Crystallization of 4'-Hydroxyacetophenone from Water: Control of Polymorphism via Phase Diagram Studies

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RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

KEYWORDS: 4'-hydroxyacetophenone / polymorphism / crystallization / phase diagram / hydrate / metastable zone width / thermal analysis

BRIEFS (WORD Style "BH_Briefs").

Supporting Information

Table S1. Solubilities of HAP in Water Determined by the Gravimetric Method.

T/K	c_{HAP}/g·kg^{-1}
Heating	
283.25	3.76±0.36
293.42	6.86±0.19
297.62	9.57±0.29
302.85	14.38±0.10
303.43	13.81±0.04
308.44	16.70±0.21
312.88	20.75±0.40
317.72	29.80±0.13
322.86	38.61±0.69
Cooling	
317.44	29.49±0.38
304.08	14.78±0.24
293.74	7.98±0.13
281.16	3.92±0.69
275.23	3.42±0.08

Table S2. Solubility (T_s), Crystallizationn (T_n), and Colloidal Phase Formation (T_{col}) Temperature Onsets as a Function of Cooling/Heating Rates, β, for Different Concentrations (c_{HAP}) of 4'-Hydroxyacetophenone in Water.[a]

c_{HAP}/g·kg^{-1}	β/K·h^{-1}								
	12			18			24		
	T_d/K	T_c/K	T_s/K	T_d/K	T_c/K	T_s/K	T_d/K	T_c/K	T_s/K
16.292		280.08	306.13			304.62			304.65
22.937		289.31	312.63		288.33	311.29		286.93	313.16
25.116			315.59			315.59			315.69
26.401		293.58	313.82		291.69	314.24		291.28	315.62
30.074	300.25	298.95	317.97	300.22	298.34	318.43	300.13	296.76	318.18
31.093	298.62	295.83	316.99		295.01	316.65	298.93	296.38	317.20
34.896	307.94	304.92		298.60		322.07	308.18	298.35	
36.183	309.81	302.29				321.41	309.85	301.62	
37.428	311.72	304.12	322.02	311.41	302.84	322.87	311.35		323.25
37.562			322.47		300.92		311.76	301.62	323.56
37.997	311.04		321.15	311.57		322.71	311.70		323.40
39.058	313.66	304.87	322.77	311.61		323.77	313.51	300.56	
42.733	317.90	305.15		317.93	302.10		318.10	300.10	
43.698	317.76			318.00			317.93		
47.18	322.47	305.01		322.37	302.97		322.29	301.45	
49.627	324.22			324.18			324.24		
50.385				325.26			325.06		
52.639	327.08	305.16		327.06	303.36		327.07	300.03	
57.416	329.85	305.21		329.22	305.06		330.64	300.85	
57.82	330.95			330.96			330.94		
58.557	331.51			331.43			331.31		
59.529	332.19	304.78		332.14	302.70		331.74		

[a] The values of c_{HAP} refer to g of anhydrous HAP per 1 kg of water.

Thermogravimetry (TG). The results of the determination of the molar fraction n of water in the H2 hydrate (HAP·nH$_2$O) by TG at a heating rate $\beta = 5$ K·min^{-1} are summarized in Table S3. Here, T_i and T_f are the initial and final temperatures of the mass loss step, m_i is the initial mass of sample, and Δm is the observed mass loss. The uncertainty indicated for $\langle n \rangle$ represents twice the standard deviation of the mean.

Table S3. Amounts of Substance n of Water in the HAP·nH$_2$O Hydrate (H2) Determined by Thermogravimetry

T_i/K	T_f/K	m_i/mg	Δm/mg	n
298	324.5	7.917	2.221	2.95
298	329.1	10.929	2.986	2.84
298	342.5	17.752	4.936	2.91
298	351.2	25.125	6.871	2.84

$\langle n \rangle = 2.9 \pm 0.1$

Table S4. Indexation of the X-ray Powder Diffraction Pattern of the Dehydrated H2 Form in Figure 4 of the Main Text. The Pattern Corresponds to the Anhydrous Form II of 4'-Hydroxyacetophenone (Oorthorhombic, Space group $P2_12_12_1$, a = 6.1296 Å, b = 9.5359 Å, c = 24.3289 Å).

