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A DTA STUDY OF PHENOLS
IV. Nitro- and amino-phenols

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

The systematic characterization of organic compounds involves the synthesis of a corresponding derivative and the determination of the melting point thereof. A DSC study by Crandall and Pennington [1] of phenol, resorcinol and eugenol and of the corresponding *p*-nitrophenylbenzoate derivatives, suggested that phenols in the solid state can be characterised via 'in situ' derivative formation in a thermal analysis system. This postulate has been extensively tested and reported as Parts 1 [2], 2 [3] and 3 [4] of a detailed DTA study of a wide variety of phenols and the corresponding *p*-phenylazobenzoylchloride (*p*-PABC), *p*-nitrobenzoylchloride (*p*-NBC) and 3,5-dinitrobenzoylchloride (3,5-dNBC) derivatives.

The final part of this comprehensive study is reported here as a DTA study of eight nitrophenols and eight aminophenols and of the corresponding *p*-PABC, *p*-NBC and 3,5-dNBC derivatives. The thermal analysis data

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and, in particular, the derivative formation temperatures (T_D), are interpreted in terms of phenol acidity, steric effects associated with the phenol and acid chloride ring substituents and second order hydrogen-bonding effects associated with the two interacting moieties in the derivative formation reaction.

Experimental

The source of acid chlorides, the DTA system used, the sample presentation procedures, the DTA experimental conditions used and the data analysis procedures with respect to DTA curve analysis and peak assignments, have been fully described in Part 1 [2]. The Thermal Optical Analysis System, used primarily to confirm derivative melting points, has also been described [2].

Results and discussion

The DTA profile analysis data for eight nitro-phenols and the corresponding *p*-PABC, *p*-NBC and 3,5-dNBC derivatives, are recorded in Table 1. Similar data for eight amino-phenols 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 by DTA. For the quick identification of these phenols, the melting points of the various nitrophenols and amino-phenols and of the corresponding *p*-PABC, *p*-NBC and 3,5-dNBC derivatives, as determined by this DTA study, are summarised in Tables 3 and 4 respectively.

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. 2-Nitrophenol, 3-nitrophenol and 4-nitrophenol decompose at 168°, 234° and 232° respectively, indicating that within the group of isomeric nitrophenols, 2-nitrophenol is the least thermally stable - thereby giving no support to the postulate of strong intramolecular hydrogen-bonding associated with 2-nitrophenol [5]. Additional ring substituents on the nitrophenol moiety marginally increase thermal stability: 2-chloro-4-nitrophenol and 2,6-dibromo-4-nitrophenol decompose at 242° and 255° respectively, compared with 4-nitrophenol, which decomposes at 232°.

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

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
2-nitro-	parent	29	45	56
		96	168	199
	p-PABC	31	44	58
		64	73	88
		88	94EXO	99
		99	117sh	
			*139	161
		188	206	232
		232	248	262
	p-NBC	28	38	61
		75	104	124
		126	*146	179
		203	262	287
	3,5-dNBC	28	44	57
		73	133	140
		143	*156	172
		208	223	232
3-nitro-	parent	84	97	106
		211	234	246
	p-PABC	73	86	107
		119	129	145
		145	*166sh	
			178	207
		207	ENDO Drift	
	p-NBC	52	69	76
		76	80	93
		114	120	129
		154	*177	182
		243	322	330
	3,5-dNBC	55	67	74
		74	83	96
		113	130	
			*161	175
		259	324	341
4-nitro-	parent	101	114	120
		196	232	269
	p-PABC	73	87	98
	EXO Drift to	114	145	152
		191	*206	220
		232	266	304

Table 1 continued

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
	p-NBC	50	70	83
		83	91	97
		97	105	118
		146	*159	178
		200	225sh	
			240	270
	3,5-dNBC	59	68	77
		80	101	
			113sh	120
		164	*190	197
		210	254sh	
			275	291
		291	EXO Drift	
2-chloro-4-nitro-	parent	93	105	112
		228	242	258
	p-PABC	66	83sh	
			90	
			sh97	
			*sh110	140
		150	195	208
	p-NBC	41	57	66
		66	80	
			sh83	92
		137	*149	154
		155	172	194
	3,5-dNBC	49	61	73
		73	98	103
		103	110	125
		125	*139	151
		163	188	223
2-methyl-3-nitro-	parent	140	146	174
		178	232	252
	p-PABC	74	95	109
		125	142	155
		155	157EXO	168
		183	*201	220
		220	ENDO Drift	

