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A DTA STUDY OF PHENOLS
III. Polyhydroxy-phenols and naphthols

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A comprehensive DTA study is reported of ten polyhydroxy-phenols and eight naphthols and of the corresponding *p*-phenylazo benzoylchloride, *p*-nitrobenzoylchloride and 3,5-dinitrobenzoylchloride derivatives, prepared 'in situ' by heating intimate mixtures of phenol and acid chloride in a conventional DTA system. The thermal analysis data and, in particular, the derivative formation temperatures, are interpreted in terms of the inductive, mesomeric and steric effects associated with the phenol and acid chloride and the extent of inter- and intramolecular hydrogen-bonding existing in these systems. The DTA data collectively, provide a comprehensive data base for the identification and characterisation of these phenols via DTA.

Parts 1 [1] and 2 [2] in this series of papers have reported a detailed DTA study of halo-, methyl-, and methyl-halo-phenols together with the 'in situ' formation in a DTA of the corresponding *p*-nitrobenzoylchloride (*p*-NBC), 3,5-dinitrobenzoylchloride (3,5-dNBC) and *p*-phenylazobenzoylchloride (*p*-PABC) derivatives. It was conclusively shown that these groups of phenols can be characterised in the solid state by DTA and that such characterisation is augmented by a DTA study of the 'in situ' phenol/acid chloride derivative formation process - a proposal which had earlier been suggested by Crandall and Pennington [3].

The third part of this comprehensive study is reported here as a DTA study of ten polyhydroxy-phenols and eight naphthols and of the corresponding *p*-PABC, *p*-NBC and 3,5-dNBC derivatives. The derivative formation temperatures (T_D) are rationalized in terms of phenol acidity, steric

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effects associated with the phenol and acid chloride ring substituents and second order effects, related to inter- and intramolecular hydrogen-bonding of the phenol and the relative extent to which these cumulative factors influence the degree of phenol/acid chloride interaction.

Experimental

The source of phenols and acid chlorides, the DTA system used, the sample presentation procedures and the data analysis procedures with respect to DTA curve analysis and peak assignments, have been fully described in Part 1 [1]. The Thermal Optical Analysis System, used separately to confirm derivative melting points, has also been described [1].

Results and discussion

The DTA profile analysis for ten polyhydroxy-phenols and the corresponding *p*-PABC, *p*-NBC and 3,5-dNBC derivatives are recorded in Table 1. Similar data for eight naphthols are recorded in Table 2. All transitions are endothermic, except when specifically identified as exothermic (Exo). These data collectively constitute a comprehensive data bank for the subsequent characterisation of these phenols in the solid-state by DTA. For the rapid identification of these phenols, the melting points of the various polyhydroxy-phenols and naphthols and of the corresponding *p*-PABC, *p*-NBC and 3,5-dNBC derivatives, are summarised in Tables 3 and 4 respectively.

Table 1 Peak definition temperatures for polyhydroxy-phenols and for the corresponding *p*-PABC, *p*-NBC and 3,5-dNBC derivatives

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
catechol	parent	100	105	115
		178	202	214
	p-PABC	73	88	96
		96	102EXO	109
		109	122	129
		134	*143	150
		190	ENDO Drift	

Table 1 continued

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
	p-NBC	38	47	58
		65	80	93
		114	145	148
		148	*163	181
		215	279	304
	3,5-dNBC	47	60	68
		73	96	103
		125	132	
			*158	173
		198	253EXO	284
4-methylcatechol	parent	55	68	85
		107	212	228
	p-PABC	51	63	76
		77	87	102
		125	133	139
		139	*146	159
		181	203	238
	p-NBC	30	46	63
		118	147	
			*160	181
		204	240	290
		290	347EXO	389
	3,5-dNBC	26	46sh	
			57	69
		132	151	
			*168	183
		240	291EXO	349
resorcinol	parent	101	110	120
		142	235	270
	p-PABC	79	94	96
		96	102EXO	106
		106	117	
			sh*145	151
		161	171	201
	p-NBC	56	73	81
		81	87	102
		121	145sh	
			*184	196
		198	222	238