h	k	l	2θ(obs)/º	$\Delta 2\theta$ / º
0	*1*	*2*	11.774	-0.009
1	*0*	*1*	14.902	0.010
1	*0*	*2*	16.177	-0.002
1	*1*	*0*	17.197	0.014
1	*1*	*1*	17.571	0.003
1	*0*	*3*	18.115	-0.012
0	*2*	*1*	18.948	-0.004
1	*1*	*3*	20.363	-0.031
0	*2*	*3*	21.566	-0.038
1	*1*	*4*	22.586	-0.003
1	*0*	*5*	23.300	-0.022
1	*2*	*0*	23.657	0.036
1	*2*	*2*	24.745	0.002
1	*1*	*5*	25.136	-0.008
1	*2*	*3*	26.071	-0.011
0	*1*	*7*	27.278	-0.011
1	*2*	*4*	27.839	-0.016
0	*3*	*1*	28.264	-0.028
0	*2*	*6*	28.910	0.028
0	*3*	*2*	29.029	0.018
1	*2*	*5*	29.981	-0.012
0	*1*	*8*	30.848	0.011
0	*3*	*4*	31.766	0.028
1	*2*	*6*	32.463	0.032
1	*3*	*2*	32.565	0.017
1	*3*	*3*	33.568	-0.033
2	*0*	*5*	34.571	0.011

Table S5. Indexation of the X-ray Powder Diffraction Pattern of the Solid Removed From the Aqueous Solution After a 48h Equilibration Time at 302.6 K (Figure 5). The Pattern Corresponds to the Anhydrous Form I of 4'-Hydroxyacetophenone (Monoclinic, Space group $P2_1/c$, a = 7.6951 Å, b = 8.3141 Å, c = 11.2577 Å, β = 95.06°).

h	*k*	*l*	2θ(obs)/°	$\Delta 2\theta$ / °
1	*0*	*0*	11.553	0.018
0	*1*	*1*	13.27	0.024
0	*0*	*2*	15.803	0.01
1	*1*	*1*	18.047	-0.008
-1	*0*	*2*	18.761	0.01
0	*1*	*2*	19.067	-0.009
1	*0*	*2*	20.41	-0.007
0	*2*	*0*	21.362	0.005
2	*0*	*0*	23.215	0.025
1	*2*	*0*	24.32	-0.018
2	*1*	*0*	25.561	-0.012
2	*1*	*-1*	26.156	-0.016
-2	*0*	*2*	26.972	-0.003
1	*1*	*-3*	27.737	-0.011
-1	*2*	*2*	28.587	0.019
-2	*1*	*3*	33.721	-0.003

Table S6: Indexation of the X-ray Powder Diffraction Pattern in Figure 11(a). The Pattern Corresponds to the Anhydrous Form II of 4'-Hydroxyacetophenone (Orthorhombic, Space Group $P2_12_12_1$, a = 6.1406 Å, b = 9.5132 Å, c = 24.3443 Å).

h	k	l	2θ(obs)/°	$\Delta 2\theta$ / °
0	*1*	*2*	11.845	0.048
0	*1*	*3*	14.420	0.085
1	*1*	*0*	17.245	0.072
1	*1*	*1*	17.560	0.002
0	*2*	*1*	18.925	-0.070
1	*1*	*3*	20.335	-0.047
0	*2*	*3*	21.640	0.001
1	*1*	*4*	22.570	-0.005
0	*2*	*4*	23.770	0.048
1	*1*	*5*	25.075	-0.054
0	*2*	*5*	26.185	0.015
0	*1*	*7*	27.280	-0.001
1	*2*	*4*	27.850	-0.017
0	*2*	*6*	28.900	0.000
1	*2*	*5*	29.995	-0.006
0	*1*	*8*	30.805	-0.020
0	*2*	*7*	31.825	-0.025
1	*2*	*6*	32.471	0.035
1	*3*	*3*	33.634	-0.011
1	*1*	*8*	34.197	0.015

Table S7. Indexation of the X-ray Powder Diffraction Pattern in Figure 13(a). The Pattern Corresponds to the Anhydrous Form I of 4'-Hydroxyacetophenone (Monoclinic, Space Group $P2_1/c$, a = 7.7070 Å, b = 8.3336 Å, c = 11.2911 Å, β = 94.91°).

h	*k*	*l*	2θ(obs)/°	$\Delta 2\theta$ / °
1	*0*	*0*	11.5361	0.0233
0	*1*	*1*	13.182	-0.0373
0	*0*	*2*	15.7821	0.006
1	*1*	*1*	17.9728	-0.0361
-1	*0*	*2*	18.8361	0.0912
0	*1*	*2*	19.0575	0.0104
1	*0*	*2*	20.3713	0.0014
0	*2*	*0*	21.3213	0.0188
1	*1*	*2*	23.002	-0.0158
2	*0*	*0*	23.1889	0.0451
1	*2*	*0*	24.3144	0.0356
2	*1*	*0*	25.4921	-0.0272
-2	*0*	*2*	26.9239	-0.0331
-1	*2*	*2*	28.5505	0.0286
1	*2*	*2*	29.618	-0.0231
2	*2*	*0*	31.712	0.0541
-2	*1*	*3*	33.7014	-0.0014