Table 1 continued

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
	p-NBC	59	68	82
		96	120	127
		127	130	141
		144	*162	186
		200	EXO Drift	
	3,5-dNBC	59	67	80
		97	133	135
		135	136	156
		189	*198	206
		217	223	231
3-methyl-4-nitro	parent	118	127	146
		155	255	276
	p-PABC	73	95	
			sh115	116
		125	*145	193
		193	ENDO Drift	
	p-NBC	54	67	77
		80	103	109
		115	*126	149
		149	EXO Drift	
	3,5-dNBC	55	60	72
		85	102sh	
			113	122
		122	*145	152
		170	189	203
2,6-dibromo-4-nitro	parent	139	145	172
		289	314	346
	p-PABC	79	89	103
		128	136	149
		149	155	176
		176	*195sh	
			206	220
	p-NBC	57	64	81
		110	112	122
		132	145	154
		172	*189	205
		256	293	331

Table 1 continued

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
	3,5-dNBC	61	67	79
		101	126	141
		141	155	170
		199	*202	218
		222	281	339
2,6-diiodo-4-nitro	parent	143	152	167
		189	246	271
	p-PABC	80	93	105
		132	159	170
		178	*191	208
		223	229	245
	p-NBC	57	66	74
		109	110	115
		130	149	166
		200	*204	226
		226	261	308
	3,5-dNBC	58	67	76
		114	137	148
		148	169	171
		171	*178	186
		230	280	314

sh shoulder, *derivate mp (Confirmed by Thermal Optical Analysis)

Interpretation of the various peaks in the DTA profiles of the phenol derivatives is generally in accordance with the sequence: acid chloride m. p., phenol m.p., derivative formation (T_D), derivative m.p. and derivative decomposition. Such a sequence of events is illustrated by the DTA profiles (Fig. 1) and corresponding peak definition temperature data (Table 1), for the 3,5-dNBC derivative of 2-nitrophenol, 3-nitrophenol and 4-nitrophenol. For example, the peaks in the DTA profile of the 3-nitrophenol/3,5-dNBC system are assigned as: depressed melting point of 3,5-dNBC and phenol at 67 and 83° respectively, derivative formation at 130°, derivative m.p. at 161°, and derivative decomposition at 324°. Similar interpretations may be given to the peaks in the DTA profiles of the 2-nitrophenol/3,5-dNBC and 4-nitrophenol/3,5-dNBC systems, also shown in Fig. 1.

The ease of derivative formation, which is essentially reflected in the magnitude of (T_D), is dependent on the relative acidic and basic strengths of the phenol and acid chloride respectively. Thus, electronic and steric effects associated with ring substituents on the phenol and acid chloride, significantly effect the ease of derivative formation. Also, second order effects, such as intra- and intermolecular hydrogen-bonding effects, associated with the phenol and intermolecular phenol/acid chloride hydrogen-bonding impede derivative formation.

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

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
2-amino-	parent	162	176	188
		188	195	224
	p-PABC	80	96	105
	EXO Drift to	137	140	
		140	145	150
		150	167	173
		173	*193	202
		223	ENDO Drift	
	p-NBC	72	75	76
		76	80EXO	115
		143	146	154
		160	186	204
		204	*208	216
		229	253	265
		265	276	305
	3,5-dNBC	65	72	80
		138	147	159
		159	164EXO	175
		185	206	208
		214	*226	238
		248	290	331
3-amino-	parent	116	127	144
		189	228	263
	p-PABC	88	98	104
	EXO Drift to	104	116	
		116	120sh	
			160	188
		212	*236	264
		264	ENDO Drift	
	p-NBC	68	75	77

