# Electronic Supplementary Information (ESI) for "Chemical equilibria in the uranyl(VI) – peroxide – carbonate system; identification of precursors for the formation of polyperoxometallates".

Pier Luigi Zanonato, Plinio Di Bernardo, Z. Szabò and Ingmar Grenthe

			Cup (	mM)	Titrant (mM)				
N	V <sub>0</sub> (mL)	$UO_2^{2+}$	$H_2O_2$	$\mathrm{H}^+$	$CO_3^{2-}$	$H_2O_2$	$CO_{3}^{2-}$	$\mathrm{H}^+$	
1	66.6	33.67	0.00	0.411	0.0	409.4	0.0	0.0	
2	60.0	7.14	35.8	3.68	20.27	0.0	241.5	0.0	
3	76.7	4.20	2.20	0.340	12.49	0.0	241.5	0.0	
4	86.2	3.71	3.91	0.316	11.13	0.0	241.5	0.0	
5	81.1	4.63	0.0	0.036	18.50	55.7	20.3	0.0	
6	93.2	2.38	0.0	0.12	9.30	55.7	20.4	0.0	
7	104.9	1.51	0.0	0.091	5.86	41.7	15.6	0.0	
8	109.0	1.14	0.0	0.293	4.41	41.4	15.8	0.0	
9	109.6	0.61	0.0	0.062	2.23	46.85	8.00	0.0	
10	111.3	1.99	0.0	-0.154	12.25	58.9	0.0	0.0	
11	134.5	2.42	2.50	0.317	7.38	0.0	241.5	0.0	
12	116.4	1.35	2.03	0.394	4.24	0.0	241.5	0.0	
13	117.6	14.94	0.0	0.441	168.4	409.4	0.0	0.0	
14	39.0	8.27	1.10	-1.14	21.68	53.11	0.0	-51.44	
15	104.9	0.427	0.0	0.14	1.67	58.9	0.0	0.0	
16	148.2	0.216	0.0	-0.034	0.838	58.9	0.0	0.0	
17	60.5	29.13	0.0	0.685	79.87	371.3	0.0	-48.75	
18	53.5	32.59	0.0	0.933	89.21	277.3	0.0	-168.7	
19	53.5	32.59	0.0	0.933	89.21	373.6	0.0	-45.77	

Table S1. Test solutions used in the potentiometric titrations at 0 °C.

			Tit	trant (mM	[)				
N	V <sub>0</sub> (mL)	UO <sub>2</sub> <sup>2+</sup>	$H_2O_2$	CO <sub>3</sub> <sup>2-</sup>	$\mathrm{H}^{+}$	$H_2O_2$	CO <sub>3</sub> <sup>2-</sup>	$\mathrm{H}^{+}$	
1	30.9	9.94	0	249.0	2.97	400.7	0	0	
2	38.1	11.18	0	96.98	5.03	246.8	0	0	
3	27.6	7.52	0	44.42	4.31	246.8	0	0	
4	70.5	30.15	0	166.8	2.07	246.8	0	0	
5	28.9	4.28	0	21.22	2.70	246.8	0	0	
6	56.0	15.24	0	73.10	0.21	246.8	0	0	
7	32.1	13.28	0	62.06	4.25	246.8	0	0	
8	27.2	8.48	9.08	35.93	-7.56	0	0	-49.8	
9	27.3	8.52	8.60	36.01	-5.27	0	0	-49.8	
10	94.4	45.97	0	184.0	4.91	246.8	0	0	
11	37.1	23.05	0	86.91	8.49	246.8	0	0	
12	30.3	9.64	9.68	32.42	-0.63	0	0	-520	
13	27.2	18.65	18.77	60.80	7.17	0	247.2	0	
14	25.2	10.08	10.32	32.53	6.71	0	247.2	0	
15	70.1	30.26	0	97.05	2.05	246.8	0	0	
16	39.4	15.19	16.17	47.08	-0.58	0	0	-520	
17	29.1	20.29	2.16	62.84	-1.30	55.1	0	0	
18	38.6	15.29	15.20	47.29	-0.97	0	0	-520	
19	27.0	7.27	1.18	22.17	-1.26	55.1	0	0	
20	28.2	7.00	0	21.31	-1.57	55.1	0	0	
21	31.8	6.21	5.69	18.90	-0.98	0	0	-520	
22	25.1	5.72	5.71	17.32	2.60	0	247.2	0	
23	23.5	2.88	3.10	8.713	1.38	0	247.2	0	

					_
Table S2	. Test solutions	used in the	potentiometric	titrations	at 25 °C.