Table 1 continued

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
	3,5-dNBC	43	69	82
		82	95	109
		116	125	133
		193	*206	232
		237	274	309
2-methylresorcinol	parent	96	116	123
		152	219	244
	p-PABC	77	92	95
		101	109	
			sh125	134
		134	*155	172
		179	204	234
	p-NBC	57	73	81
		81	94	109
		126	149sh	
			*177	211
		223	300	323
	3,5-dNBC	57	71	80
		80	90	114
		117	136sh	
			*176	190
		211	272	301
4-chlororesorcinol	parent	80	106	118
		138	210	242
	p-PABC	72	88	94
		94	96	121
		121	129EXO	130
		130	*139	143
		157	192EXO	238
	p-NBC	27	45	58
		58	70	84
		123	136	148
		154	*167	190
		197	238	251
	3,5-dNBC	50	76	88
		90	109sh	
			*171	188
		198	ENDO Drift	
hydroquinone	parent	164	172	198
		204	248	261

Table 1 continued

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
	p-PABC	86	97	104
		104	127	133
		133	134EXO	135
		135	138	149
		172	*188	190
		190	199EXO	245
	p-NBC	57	64	77
		96	125	138
		138	142EXO	151
		151	154	163
		245	*263	270
		270	294	316
	3,5-dNBC	53	61	71
		99	132	145
		152	163	173
		300	*323	334
		345	EXO Drift	
methylhydroquinone	parent	123	127	147
		157	233	252
		259	320EXO	390
	p-PABC	81	96	108
		108	120	133
		133	143	148
		148	*157	167
		200	210	230
	p-NBC	61	73	83
		83	101	123
		148	156	169
		229	*247	270
		270	276	336
	3,5-dNBC	58	66	74
		86	111	125
		154	168	179
		224	*241	254
		262	295	349
trimethylhydroquinone	parent	160	172	189
		196	242	253

Table 1 continued

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
	p-PABC	80	96	100
		112	121	139
		139	159sh	
			*178	194
		210	263	298
	p-NBC	61	73	86
		97	133	
			sh175	178
		218	*241	270
		273	310EXO	340
	3,5-dNBC	58	66	72
		97	160	173
		173	183	196
		196	*209	247
		247	292EXO	327
pyrogallol	parent	124	133	149
		168	246	263
	p-PABC	87	97	101
		107	120	124
		124	139	142
		142	*169	176
		190	223	250
	p-NBC	58	71	83
		89	97	110
		110	125EXO	128
		128	150	160
		214	*235	246
		259	EXO Drift	
	3,5-dNBC	61	69	81
		84	97	112
		133	136	154
		192	*209	226
		230	270EXO	306
phloroglucinol	parent	85	117	120
		203	222	231

Table 1 continued

Phenol	Peak definition temperatures, °C		
	onset	peak	offset
p-PABC	69	91sh	
		98	103
	103	109EXO	112
	112	124	130
	159	*182	216
	232	258	269
p-NBC	43	68	76
	93	94	95
	95	96EXO	107
	107	138	175
	275	*289	328
	338	EXO Drift	
3,5-dNBC	44	58	70
	70	88	
		sh102	104
	148	*164	177
	179	185	193

sh shoulder

*Derivative mp (Confirmed by Thermal Optical Analysis)

The peak definition temperature data (Tables 1 and 2), as related to the initial decomposition of the parent phenols, give a quantitative indication of the relative thermal stability of these compounds. For the polyhydroxyphenols, it is apparent that as the number of hydroxyl-substituents increases, thermal stability increases. Thus catechol, resorcinol and pyrogallol decompose at 202°, 235° and 246°, respectively. Methyl substituents appear to decrease the thermal stability of the phenol: 2-methyl-resorcinol decomposes at 219°, compared to the parent resorcinol, which decomposes at 235° and methyl-hydroquinone decomposes at 233° compared to the parent hydroquinone, which decomposes at 248°. Chloro substituents also appear to decrease the thermal stability of the phenol: 4-chloro-resorcinol decomposes at 210°, compared to the parent resorcinol, which decomposes at 235°. The position of the various hydroxyl group substituents also influences the thermal stability of the phenol - the isomers, pyrogallol and phloroglucinol decompose at different temperatures, 246° and 222° respectively.

