Title: A Kinetic Approach for Investigating the "Microwave Effect":Decomposition of Aqueous Potassium Persulfate

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Calibration Procedure of the Microwave Power Output:

According to the standard method (IEC/EN 60705)[37], empty flask (pyrex) container was weighed, filled with 1000 g of distilled water at the initial temperature of 10±0.5°C, and placed into the microwave (MW) reactor cavity. MW energy was supplied at 1000W. The water was stirred along the heating period by a magnetic stirrer at 160 rpm. After 60s, the final temperature of water load was measured by both FO and IR sensors. The energy balance is given by Eq. (1)[38, 39] in this section:

$$P = \frac{c_{pw}.m_w(T_2 - T_1) + c_{pc}.m_c(T_2 - T_1) + c_{pm}.m_m(T_2 - T_1)}{t} \tag{1}$$

Where; P: test power (W), m_w :mass of water (g), c_{pw} :specific heat capacity of water = 4.187 $Jg^{-1}°C^{-1}$, m_c :mass of container (g), c_{pc} :specific heat capacity of container = 0.750 $Jg^{-1}°C^{-1}$, m_m: mass of magnet (g), c_{pm} :specific heat capacity of magnet = 0.465 $Jg^{-1}°C^{-1}$, t: heating time = 60 s T_1: initial temperature of water (10±0.5°C) , T_2: final temperature of water.

The power test was further performed with a set of flasks of volume between 100 cm^3 and 1000 cm^3. Following the same procedure, a known amount of water at the initial temperature of 10±0.5°C was placed into the cavity and MW energy was supplied for 60s. The applied nominal power (P_{nom}), was chosen so that the final temperature of the water load was near the ambient temperature to minimize heat losses and to apply Eq.(1) without any heat losses term for the calculation of the test power P. The load curve[38-39] presenting the test power as a function of load size for flask containers is shown in supp.info.Figure 1. To account for the differences between the absorbed and nominal power values, a correction factor is defined as

$$p = P / P_{nom} \quad (2)$$

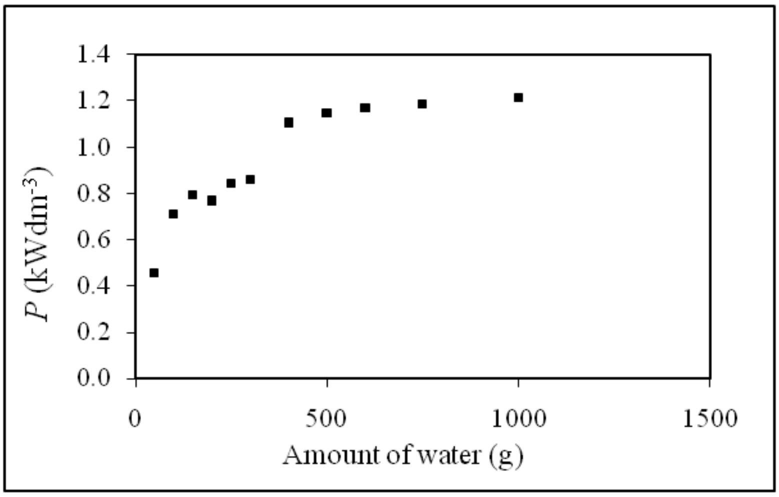

Figure 1. Load curve for flask containers

Average P_{nom} of each run was calculated as follows; the initial two minutes was not taken into account in the calculations by considering the transient state of the system to reach the steady state of constant temperature and MW power. From this point, local P_{nom} values recorded at one second time intervals until the end of the experiment were arithmetically averaged to obtain an initial estimate. Then, a statistical test was performed to detect outliers (high or low P_{nom} values due to uncontrolled disturbances) by considering their deviation from the mean value. These were removed from the data and the arithmetic mean value was recalculated as the final average P_{nom}. This was multiplied by p value (0.768 for our experimental system) to finally obtain P.

