



Data Article

Dataset and kinetic model reaction compilation for the radical-induced degradation of formic acid and formate in aqueous solution

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ABSTRACT

This article contains the individual datasets and complete reaction kinetics compilation for the formic acid/formate component of the kinetic model described in "Radiolytic Degradation of Formic Acid and Formate in Aqueous Solution: Modeling the Final Stages of Organic Mineralization under Advanced Oxidation Process Conditions" [1]. Gamma irradiation data were collected for aqueous sodium formate solutions under pH = 1.5 and 9.0 conditions. To determine the optimum conditions necessary to effectively mineralize formic acid/formate in an Advanced Oxidation Process utilized for water treatment, several solution compositions were evaluated: air, nitrogen, and nitrous oxide saturation. Data were collected by a combination of high performance liquid chromatography and gas chromatography. These measured values were used to construct a kinetic computer model, by combining with published literature rate coefficients and optimizing specific important rate coefficients to afford the best agreement with experimental data.

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Specifications Table

Subject	Environmental Science – Water Science and Technology
Specific subject area	Application of ionizing radiation as part of an advanced oxidation process for water treatment
Type of data	Table
How data were acquired	These data were acquired by exposing aqueous formic acid/formate sample solutions to cobalt-60 gamma rays for a given duration using a Nordion Gammacell 220E Cobalt-60 irradiator. Samples were subsequently analysed by a combination of high performance liquid chromatography (HPLC) and gas chromatography (GC) using a Waters Alliance (Milford, MA, USA) e2695 separations module with a Waters photodiode array (PDA) detector and an Agilent Technologies (Santa Clara, CA, USA) 7890 Series II GC with flame ionization detection (FID), respectively. Kinetic model calculations were solved using the MCPA software (Faringdon, UK) FACSIMILE numerical algorithm.
Data format	Raw, Analyzed
Parameters for data collection	Isolation of formic acid/formate was done by aqueous solution pH control. Solutions were pre-saturated or continuously sparged with specific gases to create oxidizing or reducing conditions. Gamma irradiation was used to directly generate radicals from water, eliminating other chemical additives. Advanced Oxidation Processes (AOP) water treatment conditions were studied to allow direct transfer of data to real-world systems.
Description of data collection	A combination of a HPLC and GC were used to quantify the loss of formic acid/formate and production of oxalate/oxalic acid and gaseous products as a function of absorbed gamma radiation dose. HPLC was employed for carboxylic acids analyses, exploiting their retention time and absorption at 210 nm. Headspace gas compositions were quantified by GC-FID. Kinetic computer modelling utilized the differential equation solving package FACSIMILE, built from literature reactions and rate coefficients. Some important rate coefficients were optimized to provide quantitative agreement to experimental data.
Data source location	Institution: Center for Radiation Chemistry Research, Idaho National Laboratory City/Town/Region: Idaho Falls/ID Country: USA
Data accessibility	With the article
Related research article	Gregory P. Horne, Peter R. Zalupski, Dayna L. Daubaras, Cathy Rae, Stephen P. Mezyk, and Bruce J. Mincher, Radiolytic Degradation of Formic Acid and Formate in Aqueous Solution: Modeling the Final Stages of Organic Mineralization under Advanced Oxidation Process Conditions, Water Research, DOI: 10.1016/j.watres.2020.116314

Value of the Data

- Data used to construct a quantitative computer model for the radical-induced degradation of formic acid and formate in water that allows for predictions over a wide range of water chemistry conditions.
- Water purification professionals needing enhanced mechanistic chemistry understanding of radical chemistry to enable control of process parameters for successful treatment using Advanced Oxidative Processes.

- A combined experimental/computational model approach developed from these data can be expanded to additional organic contaminants of interest in Advanced Oxidative Process treatment.
- These data are of value to all investigations into the effect of radiation chemistry on organic compounds in fields as diverse as nuclear fuel reprocessing, formation of interstellar organic species, and photolysis of atmospheric aerosols and surface waters.

1. Data Description

The aim of a water treatment Advanced Oxidation Process (AOP) is the complete mineralization of organic contaminants to water, carbon dioxide, carbonate species, and halide ions. The sequential oxidatative degradation of an organic molecule produces lower molecular weight organic species until formic acid and/or its conjugate base formate remain. This small carboxylic acid is the last stable organic species prior to complete mineralization and thus understanding and predicting its fundamental chemical behaviour is critical for the optimization of AOP water treatment technology.