Table 2 Peak definition temperatures for naphthols and for the corresponding *p*-PABC, *p*-NBC and 3,5-dNBC derivatives

Naphthol		Peak definition temperatures, °C		
		onset	peak	offset
1-naphthol	parent	83	94	113
		148	211	256
	p-PABC	64	69	75
		77	83	87
	EXO Drift to	98	105	
			*122	129
		129	145	162
		162	ENDO Drift	
	p-NBC	44	59	65
		65	66	81
		105	133sh	
			*148	159
		166	188	218
	3,5-dNBC	43	55	66
		72	84	90
		90	95EXO	100
		119	150	159
		199	*219	230
		230	239EXO	254
2-bromo-1-naphthol	parent	79	85	96
		130	235	252
	p-PABC	53	60	70
		70	77	96
		116	129	135
		154	*177	184
		214	259	265
		265	EXO Drift	
	p-NBC	39	44	53
		53	57	70
		84	120	128
		128	*144	146
		160	182	188
	3,5-dNBC	49	58	65
		70	75	83
		119	127	139
		144	*167	182
		211	239	257
2-methyl-1-naphthol	parent	32	66	80
		145	218	248

Table 2 continued

Naphthol		Peak definition temperatures, °C		
		onset	peak	offset
	p-PABC	40	57	
			sh72	81
		83	90sh	
			*102	121
		143	169	188
	p-NBC	30	40	62
		112	130	
			*138	152
		162	193	208
		217	227EXO	235
	3,5-dNBC	48	66	78
		92	140sh	
			*154	159
		167	170	179
2-nitro-1-naphthol	parent	120	129	138
		198	207	253
	p-PABC	80	94	109
		109	115sh	
			119	128
		154	*170	175
		192	213	236
	p-NBC	60	74	84
		84	97	
			sh114	120
		141	*149	160
		160	181	204
		204	213EXO	225
	3,5-dNBC	58	67	69
		94	123	130
		130	136sh	
			*165	176
		188	204EXO	212
4-chloro-1-naphthol	parent	111	120	136
		161	209	251
	p-PABC	67	76	80
		80	83sh	
			90	94
	EXO Drift to	98	103	122
		145	*151	159
		159	189	227

Table 2 continued

Naphthol		Peak definition temperatures, °C		
		onset	peak	offset
	p-NBC	56	64	66
		66	70	80
		99	126sh	
			*162	181
		272	294	308
	3,5-dNBC	65	71	80
		80	90	94
		98	139sh	
			*157	170
		211	247EXO	281
2-naphthol	parent	106	120	134
		154	212	248
	p-PABC	74	83sh	
			90	95
	EXO Drift to	106	107	108
		179	*194	199
		212	ENDO Drift	
	p-NBC	51	66	74
		74	84	106
		116	134sh	
			*171	181
		181	200	226
	3,5-dNBC	58	65	72
		96	110	119
		133	149	162
		194	*212	220
		235	244EXO	292
6-bromo-2-naphthol	parent	126	130	140
		253	277	285
	p-PABC	83	94	99
	EXO Drift to	107	114	147
		160	*188	194
		216	249	286
	p-NBC	46	66	76
		80	109	115
		115	124	139
		169	*189	218
		218	313	358

Table 2 continued

Naphthol		Peak definition temperatures, °C		
		onset	peak	offset
	3,5-dNBC	54	66	74
		91	110	118
		128	136	151
		169	*192	206
		206	219EXO	236
1,6-dibromo-2-naphthol	parent	89	106	11
		192	237	263
	p-PABC	68	73	80
		80	95	106
		121	139	146
		204	*227	250
		260	294	316
	p-NBC	58	73	91
		95	101	107
		120	127sh	
			*162	167
		186	193	249
	3,5-dNBC	58	68	75
		75	80	84
		120	126	135
		149	*165	178
		232	274	283

sh shoulder

*Derivative mp (Confirmed by Thermal Optical Analysis)