Calibration Procedure of UV:

For calibration of UV, aqueous solutions of K_2SO_4 and $K_2S_2O_8$ of various concentrations were scanned between 190 and 260 nm using a UV-Vis spectrophotometer (Perkin-Elmer, Lamda–35), as shown in supp.info.Figure 2. Calibration curves were drawn at different wavelengths, as shown in supp.info.Figure 3. The highest correlation (R^2 = 0.9994) was obtained with wavelength of 215 nm and molar absorptivities at this wavelength were calculated as $\varepsilon_1 = 0.3019$ $mM^{-1}cm^{-1}$ for $K_2S_2O_8$ and $\varepsilon_2 = 0.0030$ $mM^{-1}cm^{-1}$ for K_2SO_4 (shown in Supp. Info. Table 1). During the runs, the absorbance was measured at intervals of 6 seconds (in order to minimize random fluctuations in absorbance values), and approximately 200 absorbance-time data points were recorded. A typical experimental plot at 215 nm is shown in supp.info. Figure 4.

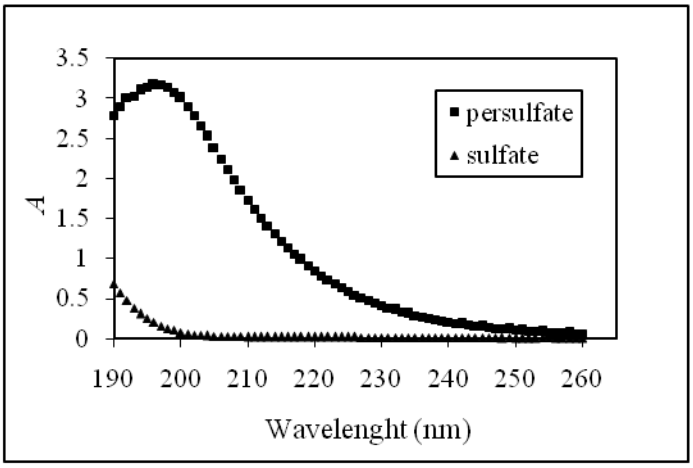

Figure 2. UV spectra of $K_2S_2O_8$ (4mM) and K_2SO_4 (8mM) between 190 - 260 nm

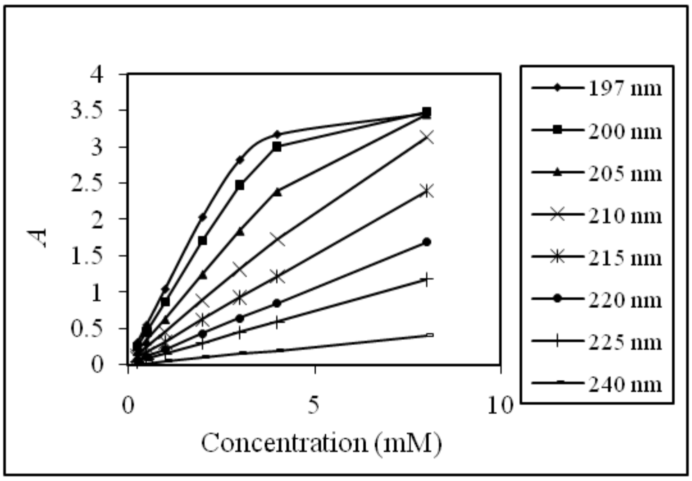

Figure 3. Calibration curves of $K_2S_2O_8$ between 190 -260 nm

Supp. Info. Table 1. Molar absorptivities of $K_2S_2O_8$ and K_2SO_4 between 190 and 260 nm.