Datasets and reaction kinetics compilations are presented for an experimental and computational gamma irradiation investigation into formic acid/formate degradation as reported by Horne *et al.* [1]. Sample vials were assessed for radiolytic gas contribution from the butyl septa comprising the crimp-cap sample vials (Table 1), and leak tested to determine the rate of molecular hydrogen (H₂) and carbon dioxide (CO₂) effusion (Tables 2 and 3, respectively). For the aqueous alkaline conditions (pH = 9.0) the concentrations of formate (Table 4) and subsequently produced oxalate (Table 5) and H₂(Table 6) are listed at all the investigated gamma radiation doses when irradiated under sealed, air-sparged, N₂-saturated, and N₂O-saturated conditions. Complementary studies under aqueous acidic conditions (pH = 1.5) were performed, and the concentrations of formic acid and subsequently produced H₂ and CO₂ are shown in Tables 7 and 8, respectively. For all irradiated acidic conditions the oxalate/oxalic acid concentrations were below the limit of experimental detection ($\sigma = 0.0001$ M). Finally, Table 9 provides a compilation of chemical reactions and associated kinetics that, when employed in combination with a standard water radiolysis model [2], may be solved using the FACSIMLE numerical algorithm (MCPA software [3]) to provide a quantitative mechanistic description for the radiation-induced chemistry underpinning the aforementioned datasets.

Table 1

Raw data for the amount of H₂ and CO₂ from the cobalt-60 gamma irradiation (~0.90 Gy min⁻¹) of empty 20 mL butyl septa crimp-cap sample vials with an air headspace as quantified by GC.

Dose (kGy)	H ₂ (ppmv)	CO ₂ (ppmv)
0	0	235.0
0	0	224.5
0.232	0	272.9
0.225	0	237.8
0.464	0	272.0
0.451	0	251.8
0.696	0	287.0
0.676	0	239.4
0.924	0	253.5
0.901	0	243.0
1.160	0	261.4
1.126	0	250.0
1.392	0	250.9
1.352	0	254.4
1.624	0	257.9
1.577	0	249.1

Table 2

Raw data for leak testing 20 mL butyl septa crimp-cap sample vials containing 4.0 mL of formic acid/formate solution from injecting known volumes of H₂ into an air headspace as quantified by GC. INV = Inverted.

Dose (kGy)	Time (hours)	H ₂ (ppmv)
0	0.00	74.3
	0.87	73.0
	2.15	72.6
	18.63	69.6
	23.67	68.8
	91.72	67.4
0.221 (INV)	0.05	71.8
	0.93	73.2
	2.20	70.8
	18.68	70.6
	23.72	67.5
	91.98	66.1
0.447	0.10	71.0
	1.00	67.8
	2.25	68.9
	18.75	72.8
	23.75	67.6
	92.05	66.3
0.467 (INV)	0.13	74.1
	1.05	73.3
	2.30	72.9
	18.80	70.3
	23.80	69.3
	92.17	68.3
0.677	0.18	72.3
	1.08	73.2
	2.35	72.5
	18.85	71.1
	23.83	72.5
	92.22	67.2
0.704 (INV)	0.23	78.2
	1.13	78.0
	2.40	76.6
	18.90	76.6
	23.87	74.7
	92.27	73.3
0.899	0.28	77.6
	1.18	76.6
	2.45	76.6
	18.95	74.8
	23.92	77.2
	92.32	73.0
0.940 (INV)	0.33	87.3
	1.23	85.4
	2.50	83.7
	19.02	82.0
	23.95	84.4
	92.37	80.6
1.125	0.37	84.1
	1.28	81.1
	2.53	83.3
	19.05	81.6
	24.00	82.0
	92.42	79.0

(continued on next page)

Table 2 (continued)

Dose (kGy)	Time (hours)	H ₂ (ppmv)
1.176 (INV)	0.42	95.2
	1.35	92.1
	2.58	94.5
	19.10	93.2
	24.03	93.0
	92.47	84.1
1.351	0.45	94.1
	1.40	90.3
	2.63	90.5
	19.15	88.8
	24.08	87.6
	92.50	87.8
1.577 (INV)	0.50	107.1
	1.45	103.2
	2.68	102.9
	19.20	100.2
	24.13	101.5
	92.55	95.0
1.648	0.57	105.3
	1.50	105.7
	2.72	102.6
	19.23	100.7
	24.17	101.5
	92.63	98.2

2. Experimental Design, Materials, and Methods

Sample Preparation. Formate/formic acid solutions were prepared gravimetrically at 1.0 mM using sodium formate (Aldrich, 99.998% trace metals basis) and HPLC-grade water (J.T. Baker). The appropriate aqueous pH=9.0 and 1.5 conditions were afforded using sodium hydroxide (Aldrich, 50 % w/w) or either perchloric (Aldrich, 99.999 % trace metals basis) or sulfuric (Aldrich, 99.999 %) acids, respectively. Each irradiation sample contained 4.0 mL of aqueous mixture sealed in 20 mL crimp-cap vial (Aldrich). The sealed condition refers to aerated samples prepared on the bench, without any additional sample conditioning. The air-sparged condition refers to aerated samples prepared on the bench but also continuously sparged with tank compressed air, regulated by a mass flow controller at 1 mL min⁻¹ during gamma irradiation. To examine deaerated or highly oxidizing conditions, samples were pre-saturated inside an equilibrated environmental chamber prior to irradiation with N₂ or N₂O, respectively. The chamber was flushed with the appropriate gas for 30 minutes prior to the preparation of all samples. Each vial was flushed to displace the O₂. The formate/formic acid solutions were sparged for 20 minutes prior to transfer and sealing of vials. This equilibration treatment lowered the average oxygen content in each vial to ≤ 0.6 %, as determined by GC. Compressed air, N₂, and N₂O were purchased in their highest available purity from Norco.