It has been well documented [1, 2] that the ease of derivative formation, as reflected in the magnitude of T_D, is dependent on the relative acidic and basic strengths of the acid chloride and phenoxide ion respectively, although it appears that phenol acidity is the dominant effect in this synergistic interaction. Thus, on this basis, derivative formation is directly favoured by electron withdrawing ring substituents of the phenol and electron releasing ring substituents of the acid chloride. This primary interaction is impeded by steric effects of ring substituents adjacent to the reactive groups of each moiety. Also, intra- and intermolecular, second-order hydrogen-bonding effects, associated with the phenol and intermolecular phenol/acid chloride hydrogen-bonding, impede derivative formation.

For both the polyhydroxy-phenols and naphthols, the ease of derivative formation for a given phenol, is in the order *p*-PABC < *p*-NBC < 3,5-dNBC. For example, the T_D for these derivatives of hydroquinone is 138°, 154° and 163° respectively and for 1-naphthol, 105°, 133° and 150° respectively. This trend reflects the progressive increase in electron withdrawing capacity of ring substituents of the acid chloride.

Several sets of T_D data for these phenol derivatives illustrate that electronic effects associated with the phenol moiety dominate the ease of derivative formation. For example, the T_D for the 3,5-dNBC derivatives of hydroquinone, methyl-hydroquinone and trimethyl-hydroquinone are 163°, 168° and 183° respectively, which illustrates a progressive decrease in ease of derivative formation, due to a progressive increase in methyl ring substituent electron releasing effect associated with the phenol. The trend is a general one: T_D for the *p*-PABC derivative of 2-methyl-resorcinol is 125° that for the *p*-PABC derivative of resorcinol is 117°; T_D for the p-PABC derivative of 4-methyl-catechol is 133°, that for the *p*-PABC derivative of catechol is 122°. The opposite effect is shown by a chloro substituent on the phenol: T_D for the *p*-NBC derivative of 4-chloro-resorcinol is 136°, whereas that for the *p*-NBC derivative of resorcinol is 145°.

Table 3 Melting points of polyhydroxy-phenols and of the corresponding derivatives

Phenol	Melting point, °C			
	parent	*p*-PABC	*p*-NBC	3,5-dNBC
catechol	105	143	163	158
			159[a]	152[a]
4-methylcatechol	68	146	160	168
resorcinol	110	145	184	206
			182[a]	201[a]
2-methylresorcinol	116	155	177	176
4-chlororesorcinol	106	139	167	171
hydroquinone	172	188	263	323
			258[a]	317[a]
methylhydroquinone	127	157	247	241
trimethylhydroquinone	172	178	241	209
pyrogallol	133	169	235	209
			230[a]	205[a]
phloroglucinol	117	182	289	164
			283[a]	162[a]

[a] From Refs 5,6

The steric effect of adjacent ring substituents to the reaction site is revealed by the T_D values of the *p*-PABC derivatives of catechol and resorcinol, 122° and 117° and more dramatically by the T_D values of the *p*-NBC derivatives of pyrogallol and phloroglucinol, 150° and 138° respectively.

For the naphthols, the positions of the single hydroxyl ring substituent appears to have little effect on the thermal stability of the parent phenol, since 1-naphthol and 2-naphthol decompose at essentially the same temperature, 211° and 212° respectively.

An anomalous trend in T_D data is apparent in the case of ring substituents in the 2 position of 1-naphthol.