Table 2 continued

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
	EXO Drift to	77	94	
		94	106	116
		145	170sh	
			*195	208
		216	259	336
	3,5-dNBC	51	59	66
		88	104	121
		157	186	197
		197	*204	210
		227	253	279
4-amino-	parent	159	187	198
		198	216	247
	p-PABC	88	98	110
	EXO Drift to	148	177	
		177	178	180
		180	181EXO	185
		188	208	244
		258	*277	287
		299	ENDO Drift	
	p-NBC	72	76	88
	EXO Drift to	151	159	
		159	167	176
		180	198	226
		260	*276	295
		298	ENDO Drift	
	3,5-dNBC	58	70	80
	EXO Drift to	121	145	
		145	166	173
		173	175EXO	181
		181	194	211
		241	*258	270
		298	343	380
2-amino-4-chloro-	parent	121	136	149
		178	209EXO	260
	p-PABC	82	96	113
		113	129	134
		134	173	182
		182	*211	220
		240	316	348

Table 2 continued

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
	p-NBC	66	70	77
		108	115	126
		157	179sh	
			*192	203
		259	305	337
	3,5-dNBC	67	72	79
		109	118	128
		155	169	181
		181	*204	217
		280	328	366
2-amino-4-nitro	parent	137	148	161
		173	203EXO	237
	p-PABC	85	98	106
		109	121	131
		160	179	182
		182	*225	230
		235	274	276
	p-NBC	68	74	87
		106	128EXO	133
		133	141	150
		150	189	195
		195	*204	221
		225	273	290
	3,5-dNBC	65	73	82
		131	140	148
		160	178	183
		183	*200	208
		240	266	279
6-amino-2,4-dimethyl-	parent	114	134	145
		168	193	237
	p-PABC	85	95	99
	EXO Drift to	106, 112	124	134
		134	137EXO	141
		147	156	170
		176	*189	215
		228	ENDO Drift	
	p-NBC	67	68	69
		69	72EXO	84
		95	123	134
		152	165	202

Table 2 continued

Phenol		Peak definition temperatures, °C		
		onset	peak	offset
	EXO Drift to	206	*217	226
		226	230	243
	3,5-dNBC	60	67	76
		76	93EXO	101
		107	125	134
		134	150	170
		170	*187	195
		195	213EXO	224
3-amino-2-naphthol	parent	209	227	
			236sh	248
	p-PABC	86	96	104
		104	160	169
		189	191	197
		197	207	214
		226	*241	253
	p-NBC	68	69	71
		71	75EXO	104
		187	198	206
		206	216	232
		232	*244	259
		314	327	336
	3,5-dNBC	64	67	72
		182	187	190
		190	199	203
		203	*229	255
8-amino-2-naphthol	parent	195	206	218
		255	276	336
	p-PABC	86	96	106
	EXO Drift to	173	186	
		186	202	205
		213	*223	240
		243	ENDO Drift	
	p-NBC	67	72	73
		73	79EXO	103
		195	205	216
		232	*248	259
		263	318EXO	336

Table 2 continued

Phenol	Peak definition temperatures, °C		
	onset	peak	offset
3,5-dNBC	61	67	88
	167	182	193
	193	199	205
	205	*218	227
	266	303	EXO Drift

sh shoulder, *derivate mp (Confirmed by Thermal Optical Analysis)

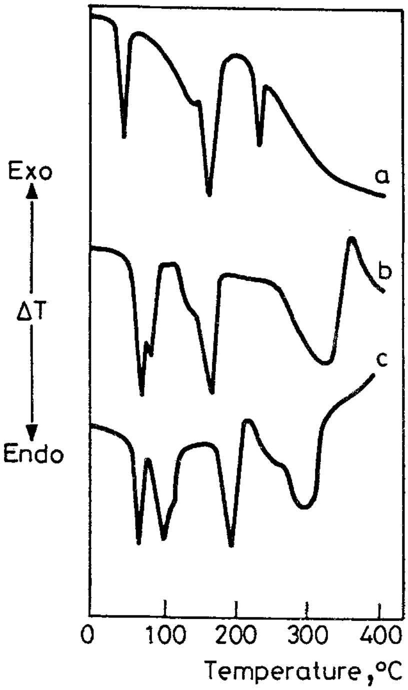


Fig. 1 DTA Profiles of the 3,5-dNBC derivatives of: a) 2-nitrophenol, b) 3-nitrophenol, c) 4-nitrophenol

With respect to a particular nitro-phenol, the general trend in corresponding derivative formation temperatures (T_D), (Table 1), is: p-NBC < p-PABC ≤ 3,5-dNBC. This trend is simply a reflection of the cumulative electronic, steric and second-order effects operating in the derivative formation process.