As each gamma radiation dose was delivered in quintuplet, the head space analysis for three irradiated samples was performed using GC. To minimize the diffusion of H₂ through the Teflon vial seal, GC analysis was typically performed on the same day as the irradiation experiment, or the following morning at the latest. The remaining two samples per received dose were analysed using HPLC. After head space GC analysis each sample was also analysed using HPLC.

Gamma Irradiation Parameters. A Nordion Gammacell 220E Cobalt-60 irradiator was used to irradiate the formic acid/formate samples with gamma rays (⁶⁰Co E_{γ1} = 1.17 MeV and E_{γ2} = 1.35 MeV) at ambient temperature. Samples were located in a bespoke, 13 position, cylindrical aluminium holder prior to loading into the irradiator's sample column. To account for small changes in dose rate – arising from sample positioning relative to the centreline dose rate and contributions to attenuation by the aluminium and the samples – gamma dose rates were

Table 3

Raw data for leak testing non-irradiated 20 mL butyl septa crimp-cap sample vials from injecting known volumes of CO₂ into an air headspace as quantified by GC.

Time (hours)	CO ₂ (ppmv)
0.05	9975.0
1.05	10032.1
2.67	9882.9
6.33	9637.8
24.30	9505.1
48.50	9105.2
0.10	10081.9
1.10	10378.6
2.72	9905.0
6.42	9805.5
24.37	9538.3
48.55	9713.3
0.17	10091.1
1.15	10395.2
2.77	9958.4
6.48	9779.7
24.43	9547.5
48.63	9650.7
0.20	10074.5
1.18	10048.7
2.82	9919.7
6.52	9893.9
24.50	9608.3
48.67	9595.4
0.25	9936.3
1.23	10118.8
2.87	9914.2
6.57	9698.6
24.57	9575.1
48.72	9448.0
0.30	10019.2
1.28	10061.6
2.92	9958.4
6.62	9665.4
24.62	9549.3
48.83	9239.7
0.35	10034.0
1.33	10085.6
2.98	10045.0
6.68	9916.0
24.67	9484.8
48.87	9239.7
0.40	10006.3
1.38	9949.2
3.03	9975.0
6.73	9849.7
24.72	9525.4

calculated for each of the 13 sample positions standardized using Fricke dosimetry [26]. Aerated Fricke solutions consisting of 1.0 mM iron(II) sulfate heptahydrate (FeSO₄·7H₂O, Aldrich ≥99%) in 0.4 M H₂SO₄ were irradiated in the same crimp-cap sample vials in each of 13 positions for multiple 1 min increments. At each time increment all Fricke solution samples were analysed for the product Fe(III) absorption peak at 304 nm using an Agilent Technologies (Santa Clara, CA, USA) Cary 6000i UV-vis-NIR Spectrophotometer, from which dose rate curves were generated. These measured values were subsequently corrected for ⁶⁰Co decay (⁶⁰Co τ_{1/2} = 5.27 years) for the duration of these reported experiments, affording average dose rates of 1.13 Gy min⁻¹ for

Table 4

Raw data for the concentration of formate as quantified by HPLC from the cobalt-60 gamma radiolysis ($\sim 1.13 \text{ Gy min}^{-1}$) of aqueous, pH=9.0 sodium formate solutions pre-saturated or continuously sparged with different gases.

Sealed		Air-Sparged		N_2 -Saturated		N_2O -Saturated	
Dose (kGy)	$[\text{HCO}_2^-]$ (mM)	Dose (kGy)	$[\text{HCO}_2^-]$ (mM)	Dose (kGy)	$[\text{HCO}_2^-]$ (mM)	Dose (kGy)	$[\text{HCO}_2^-]$ (mM)
0	1.021	0	1.007	0	1.016	0	1.016
0	1.025	0	1.007	0	1.011	0	1.011
0	1.018	0	1.007	0	1	0	1
0	1.028	0	1.018	0	1.004	0	1.004
0	1.02	0	0.999	0	0.997	0	0.997
0.283	0.941	0.232	0.945	0.283	0.896	0.283	0.835
0.287	0.947	0.235	0.943	0.287	0.889	0.287	0.823
0.283	0.948	0.232	0.935	0.283	0.89	0.283	0.831
0.288	0.949	0.235	0.94	0.288	0.908	0.288	0.827
0.275	0.946	0.225	0.943	0.275	0.895	0.275	0.645
0.567	0.848	0.464	0.877	0.567	0.792	0.575	0.631
0.575	0.855	0.47	0.875	0.575	0.795	0.566	0.652
0.566	0.856	0.463	0.88	0.566	0.793	0.575	0.648
0.575	0.856	0.471	0.871	0.575	0.796	0.85	0.44
0.55	0.855	0.451	0.876	0.55	0.808	0.862	0.452
0.85	0.736	0.696	0.79	0.85	0.703	0.849	0.472
0.862	0.747	0.706	0.796	0.862	0.711	0.863	0.463
0.849	0.751	0.695	0.792	0.849	0.713	1.133	0.275
0.863	0.745	0.706	0.779	0.863	0.701	1.149	0.273
0.826	0.753	0.676	0.796	0.826	0.69	1.132	0.294
1.133	0.509	0.928	0.706	1.149	0.615	1.15	0.276
1.149	0.497	0.941	0.703	1.132	0.625	1.101	0.282
1.132	0.537	0.927	0.706	1.15	0.596	1.417	0.108
1.15	0.522	0.942	0.715	1.101	0.603	1.437	0.098
1.101	0.537	0.901	0.715	1.417	0.53	1.415	0.121
1.417	0.327	1.16	0.612	1.437	0.526	1.438	0.053
1.415	0.344	1.176	0.61	1.415	0.539	1.376	0.131
1.438	0.334	1.159	0.627	1.438	0.528		
1.376	0.344	1.177	0.614	1.376	0.528		
1.7	0.213	1.127	0.634	1.7	0.439		
1.724	0.211	1.392	0.519	1.724	0.442		
1.698	0.219	1.411	0.511	1.698	0.437		
1.725	0.217	1.39	0.545	1.725	0.44		
1.651	0.226	1.413	0.525	1.651	0.447		
1.983	0.111	1.352	0.525	1.983	0.329		
2.012	0.116	1.624	0.396	2.012	0.329		
1.981	0.124	1.647	0.429	1.981	0.335		
2.013	0.12	1.622	0.456	2.013	0.336		
1.926	0.125	1.648	0.426	1.926	0.335		
		1.577	0.451				