24	40.8	14.53	14.96	43.85	-1.43	0	0	-520
25	53.0	21.60	0	250.8	7.46	423.7	0	0
26	85.0	7.50	0	73.19	0.05	60.96	0	0
27	25.0	44.04	0	182.6	4.41	0	423.7	0

**Table S3.** Equilibrium constants for the binary and ternary U(VI) complexes that do not contain peroxide. Only the equilibrium constants denoted with a star are required in the modeling of the uranyl(VI) – peroxide – carbonate system. These values were kept constant at the values given in the table during the minimation process. The other species do not influence the speciation. The equilibrium constants within parentheses refer to 0 °C, the remaining ones to 25 °C. The components are given in the order UO<sub>2</sub><sup>2+</sup>, H<sub>2</sub>O<sub>2</sub>, CO<sub>3</sub><sup>2-</sup>, H<sup>+</sup>. The values denoted by ‡ have been determined separately in the present study.

Complex	Notation	log β
0, 0,0, -1*	$pK_W$	$-13.72(-14.67 \pm 0.02 \ddagger)$
0, 1, 0, -1	$HO_2^-$	$-11.29(-11.83 \pm 0.01 \ddagger)$
2, 0, 0, -2	$(UO_2)_2(OH)_2^{2+}$	-6.07
1, 0, 0, -3	$UO_2(OH)_3$	-19.69
0, 0, 1, 2*	$H_2CO_3$	$15.60~(16.47\pm0.05\ddagger)$
0, 0, 1, 1*	HCO <sub>3</sub> <sup>-</sup>	$9.69~(9.945\pm0.01\ddag)$
1, 0, 1, 0	$UO_2CO_3$	8.57
1, 0, 2, 0	$UO_2(CO_3)_2^{2-1}$	14.93
1, 0, 3, 0*	$UO_2(CO_3)_3^{4-}$	21.76 (22.30)
3, 0, 6, 0	$(UO_2)_3(CO_3)_6^{-6-1}$	53.82
2, 0, 1, -3	$(UO_2)_2(CO_3)(OH)_3$ -	-1.89
1, 1, 0, -2	$UO_2(O_2)(OH)^-$	-2.67
2, 2, 0, -3	$(UO_2)_2(O_2)(OH)^-$	7.16

**Table S4**. NMR experiments by increasing the total peroxide concentration measured at 0  $^{\circ}$ C at approximately constant pH of 8.8. By using the <sup>17</sup>O peak integrals the concentrations of the complexes with known ratio uranium: carbonate (denoted *p*:*r* in the main text) can be calculated. A distribution diagram based on these experiments is shown in the main text, Figure 3b.

				Concentration based on 170 NMR Integral mM				Uranyl fraction %					
[UO22+]tot mM	[CO32-]tot mM	[peroxide]tot mM	[CO32-]coord. mM	Α	В	C	D	E	Α	В	С	D	E
33.8	130.7	22	64.4	0	25.5	1.2	5.5	1.6	0	79.19	3.73	17.08	4.97
32.2	124.3	36	43.7	18.7	10.4	0.86	2.2	0	58.15	32.34	2.67	6.84	0
30.6	113.3	48.6	34.9	23.8	4.32	1.28	1.15	0	77.91	14.14	4.19	3.76	0
29.3	108.4	60	31.5	24.8	3	0.86	0.63	0	84.67	10.24	2.94	2.15	0
28	103.8	70	29.3	24.6	1.9	0.92	0.6	0	87.79	6.78	3.28	2.14	0
26.9	99.6	79.4	27.7	24.2	1.35	1.1	0.34	0	89.66	5	4.08	1.26	0

**Table S 5**. NMR experiments at 0  $^{\circ}$ C where the pH varies; by using the  $^{17}$ O peak integrals the concentrations of the complexes with known ratio uranium: carbonate (denoted *p*:*r* in the main text) can be calculated. The values in bold refer a sample with increased peroxide concentration. A distribution diagram based on these experiments is shown in the main text, Figure 3a.