Wavelength(nm)	ε_1	ε_2	R^2 (curves of $K_2S_2O_8$)
197	0.5765	0.0240	0.5690
200	0.5502	0.0120	0.7268
205	0.4874	0.0040	0.9258
210	0.4067	0.0030	0.9934
215	**0.3019**	**0.0030**	**0.9994**
220	0.2119	0.0030	0.9996
225	0.1425	0.0030	0.9994
240	0.0517	0.0010	0.9985

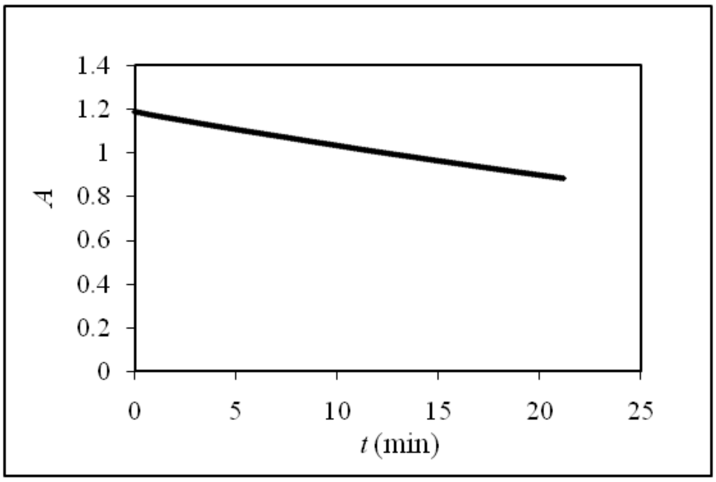

Figure 4. Experimental plot for MW-assisted decomposition of $K_2S_2O_8$ at 215nm

(Experiment no 5 in Supp. Info. Table 2)

Supp. Info.Table 2. Microwave Experimental Data

Exp . no	flow rate (cm^3min^{-1})	t (min)	T (^oC)	P ($kWdm^{-3}$)	k_{mw} 10^{-4} (s^{-1})	R^2
1	9.5	20.9	92.0	0.221	4.883	0.9989
2	9.5	20.6	90.9	0.217	4.255	0.9996
3	9.5	21.0	88.2	0.224	3.017	0.9999
4	9.5	22.8	87.8	0.244	2.832	0.9997
5	**9.5**	**21.2**	**85.8**	**0.196**	**2.422**	**0.9999**
6	9.5	21.1	81.0	0.184	1.277	0.9995
7	9.5	180.0	79.4	0.262	0.785	0.9995
8	9.5	56.0	76.2	0.195	0.615	0.9997
9	9.5	44.4	75.0	0.213	0.596	0.9998
10	9.5	53.9	71.1	0.212	0.329	0.9994
11	17.0	22.3	69.8	0.379	0.272	0.9989
12	17.0	21.5	74.6	0.355	0.493	0.9988
13	17.0	19.8	79.8	0.379	1.006	0.9999
14	17.0	22.3	84.4	0.427	1.812	0.9992

15	17.0	20.3	86.6	0.446	2.257	0.9983
16	17.0	19.3	89.0	0.521	3.110	0.9994
17	17.0	20.1	91.4	0.487	4.390	0.9982
18	21.0	19.1	69.8	0.399	0.196	0.9970
19	21.0	19.8	74.6	0.438	0.418	0.9972
20	21.0	19.6	79.4	0.469	0.896	0.9993
21	21.0	20.5	84.2	0.547	1.614	0.9982
22	21.0	20.2	86.1	0.528	2.160	0.9972
23	21.0	18.0	89.0	0.584	2.923	0.9967
24	21.0	20.6	90.6	0.604	3.745	0.9974
25	6.0	18.3	70.6	0.164	0.356	0.9991
26	6.0	19.7	75.4	0.188	0.576	0.9996
27	6.0	20.2	80.2	0.207	1.105	0.9996
28	6.0	21.0	85.8	0.204	2.178	0.9999
29	6.0	20.1	87.4	0.223	2.667	0.9988
30	6.0	20.0	90.6	0.236	3.898	0.9995
31	6.0	20.9	92.3	0.211	5.383	0.9997
32	13.5	18.5	69.8	0.307	0.280	0.9971
33	13.5	18.9	75.4	0.303	0.516	0.9994
34	13.5	19.0	80.0	0.373	0.945	0.9982
35	13.5	20.3	84.8	0.383	1.870	0.9993
36	13.5	20.5	86.6	0.392	2.410	0.9999
37	13.5	19.7	89.8	0.399	3.542	0.9998
38	3.5	21.4	75.4	0.141	0.425	0.9993
39	3.5	20.6	80.3	0.155	1.186	0.9996
40	3.5	20.7	85.0	0.202	1.943	0.9975
41	3.5	19.2	90.1	0.206	3.445	0.9997
42	3.5	19.2	92.2	0.221	4.578	0.9996