formate samples and 0.90 Gy min^{-1} for formic acid samples. Fricke solution irradiations were run in triplicate, and formic acid/formate sample irradiations in quintuplicate.

High Performance Liquid Chromatography (HPLC). Quantification of all carboxylic acids (formic acid/formate and oxalic acid/oxalate) was performed by HPLC using a Waters Alliance e2695 separations module with a Waters photodiode array (PDA) detector. The analysis was carried out on a BioRad Aminex HPX-87H column ($300 \text{ mm} \times 7.8 \text{ mm}$, $5 \mu\text{m}$ particle size). The method used $0.022 \text{ M H}_2\text{SO}_4$ in water as the mobile phase, with a flow rate of 0.6 mL min^{-1} and a column temperature of $35 \text{ }^\circ\text{C}$. The chromatographic conditions ensured reproducible retention times of $14.0 \pm 0.2 \text{ min}$ for formic acid/formate, $6.5 \pm 0.1 \text{ min}$ for oxalic acid/oxalate. The PDA measurements were extracted from the 210 nm channel using retention times and peak heights compared to standards.

Standard solutions of sodium formate (Sigma Aldrich 99.998% trace metals basis) were prepared in HPLC grade water at 3.0, 2.0, 1.0, 0.5, and 0.1 mM concentrations. The HPLC analysis of

Table 5

Raw data for the concentration of oxalate as quantified by HPLC from the cobalt-60 gamma radiolysis ($\sim 1.13 \text{ Gy min}^{-1}$) of aqueous, pH=9.0 sodium formate solutions pre-saturated or continuously sparged with different gases. ND=Not Detected.

Sealed		Air-Sparged		N ₂ - Saturated		N ₂ O- Saturated	
Dose (kGy)	[oxalate] (mM)	Dose (kGy)	[oxalate] (mM)	Dose (kGy)	[oxalate] (mM)	Dose (kGy)	[oxalate] (mM)
0	ND	0	ND	0	ND	0	ND
0	ND	0	ND	0	ND	0	ND
0	ND	0	ND	0	ND	0	ND
0	ND	0	ND	0	ND	0	ND
0	ND	0	ND	0	ND	0	ND
0.283	0.035	0.232	0.028	0.283	0.034	0.065	0.283
0.287	0.033	0.235	0.025	0.287	0.037	0.064	0.287
0.283	0.033	0.232	0.027	0.283	0.033	0.062	0.283
0.288	0.034	0.235	0.028	0.288	0.041	0.059	0.288
0.275	0.033	0.225	0.029	0.275	0.032	0.125	0.567
0.567	0.04	0.464	0.038	0.567	0.067	0.124	0.575
0.575	0.04	0.47	0.034	0.575	0.063	0.121	0.566
0.566	0.039	0.463	0.031	0.566	0.063	0.124	0.575
0.575	0.04	0.471	0.032	0.575	0.066	0.183	0.85
0.55	0.04	0.451	0.03	0.55	0.064	0.189	0.862
0.85	0.05	0.696	0.036	0.85	0.096	0.176	0.849
0.862	0.047	0.706	0.034	0.862	0.1	0.183	0.863
0.849	0.047	0.695	0.032	0.849	0.099	0.241	1.133
0.863	0.047	0.706	0.036	0.863	0.093	0.24	1.149
0.826	0.061	0.676	0.036	0.826	0.091	0.239	1.132
1.133	0.058	0.928	0.024	1.149	0.127	0.242	1.15
1.149	0.058	0.941	0.039	1.132	0.127	0.234	1.101
1.132	0.062	0.927	0.021	1.15	0.125	0.291	1.417
1.15	0.059	0.942	0.023	1.101	0.117	0.292	1.437
1.101	0.06	0.901	0.038	1.417	0.146	0.28	1.415
1.417	0.077	1.16	0.04	1.437	0.147	0.142	1.438
1.415	0.073	1.176	0.037	1.415	0.148	0.285	1.376
1.438	0.074	1.159	0.03	1.438	0.149	0.313	1.7
1.376	0.07	1.177	0.02	1.376	0.145	0.31	1.724
1.7	0.112	1.127	0.038	1.7	0.169	0.304	1.698
1.724	0.112	1.392	0.041	1.724	0.17	0.311	1.725
1.698	0.109	1.411	0.039	1.698	0.167	0.305	1.651
1.725	0.107	1.39	0.038	1.725	0.172	0.309	1.983
1.651	0.106	1.413	0.02	1.651	0.17	0.293	2.012
1.983	0.144	1.352	0.039	1.983	0.208	0.293	1.981
2.012	0.139	1.624	0.046	2.012	0.193	0.305	2.013
1.981	0.137	1.647	0.037	1.981	0.202	0.299	1.926
2.013	0.139	1.622	0.036	2.013	0.21		
1.926	0.125	1.648	0.018	1.926	0.2		
		1.577	0.041				

