃)₂OH

2. γ -Radiolysis Experiments

Table S2. Radiation chemical yield G . Dose rate of the ^{60}Co source at the time of measurement: 89.8 Gy h^{-1} .

Radical	G ($\mu\text{mol/J}$)
$\text{HO}^\bullet$	0.28
$\text{e}^-(\text{aq})$	0.28
$\text{H}^\bullet$	0.063
Total (Σ)	0.623

Table S3. Conditions and concentrations used in radiolysis experiments.

Gas	pH	BPS, DPS (mM)	H_2SO_4 (mM)	Na_2SO_4 (mM)	tBuOH (M)	DMSO (mM)
N_2	0	1	1'000	—	1	10
N_2	2	1	10	330	1	10
O_2	0	1	1'000	—	1	10
O_2	2	1	10	330	1	10

3. Experimental Results

In the following tables, the numerical results of the γ -radiolysis experiments are given. The extent of degradation of the model compounds are measured using HPLC-UV. For experiments in O₂-rich atmosphere, solutions were saturated in air with enriched O₂ content of ~60%, yielding an estimated dissolved O₂ content of ~0.7 mM.

Table S4. BPS in N₂ saturated solution.

Compound:			BPS					
Gas:			N ₂					
pH:			2			0		
Additive:			–	tBuOH	DMSO	–	tBuOH	DMSO
Time (h)	Dose (Gy)	[•] mM	Degradation					
			(%)	(%)	(%)	(%)	(%)	(%)
0.56	50	0.031	3.7	–6.4	4.5	–5.4	–8.2	8.6
1.12	101	0.063	17.4	–8.6	0.1	–4.8	2.8	9.0
2.23	200	0.125	–5.4	–4.7	3.9	–4.4	–5.3	8.9
4.46	401	0.250	33.0	–2.3	5.2	8.0	–5.2	7.3
8.91	800	0.498	43.0	4.9	19.4	32.6	–2.6	17.2
13.36	1200	0.747	52.5	11.7	25.5	39.8	5.5	20.3

Table S5. BPS in O₂ containing solution.

Compound:			BPS					
Gas:			O ₂					
pH:			2			0		
Additive:			–	tBuOH	DMSO	–	tBuOH	DMSO
Time (h)	Dose (Gy)	[•] mM	Degradation					
			(%)	(%)	(%)	(%)	(%)	(%)
0.56	50	0.031	10.4	–4.0	–3.4	0.0	–2.0	–0.8
1.12	101	0.063	13.8	–2.1	–5.0	0.6	0.1	3.6
2.23	200	0.125	21.3	–2.8	1.1	4.2	–1.0	3.6
4.46	401	0.250	33.4	–2.1	4.3	19.7	–2.5	1.9
8.91	800	0.498	55.1	0.2	13.6	37.4	0.2	6.0
13.36	1200	0.747	72.1	0.3	15.7	45.8	1.3	9.0

Table S6. DPS in N₂ saturated solution.

Compound:			DPS					
Gas:			N ₂					
pH:			2			0		
Additive:			–	tBuOH	DMSO	–	tBuOH	DMSO
Time (h)	Dose (Gy)	[•] mM	Degradation					
			(%)	(%)	(%)	(%)	(%)	(%)
0.56	50	0.031	3.1	–0.6	0.3	5.3	–0.1	2.1
1.12	101	0.063	4.1	2.5	3.5	3.1	5.3	2.7
2.23	200	0.125	6.4	4.7	2.5	5.4	6.5	–0.1
4.46	401	0.250	8.9	8.3	8.9	6.2	7.7	5.6
8.91	800	0.498	17.9	15.7	19.4	10.9	11.1	12.3
13.36	1200	0.747	21.4	23.1	27.0	14.5	16.6	16.2

Table S7. DPS in O₂ containing solution.

Compound:			DPS					
Gas:			O ₂					
pH:			2			0		
Additive:			–	tBuOH	DMSO	–	tBuOH	DMSO
Time (h)	Dose (Gy)	[•] mM	Degradation					
			(%)	(%)	(%)	(%)	(%)	(%)
0.56	50	0.031	1.4	–0.6	–0.1	–1.4	–0.7	–1.4
1.12	101	0.063	3.3	–1.2	–1.7	0.6	1.6	–1.3
2.23	200	0.125	6.7	2.4	1.7	2.9	1.4	0.9
4.47	401	0.250	13.8	3.3	1.4	4.5	0.9	0.6
8.94	803	0.500	25.4	4.2	8.4	10.5	3.9	3.8
13.41	1204	0.750	35.6	5.7	11.7	14.6	3.4	7.9