43	11.0	21.1	84.2	0.311	1.910	0.9997
44	8.0	20.3	89.8	0.283	3.352	0.9993
45	25.0	18.1	73.5	0.452	0.451	0.9992
46	9.0	18.9	89.8	0.299	3.428	0.9996
47	16.0	18.9	88.6	0.430	3.020	0.9995
48	19.0	18.6	78.6	0.435	0.796	0.9997
49	12.0	18.8	77.5	0.307	0.835	0.9997
50	11.5	19.3	82.4	0.319	1.383	0.9989
51	25.0	19.0	76.2	0.499	0.608	0.9977
52	25.0	19.3	80.2	0.507	1.114	0.9995
53	3.0	19.4	88.2	0.181	2.987	0.9990
54	7.0	19.6	77.8	0.222	0.872	0.9998
55	5.0	19.1	83.4	0.203	1.571	0.9999
56	3.0	21.0	83.4	0.145	1.556	0.9999
57	5.0	21.7	77.5	0.158	0.678	0.9982
58	7.0	19.9	73.2	0.154	0.398	0.9989
59	3.0	17.9	80.3	0.146	1.091	0.9999
60	3.0	18.7	73.6	0.131	0.459	0.9981
61	3.0	18.6	70.6	0.129	0.301	0.9977
62	3.0	18.0	74.6	0.135	0.470	0.9962
63	3.0	18.0	70.6	0.133	0.293	0.9945
64	35.0	23.0	70.0	0.513	0.270	0.9916
65	35.0	20.5	70.0	0.501	0.244	0.9985
66	35.0	20.1	86.8	0.709	2.680	0.9996
67	35.0	20.1	86.9	0.689	2.855	0.9994
68	35.0	21.1	86.8	0.755	2.533	0.9996
69	35.0	20.3	86.8	0.715	2.628	0.9996
70	32.0	20.1	87.1	0.654	2.787	0.9999

71	35.0	21.1	77.2	0.570	0.725	0.9999
72	35.0	19.9	77.1	0.581	0.747	0.9998
73	35.0	20.8	77.2	0.557	0.781	0.9992
74	5.0	19.5	88.4	0.229	3.022	0.9996
75	5.0	19.0	88.4	0.224	3.075	0.9990
76	5.0	19.1	88.4	0.225	3.152	0.9993
77	5.0	18.0	66.8	0.142	0.182	0.9977
78	5.0	22.0	88.4	0.233	2.985	0.9993
79	35.0	20.5	86.8	0.768	2.627	0.9996
80	35.0	18.6	76.4	0.581	0.572	0.9968
81	5.0	20.3	75.6	0.149	0.635	0.9880
82	35.0	22.2	76.4	0.609	0.573	0.9994
83	5.0	21.9	75.6	0.148	0.604	0.9989
84	10.0	18.0	69.6	0.098	0.413	0.9944
85	35.0	25.5	82.0	0.661	1.615	0.9999
86	35.0	24.3	85.2	0.689	2.185	0.9997