each standard solution was performed in triplicate. Using peak height parameters, the average PDA response was correlated with sodium formate concentration to produce a calibration curve utilized during the quantification of formate in the irradiated samples. The relative standard deviation (RSD) for the peak height measurement was less than 1% for each concentration. Fresh standards were prepared and analysed prior to the quantification of each experimental sample series.

Gas Chromatography (GC). A series of gas generation and diffusivity tests were performed on the butyl septa crimp-cap vials prior to analysing irradiated formic acid/formate samples. To account for the potential radiolytic formation of H₂ and CO₂ from the degradation of the butyl septa, sealed vials containing an air headspace were first irradiated to doses up to $\sim 1.6 \text{ kGy}$ and their contents analysed by GC (Table 1). After correcting for ambient air CO₂ concentration, the values in Table 1 were used to correct gas data gathered from irradiated formic acid/formate

Table 6

Raw data for the volume of H₂ as quantified by GC from the cobalt-60 gamma radiolysis (~1.13 Gy min⁻¹) of aqueous, pH=9.0 sodium formate solutions pre-saturated or continuously sparged with different gases.

Sealed		N ₂ O- Saturated	
Dose (kGy)	H ₂ (μL)	Dose (kGy)	H ₂ (μL)
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0.283	0.013
0	0	0.287	0.014
0.283	0.007	0.283	0.012
0.287	0.008	0.567	0.026
0.283	0.009	0.575	0.027
0.288	0.008	0.566	0.026
0.275	0.01	0.85	0.04
0.567	0.015	0.862	0.042
0.575	0.014	0.849	0.039
0.566	0.014	1.133	0.054
0.575	0.015	1.149	0.053
0.55	0.014	1.132	0.053
0.85	0.023	1.417	0.063
0.862	0.024	1.415	0.065
0.849	0.022	1.438	0.062
0.863	0.024	1.724	0.067
0.826	0.023	1.698	0.069
1.133	0.036	1.725	0.067
1.149	0.036	2.012	0.057
1.132	0.034	1.981	0.06
1.15	0.034	2.013	0.063
1.101	0.033		
1.417	0.048		
1.415	0.047		
1.438	0.046		
1.376	0.047		
1.7	0.065		
1.724	0.066		
1.698	0.063		
1.725	0.062		
1.651	0.061		
1.983	0.079		
2.012	0.075		
1.981	0.075		
2.013	0.076		

samples, [Tables 6](#) and [8](#), respectively. Sample vial leak tests were implemented to determine the rate of effusion for H₂ and CO₂. For H₂, irradiated sample vials containing 4.0 mL of formic acid/formate solution were injected with known volumes of H₂ and allowed to equilibrate for 30 min. These vials were sampled several times over a 4-day period, covering the maximum sampling window for irradiated formic acid/formate samples, [Table 2](#). To account for the contribution of repeated puncturing of the butyl septa to effusion rate, half of the sample H₂ spiked vials were inverted after each analysis, allowing the 4.0 mL of formic acid/formate solution to cover the septa. Negligible difference in gas effusion rate was seen. For CO₂, empty pristine vials were injected with known volumes of CO₂ and allowed to equilibrate for 30 min before sampling several times over a 48 hour period, [Table 3](#).

Headspace gas of post-irradiation non-air-sparged samples was analysed for H₂ and CO₂ by GC as reported in [\[1\]](#). Certified standards (Norco, Inc.) were used for calibrations and quality control to ensure the validity of the H₂ and CO₂ calibration curves throughout the entire measurement period.

Table 7

Raw data for the concentration of formic acid as quantified by HPLC from the cobalt-60 gamma radiolysis (~ 0.90 Gy min^{-1}) of aqueous, pH = 1.5 sodium formate solutions pre-saturated or continuously sparged with different gases.