Table 4 Melting points of naphthols and of the corresponding derivatives

Naphthol	Melting point, °C			
	parent	*p*-PABC	*p*-NBC	3,5-dNBC
1-naphthol	94	122	148	219
		118[a]	143[b]	217[b]
1-bromo-2-naphthol	85	177	144	167
2-methyl-1-naphthol	66	102	138	154
2-nitro-1-naphthol	129	170	149	145
4-chloro-1-naphthol	120	151	162	157
2-naphthol	123	194	171	212
		190[a]	169[b]	210[b]
6-bromo-1-naphthol	130	188	189	192
1,6-dibromo-2-naphthol	106	227	162	165

[a]From Ref. 7, [b] from Refs 5, 6, 8

Thus the T_D values for the *p*-PABC derivatives of naphthol, 2-bromonaphthol, 2-methyl-naphthol and 2-nitro-naphthol are 105°, 129°, 90° and 119° respectively and this trend is explained in terms of the net electronic/steric effect associated with the phenol ring substituent in the 2 position. The normal trend is apparent when the steric effect of the phenol ring substituent is eliminated: the T_D values for the *p*-NBC derivatives of 2-naphthol and 6-bromo-2-naphthol are 134° and 124° respectively.

It is more difficult to identify the second-order hydrogen-bonding effects within the T_D data associated with these phenol derivatives. It is known [4] that polyhydroxyphenols are extensively inter- and intramolecularly hydrogen-bonded in the solid state, and halogen ring substituents, ortho to the hydroxyl reactive group are expected to contribute significantly to the intramolecular hydrogen-bonding of the phenol. These effects account for the relative magnitudes of the *T*D values for the *p*-PABC derivatives of resorcinol, 117° and 4-chloro-resorcinol, 129°; 1-naphthol, 105°, 2-bromo-1-naphthol, 129° and 2-nitro-1-naphthol, 119° and also 2-naphthol, 107° and 1,6-dibromo-2-naphthol, 139°.

Although many effects contribute to the ease of phenol derivative formation, it has been stated that phenol acidity is the dominant effect and this is essentially revealed by the linear *p*Ka/*T* relationships shown in Figs 1 and 2, as derived from the data given in Tables 5 and 6.

Table 5 *p*Ka data for polyhydroxy-phenols and *T*D data for the corresponding derivatives

Phenol	*p*Ka[a]	Derivative formation temperature, *T*D, °C		
		p-PABC	*p*-NBC	3,5-dNBC
phloroglucinol	7.97	124	138	102
pyrogallol	9.05	139	150	136
resorcinol	9.20	117	145	125
catechol	9.37	122	145	132
4-methylcatechol	9.84	133	147	151
hydroquinone	9.91	138	154	163
methylhydroquinone	10.21	143	156	168

[a]From Refs 9-11

Table 6 *p*Ka data for naphthols and *T*D data for the corresponding derivatives

Naphthol	*p*Ka[a]	Derivative formation temperature, *T*D, °C		
		p-PABC	*p*-NBC	3,5-dNBC
2-nitro-1-naphthol	5.89	119	114	136
4-chloro-1-naphthol	8.86	103	126	139
1-naphthol	9.39	105	133	150
2-naphthol	9,52	107	134	149

[a]From Refs 9-11

As phenol acidity increases, the *T*D for a corresponding derivative decreases. For cases involving significant steric and second-order hydrogen-bonding interactions, non-conformity with this trend results. This is particularly apparent for the 3,5-dNBC derivatives generally, and for the derivatives of 2-nitro-1-naphthol.