					Concentration based on 170 NMR Integral mM						Ura	nyl fracti	on %							
[UO22+]tot mM	[CO32-]tot mM	[peroxide]tot mM	[CO32-]coord. mM	pH (meas.)	Α	В	С	D	Ε	F	G	н	Α	В	С	D	Ε	F	G	н
34.8	151.8	39.2	53.6	8.88	14.2	11.2	4.1	3.7	0	0	1.1	0	41.4	32.65	11.95	10.79	0	0	3.21	0
34.4	150.1	38.7	52.1	9.2	13.3	9.7	6.2	2.6	0	0	1.6	0	39.82	29.04	18.56	7.78	0	0	4.79	0
33.3	145.2	37.5	51.8	9.7	9.4	6	11.5	3.2	0	0.8	2.4	0	28.23	18.02	34.53	9.61	0	2.4	7.21	0
32.4	141.3	36.5	50.5	10.2	6.2	3.7	14.6	3.1	0	1.8	2.8	0	19.25	11.49	45.34	9.63	0	5.59	8.7	0
31.6	137.6	35.5	46.9	10.9	2.9	2.6	17.5	3.2	0	2.4	2.9	0	9.21	8.25	55.56	10.16	0	7.62	9.21	0
27.3	119.1	67.6	27.5	10.2	0	0	8.9	0.7	0	11.6	0	6.1	0	0	32.6	2.56	0	42.49	0	22.34

	-1, 1, 4, -2	-1, 1, 1, -2	-1, 1, 2, -2	-2, 1, 2, -2	-2, 2, 1, -4	5, 5, 5, -10
1 1 1 2	0.740					
1, 1, 1, -2	0.740					
1, 1, 2, -2	0.986	0.801				
	0.07.6	0.710	0.040			
2, 1, 2, -2	0.956	0.710	0.940			
2, 2, 1, -4	0.909	0.894	0.955	0.850		
5, 5, 5, -10	0.887	0.819	0.939	0.840	0.968	
	1			1		1

**Table S6.** Correlation matrix for the different complexes in the "best" model selected from the potentiometric data.



**Figure S1.** The pH dependence of the <sup>13</sup>C-NMR spectra measured in the ternary uranylcarbonate-peroxide system at 273 K. The total uranium(VI) and carbonate concentrations are changing between 34.8 and 31.6 mM, and 152 and 138 mM, respectively. The total peroxide concentration is changing between 39 and 35.5 mM. The spectrum at the top was recorded after increasing the total peroxide concentration to 67.6 mM. The notation of the different peaks is given in the main text.



**Figure S2.** The peroxide concentration dependence of the <sup>17</sup>O-NMR spectra measured in the ternary uranyl-carbonate-peroxide system at 273 K. The total uranium(VI) and carbonate concentrations are changing between 33.8 and 27 mM, and 131 and 100 mM, respectively. The total peroxide concentration is increased gradually from bottom to top between 22 and 79 mM. The pH of the samples was approximately constant at a value of 8.8.



**Figure S3.** The peroxide concentration dependence of the  ${}^{13}$ C NMR spectra measured in the ternary uranyl-carbonate-peroxide system at 273 K. The total uranium(VI) and carbonate concentrations are changing between 33.8 and 27 mM, and 131 and 100 mM, respectively. The total peroxide concentration is increased gradually from bottom to top between 22 and 79 mM. The pH values of the samples were approximately constant at a value of 8.8. The free carbonate signal at 160.5 ppm is not shown.



Obs - calc pH







Obs - calc pH







Obs - calc pH







Obs - calc pH



Obs - calc pH







#### Obs - calc pH











Obs - calc pH



Obs - calc pH



Obs - calc pH



Obs - calc pH



Figure S4. Comparison of experimental and calculated data for the different titrations given in Table S 1  $^{\circ}$ C at 0. The speciation is shown using the following color code: 1 0 3 0, 2 1 4 -2, 1 1 1 -2, -1 1 2 -2, 2 1 2, -2, 2 2 1 -4, 5 5 5 -10.

Electronic Supplementary Material (ESI) for Dalton Transactions This journal is O The Royal Society of Chemistry 2012



(b)

**Figure S5.** Agreement between the selected chemical model in Table 2 and the experimental data for titrations (9) and (14), at 25°C. The agreement is less good than in the 0 °C data, particularly at the higher concentrations of  $H_2O_2$  as seen in titration 9.



**Figure S6.** Comparison of the fit between model and experiment in titration T 4 using the selected model (the red curve) and a fit where the constants for the complex 5, 5, 5, -10 has been increased by  $2\sigma$  and the one for 2, 2, 4, -2 has been decreased by  $2\sigma$ , deviations (black curve). The deviation (Obs – calc pH) is small and significant only in the very first part of the titration.