Sealed		Air-Sparged		N ₂ - Saturated		N ₂ O- Saturated	
Dose (kGy)	[HCOOH] (mM)	Dose (kGy)	[HCOOH] (mM)	Dose (kGy)	[HCOOH] (mM)	Dose (kGy)	[HCOOH] (mM)
0	1	0	1.007	0	1.023	0	0.979
0	1.02	0	1.019	0	1.019	0	0.98
0	1.02	0	1.008	0	1.008	0	0.984
0	1.03	0	0.998	0	1.009	0	0.981
0	1	0	0.997	0.287	0.907	0.283	0.867
0.38	0.903	0.38	0.922	0.283	0.902	0.287	0.854
0.38	0.919	0.38	0.917	0.288	0.921	0.283	0.855
0.367	0.917	0.367	0.92	0.275	0.939	0.288	0.857
0.372	0.917	0.372	0.906	0.575	0.792	0.275	0.857
0.377	0.922	0.377	0.905	0.566	0.814	0.567	0.745
0.76	0.812	0.759	0.82	0.575	0.875	0.575	0.75
0.76	0.816	0.76	0.844	0.55	0.88	0.566	0.741
0.734	0.825	0.734	0.811	0.862	0.726	0.575	0.726
0.745	0.839	0.744	0.811	0.849	0.721	0.55	0.74
0.754	0.832	0.754	0.816	0.863	0.793	0.85	0.64
1.14	0.577	1.139	0.74	0.826	0.803	0.862	0.616
1.14	0.574	1.14	0.708	1.149	0.631	0.849	0.646
1.101	0.617	1.101	0.733	1.132	0.624	0.863	0.617
1.117	0.608	1.117	0.732	1.15	0.608	0.826	0.626
1.132	0.605	1.131	0.727	1.101	0.626	1.149	0.51
1.519	0.398	1.519	0.657	1.437	0.546	1.132	0.521
1.52	0.434	1.52	0.638	1.415	0.553	1.15	0.518
1.469	0.424	1.468	0.652	1.438	0.541	1.101	0.531
1.489	0.432	1.489	0.655	1.376	0.551	1.417	0.413
1.509	0.407	1.508	0.649	1.724	0.433	1.437	0.408
1.899	0.298	1.899	0.57	1.698	0.461	1.415	0.425
1.9	0.26	1.9	0.557	1.725	0.481	1.438	0.422
1.836	0.287	1.835	0.578	1.651	0.453	1.376	0.405
1.862	0.285	1.861	0.574	2.012	0.376	1.7	0.32
1.886	0.263	1.885	0.59	1.981	0.392	1.724	0.313
				2.013	0.393	1.698	0.319
				1.926	0.413	1.725	0.326
						1.651	0.331
						1.983	0.257
						2.012	0.239
						1.981	0.238
						2.013	0.241
						1.926	0.229

Table 8

Raw data for the volume of H₂ and CO₂ as quantified by GC from the cobalt-60 gamma radiolysis (~1.13 Gy min⁻¹) of aqueous, pH = 1.5 sodium formate solutions pre-saturated or continuously sparged with different gases.

Sealed			N ₂ - Saturated			N ₂ O- Saturated	
Dose (kGy)	H ₂ (μL)	CO ₂ (μL)	Dose (kGy)	H ₂ (μL)	CO ₂ (μL)	Dose (kGy)	H ₂ (μL)
0	0	0	0	0	0	0	0
0	0	0.002	0	0	0.001	0	0
0	0	0.003	0	0	0.002	0	0
0.38	0.007	0.04	0.379	0.046	0.036	0.305	0.026
0.38	0.006	0.032	0.379	0.046	0.04	0.305	0.026
0.367	0.007	0.03	0.366	0.045	0.039	0.295	0.023
0.76	0.015	0.062	0.758	0.094	0.071	0.61	0.044
0.76	0.016	0.07	0.759	0.092	0.071	0.61	0.044
0.734	0.016	0.07	0.733	0.092	0.07	0.59	0.044
1.14	0.032	0.165	1.137	0.147	0.119	0.915	0.057
1.14	0.033	0.145	1.138	0.148	0.111	0.915	0.061
1.101	0.028	0.149	1.099	0.133	0.12	0.884	0.059
1.519	0.053	0.194	1.517	0.192	0.166	1.22	0.079
1.52	0.056	0.215	1.517	0.207	0.158	1.22	0.079
1.469	0.052	0.195	1.466	0.184	0.156	1.179	0.076
1.899	0.104	0.274	1.896	0.239	0.172	1.525	0.089
1.9	0.086	0.233	1.897	0.256	0.174	1.526	0.092
1.836	0.081	0.241	1.832	0.26	0.192	1.474	0.086
						1.83	0.108
						1.831	0.106
						1.769	0.103
						2.063	0.106

Table 9

Formic acid/formate radiolysis chemical reaction compilation employed by the kinetic model reported by Horne *et al.* [1].