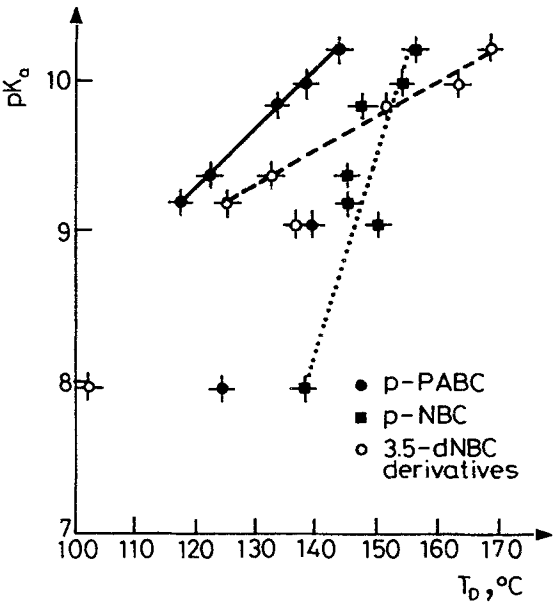

Fig. 1 pKa/T_D relationships for the polyhydroxy-phenol systems

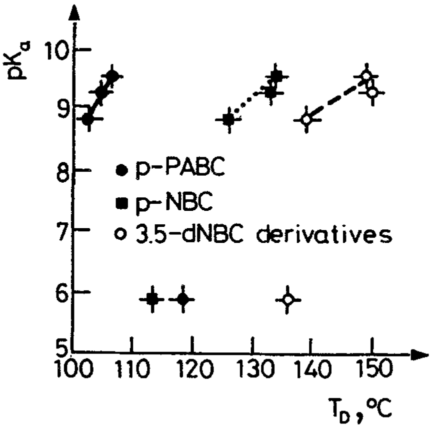

Fig. 2 pKa/T_D relationships for the naphthol systems

Thus, in summary, it is apparent that the T_D data for the derivatives of polyhydroxy-phenols and naphthols can be rationalized in terms of primary electronic effects and secondary steric effects and hydrogen-bonding interactions, associated with the phenol and derivative-forming agent. The DTA method appears to be of considerable value for the qualitative revelation of these solid state intermolecular effects.

References

1 N. G. Buckman, J. O. Hill and R. J. Magee, J. Therm. Anal., 36 (1990). 289.
2 N. G. Buckman, J. O. Hill and R. J. Magee, J. Therm. Anal., 36 (1990). 2555.
3 E. W. Crandall and M. Pennington, J. Chem. Educ., 57 (1980) 824.
4 G. E. Bacon and N. A. Curry, Proceed. Roy. Soc., A235 (1956) 552.
5 N. D. Cheronis, J. B. Entrikin and E. M. Hodnett, 'Semimicro Qualitative Organic Analysis', 3rd Edn., Wiley-Interscience, N. Y. 1965.
6 A. I. Vogel, 'Textbook of Practical Organic Chemistry'. 4th Edn., Longman, N. Y. 1981.
7 E. O. Woolfolk and J. M. Taylor, J. Org. Chem., 22 (1957) 827.
8 M. Phillips and G. L. Keenan, J. Amer. Chem. Soc., 53 (1931) 1924.
9 E. P. Serjeant and B. Dempsey, IUPAC Chemical Data Series No 23: 'Ionisation Constants of Organic Acids in Aqueous Solutions', Pergamon Press, N. Y. 1979.
10 P. J. Pearce and R. J. J. Simkins, Canad. J. Chem., 46 (1968) 241.
11 G. Kortum, W. Vogel and K. Andrussow, Pure and Appl. Chem., 1 (1960) 187.

Zusammenfassung — Dies ist eine umfassende DTA-Untersuchung von zehn Polyhydroxyphenolen und acht Naphtholen sowie der entsprechenden *p*-Phenylazobenzoylchlorid-, *p*-Nitrobenzoylchlorid- und 3,5-Dinitrobenzoylchlorid-Derivate, die durch Erhitzen inniger Gemische des jeweiligen Phenoles und Säurechlorides "in situ" in einem herkömmlichen DTA-Gerät hergestellt wurden. Die bei der Thermoanalyse erhaltenen Angaben, insbesondere die Bildungstemperatur der Derivate wurde bezüglich des induktiven, mesomeren und sterischen Effektes bei Phenol und Säurechlorid sowie der Stärke der in diesem System existierenden inter- und intramolekularen Wasserstoffbrückenbindungen interpretiert. Die Gesamtheit der DTA-Daten bietet eine umfassende Datensammlung für Identifizierung und Charakterisierung dieser Phenole mittels DTA.