Supp. Info.Table 3. Thermal (Conventional) Experimental Data

Exp. no	flow rate (cm^3min^{-1})	*t* (min)	*T* (^oC)	$k_{th}.10^{-4}$ (s^{-1})	R^2
1	9.5	19.5	58.0	0.053	0.9742
2	9.5	27.2	60.5	0.077	0.9782
3	9.5	23.3	65.5	0.129	0.9855
4	9.5	27.6	69.6	0.209	0.9862
5	9.5	30.0	75.5	0.437	0.9952
6	9.5	30.0	80.5	0.689	0.9959
7	9.5	20.0	88.7	2.000	0.9996
8	9.5	33.0	85.1	1.467	0.9997

Supp. Info.Table 4. Experimental Data for Mathematical Modeling

Exp. no	$10^3/T$ (K^{-1})	P ($kWdm^{-3}$)	$k.10^{-4}$ (s^{-1})
1	2.7673	0.224	3.017
2	2.7707	0.244	2.832
3	2.7858	0.196	2.422
4	2.8236	0.184	1.277
5	2.8624	0.195	0.615
6	2.8721	0.213	0.596
7	2.9048	0.212	0.329
8	2.9158	0.379	0.272
9	2.8755	0.355	0.493
10	2.8334	0.379	1.006
11	2.7965	0.427	1.812
12	2.7796	0.446	2.257
13	2.7612	0.521	3.110
14	2.9158	0.399	0.196
15	2.8755	0.438	0.418
16	2.8364	0.469	0.896
17	2.7983	0.547	1.614
18	2.7833	0.528	2.160
19	2.7612	0.584	2.923
20	2.7491	0.604	3.745
21	2.9090	0.164	0.356
22	2.8689	0.188	0.576
23	2.8299	0.207	1.105
24	2.7858	0.204	2.178
25	2.7735	0.223	2.667

26	2.7491	0.236	3.898
27	2.9158	0.307	0.280
28	2.8689	0.303	0.516
29	2.8312	0.373	0.945
30	2.7936	0.383	1.870
31	2.7796	0.392	2.410
32	2.7551	0.399	3.542
33	2.8689	0.141	0.425
34	2.8294	0.155	1.186
35	2.7920	0.202	1.943
36	2.7532	0.206	3.445
37	2.7370	0.221	4.578
38	2.7983	0.311	1.910
39	2.7551	0.283	3.352
40	2.8847	0.452	0.451
41	2.7551	0.299	3.428
42	2.7646	0.430	3.020
43	2.8428	0.435	0.796
44	2.8514	0.307	0.835
45	2.8122	0.319	1.383
46	2.8624	0.499	0.608
47	2.8300	0.507	1.114
48	2.7673	0.181	2.987
49	2.8493	0.222	0.872
50	2.8048	0.203	1.571
51	2.8046	0.145	1.556
52	2.8518	0.158	0.678
53	2.8874	0.154	0.398

54	2.8290	0.146	1.091
55	2.8840	0.131	0.459
56	2.9090	0.129	0.301
57	2.8755	0.135	0.470
58	2.9090	0.133	0.293
59	2.9141	0.513	0.270
60	2.9141	0.501	0.244
61	2.7781	0.709	2.680
62	2.7781	0.755	2.533
63	2.7781	0.715	2.628
64	2.8542	0.570	0.725
65	2.8549	0.581	0.747
66	2.8542	0.557	0.781
67	2.7660	0.229	3.022
68	2.7658	0.224	3.075
69	2.7658	0.225	3.152
70	2.9415	0.142	0.182
71	2.7658	0.233	2.985
72	2.7781	0.768	2.627
73	2.8607	0.581	0.572
74	2.8673	0.149	0.635
75	2.8607	0.609	0.573
76	2.8673	0.148	0.604
77	2.9175	0.098	0.413
78	2.8156	0.661	1.615
79	2.7905	0.689	2.185
80	3.0197	0.000	0.053
81	2.9971	0.000	0.077

82	2.9528	0.000	0.129
83	2.9175	0.000	0.209
84	2.8681	0.000	0.437
85	2.8276	0.000	0.689
86	2.7635	0.000	2.000
87	2.7913	0.000	1.467