Reaction	Rate Coefficient (k)	Source
HCOOH → HCO ₂ ⁻ + H _{aq} ⁺	3.6 × 10 ⁶ s ⁻¹	Adapted from pKa = 3.77, [4]
HCO ₂ ⁻ + H _{aq} ⁺ → HCOOH	2.0 × 10 ¹⁰ M ⁻¹ s ⁻¹	Assumed diffusion-controlled, [4]
HCOOH + e _{aq} ⁻ + H ₂ O → HCO ₂ ⁻ + H ₂ + OH ⁻	1.4 × 10 ⁸ M ⁻¹ s ⁻¹	[5]
HCOOH + ·H → ·COOH + H ₂	6.8 × 10 ⁵ M ⁻¹ s ⁻¹	[6]
HCOOH + ·OH → ·COOH + H ₂ O	1.4 × 10 ⁸ M ⁻¹ s ⁻¹	[4]
HCO ₂ ⁻ + e _{aq} ⁻ + H ₂ O → ·CO ₂ ⁻ + H ₂ + OH ⁻	8.0 × 10 ³ M ⁻¹ s ⁻¹	Proposed products, [7]
HCO ₂ ⁻ + ·H → ·CO ₂ ⁻ + H ₂	2.1 × 10 ⁸ M ⁻¹ s ⁻¹	[4]
HCO ₂ ⁻ + ·OH → ·CO ₂ ⁻ + H ₂ O	2.6 × 10 ⁹ M ⁻¹ s ⁻¹	[8]
HCO ₂ ⁻ + ·O ⁻ → ·CO ₂ ⁻ + OH ⁻	1.4 × 10 ⁹ M ⁻¹ s ⁻¹	Proposed products, [9]
HCO ₂ ⁻ + ·O ₂ ⁻ → ·CO ₂ ⁻ + HO ₂ ⁻	1.0 × 10 ⁻² M ⁻¹ s ⁻¹	Proposed products, [10]
·COOH → ·CO ₂ ⁻ + H _{aq} ⁺	1.0 × 10 ⁸ s ⁻¹	Adapted from pKa = 2.3, [11]
·CO ₂ ⁻ + H _{aq} ⁺ → ·COOH	2.0 × 10 ¹⁰ M ⁻¹ s ⁻¹	Assumed diffusion-controlled [11]
·COOH + e _{aq} ⁻ + H ₂ O → HCOOH + OH ⁻	9.0 × 10 ⁹ M ⁻¹ s ⁻¹	Proposed reaction
·COOH + ·H → HCOOH	9.0 × 10 ⁹ M ⁻¹ s ⁻¹	Proposed reaction
·COOH + H ₂ O ₂ → CO ₂ + ·OH + H ₂ O	5.0 × 10 ⁷ M ⁻¹ s ⁻¹	Proposed reaction
·COOH + ·CO ₂ ⁻ → CO ₂ + HCO ₂ ⁻	1.0 × 10 ⁹ M ⁻¹ s ⁻¹	Adapted from [11]
2·COOH → CO ₂ + HCOOH	1.7 × 10 ⁹ M ⁻¹ s ⁻¹	Adapted from [11]
·CO ₂ ⁻ + e _{aq} ⁻ + H ₂ O → HCO ₂ ⁻ + OH ⁻	9.0 × 10 ⁹ M ⁻¹ s ⁻¹	[7]
·CO ₂ ⁻ + ·H → HCOOH	9.0 × 10 ⁹ M ⁻¹ s ⁻¹	Proposed reaction
·CO ₂ ⁻ + O ₂ → CO ₂ + ·O ₂ ⁻	2.4 × 10 ⁹ M ⁻¹ s ⁻¹	[12]
·CO ₂ ⁻ + H ₂ O ₂ → CO ₂ + ·OH + OH ⁻	6.0 × 10 ⁵ M ⁻¹ s ⁻¹	[7]
2·CO ₂ ⁻ → X	7.5 × 10 ⁸ M ⁻¹ s ⁻¹	[13]

(continued on next page)

Table 9 (continued)

Reaction	Rate Coefficient (k)	Source
$X \rightarrow ^-OOC-COO^-$	$1.0 \times 10^9 \text{ s}^{-1}$	Adapted from [11]
$X \rightarrow OCOCOO^{2-}$	$9.0 \times 10^9 \text{ s}^{-1}$	Adapted from [11]
$OCOCOO^{2-} \rightarrow ^-OOC-COO^-$	$1.6 \times 10^6 \text{ s}^{-1}$	Adapted from [11]
$OCOCOO^{2-} + H_{aq}^+ \rightarrow OCOCOOH^-$	$1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Assumed diffusion-controlled
$OCOCOOH^- \rightarrow OCOCOO^{2-} + H_{aq}^+$	$1.0 \times 10^6 \text{ s}^{-1}$	Adapted from [11]
$OCOCOOH^- \rightarrow CO_2 + HCO_2^-$	$1.0 \times 10^{10} \text{ s}^{-1}$	Adapted from [11]
$HOOC-COOH \rightarrow HOOC-COO^- + H_{aq}^+$	$1.1 \times 10^9 \text{ s}^{-1}$	Adapted from pKa = 1.25, [14]
$HOOC-COO^- + H_{aq}^+ \rightarrow HOOC-COOH$	$2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Assumed diffusion controlled, [14]
$HOOC-COO^- \rightarrow ^-OOC-COO^- + H_{aq}^+$	$1.1 \times 10^5 \text{ s}^{-1}$	Adapted from pKa = 4.28, [14]
$^-OOC-COO^- + H_{aq}^+ \rightarrow HOOC-COO^-$	$2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Assumed diffusion controlled, [14]
$HOOC-COOH + ^\bullet OH \rightarrow ^\bullet CO_2^- + CO_2 + H_{aq}^+$	$1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	[15]
$HOOC-COOH + e_{aq}^- + H_2O \rightarrow HOOC-C(OH)_2^\bullet + OH^-$	$2.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	[15]
$HOOC-COOH + ^\bullet H \rightarrow HOOC-C(OH)_2^\bullet$	$3.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	[15]
$HOOC-COO^- + ^\bullet OH \rightarrow ^\bullet CO_2^- + CO_2 + H_2O$	$1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	[15]
$HOOC-COO^- + e_{aq}^- + H_2O \rightarrow HOOC-C(OH)_2^\bullet + 2OH^-$	$3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[15]
$HOOC-COO^- + ^\bullet H + H_2O \rightarrow HOOC-C(OH)_2^\bullet + OH^-$	$1.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	[15]
$^-OOC-COO^- + ^\bullet OH \rightarrow ^\bullet CO_2^- + CO_2 + OH^-$	$9.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	[15]
$^-OOC-COO^- + e_{aq}^- + 3H_2O \rightarrow HOOC-C(OH)_2 + 3OH^-$	$4.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	[15]
$^-OOC-COO^- + ^\bullet H + 2H_2O \rightarrow HOOC-C(OH)_2^\bullet + 2OH^-$	$1.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	[15]
$^-OOC-COO^- + ^\bullet O_2^- + H_2O \rightarrow ^\bullet CO_2^- + CO_2 + HO_2^\bullet + OH^-$	$200 \text{ M}^{-1} \text{ s}^{-1}$	Adapted from [15]
$2HOOC-C(OH)_2^\bullet \rightarrow HOOC-COOH + HOOC-CHO$	$1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[15]
$HOOC-C(OH)_2^\bullet + O_2 \rightarrow HOOC-COOH + HO_2^\bullet$	$1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	[15]
$CO_2 + e_{aq}^- \rightarrow ^\bullet CO_2^-$	$7.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[5]
$CO_2 + ^\bullet H \rightarrow ^\bullet COOH$	$1.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	[16]
$CO_2 + ^\bullet OH \rightarrow ^\bullet CO_3^- + H_{aq}^+$	$1.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	[16]
$CO + e_{aq}^- \rightarrow CO^\bullet$	$1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[17]
$CO + ^\bullet H \rightarrow HCO^\bullet$	$1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	[18]
$CO + ^\bullet OH \rightarrow ^\bullet COOH$	$2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[19]
$CO_2 + H_2O \rightarrow HCO_3^- + H_{aq}^+$	$3.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$	[20]
$HCO_3^- + H_{aq}^+ \rightarrow CO_2 + H_2O$	$2.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	[20]
$CO_2 + OH^- \rightarrow HCO_3^-$	$2.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	[20]
$HCO_3^- \rightarrow CO_2 + OH^-$	$9.7 \times 10^{-5} \text{ s}^{-1}$	[20]
$CO_3^{2-} + H_{aq}^+ \rightarrow HCO_3^-$	$5.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	[20]
$HCO_3^- \rightarrow CO_3^{2-} + H_{aq}^+$	59.4 s^{-1}	[20]
$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$	$6.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[20]
$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$	$3.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	[20]
$HCO_3^- + ^\bullet CO_2^- \rightarrow ^\bullet CO_3^- + HCO_2^-$	$2.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	[21]
$HCO_3^- + ^\bullet OH \rightarrow ^\bullet CO_3^- + H_2O$	$8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	[4]
$CO_3^{2-} + ^\bullet OH \rightarrow ^\bullet CO_3^- + OH^-$	$3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	[4]
$^\bullet CO_3^- + ^\bullet O_2^- \rightarrow CO_3^{2-} + O_2$	$6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	[22]
$^\bullet CO_3^- + ^\bullet OH \rightarrow CO_2 + HO_2^-$	$3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[23]
$^\bullet CO_3^- + ^\bullet CO_2^- \rightarrow CO_3^{2-} + CO_2$	$5.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	[21]
$^\bullet CO_3^- + HO_2^- \rightarrow HCO_3^- + ^\bullet O_2^-$	$3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	[24]
$^\bullet CO_3^- + ^\bullet CO_3^- \rightarrow ^\bullet CO_2^- + ^\bullet CO_2^- + O_2$	$1.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Proposed products, [25]
$^\bullet CO_3^- + HCO_2^- \rightarrow HCO_3^- + ^\bullet CO_2^-$	$1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	[21]
$^\bullet CO_3^- + H_2O_2 \rightarrow HCO_3^- + ^\bullet HO_2$	$4.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	[21]

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have, or could be perceived to have, influenced the work reported in this article.

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