With respect to T_D generally, several trends are evident.

T_D for the *p*-PABC derivatives of 2-nitrophenol, 3-nitrophenol and 4-nitrophenol are 117°, 129° and 145° respectively, which is consistent with insignificant intramolecular hydrogen-bonding associated with 2-nitrophenol.

The steric effect of groups ortho to the reaction site of the phenol is apparent from the T_D values for 4-nitrophenol, 2,6-dibromo-4-nitrophenol and 2,6-diiodo-4-nitrophenol: 105°, 145° and 149° respectively. The steric effect of ortho halogen groups on the phenol inhibits the derivative formation reaction, as reflected in relatively high T_D values for the tri-substituted phenols. However, it appears that one ortho chloro ring substituent on the phenol exerts an insignificant steric effect: T_D for the 3,5-dNBC derivatives of 4-nitrophenol and 2-chloro-4-nitrophenol are essentially identical: 113° and 110° respectively.

Table 3 Melting point of nitro-phenols and of the corresponding derivatives

	Melting point, °C			
	Parent	*p*-PABC	*p*-NBC	3,5-dNBC
2-nitro-	45	139	146	156
		137[a]	141[b]	155[b]
3-nitro-	97	166	177	161
		162[a]	174[b]	159[b]
4-nitro-	114	206	159	190
		203[a]	159[b]	186[b]
2-chloro-4-nitro-	105	110	149	138
2-methyl-3-nitro-	146	201	162	198
3-methyl-4-nitro-	127	145	126	145
2,6-dibromo-4-nitro-	145	195	189	202
2,6-diiodo-4--nitro	152	191	204	178

[a] From Ref. 10, [b] From Ref. 11

The electronic effects associated with phenol ring substituents are readily revealed from the T_D data (Table 1). T_D for the *p*-NBC derivatives of 4-nitrophenol and 2-chloro-4-nitrophenol are 105° and 83° respectively, which are consistent with the -I effect of the chloro ring substituent increasing phenol acidity and thereby facilitating derivative formation in the case of 2-chloro-4-nitrophenol/*p*-NBC. The opposite trend is shown in the case of T_D for the *p*-PABC derivatives of 3-nitrophenol and 2-methyl-3-nitrophenol:

129° and 157°, respectively. This trend in *T*D reflects the +I inductive effect of the methyl ring substituent of the phenol decreasing phenol acidity and thereby impeding derivative formation in the case of 2-methyl-3-nitrophenol/*p*-PABC derivative. This effect is less apparent for a meta methyl ring substituent on the phenol: *T*D for the *p*-NBC derivatives of 4-nitrophenol and 3-methyl-4-nitrophenol are 105° and 103° respectively.

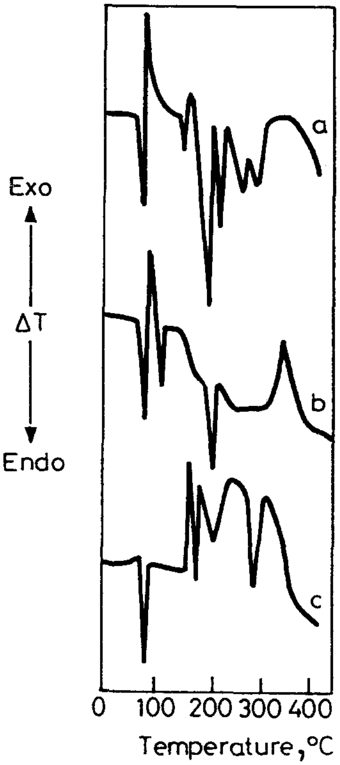
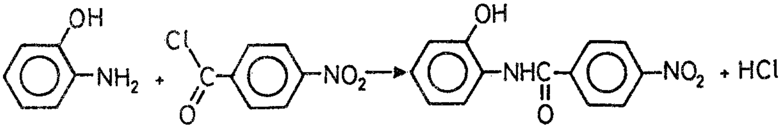


Fig. 2 DTA Profiles of the *p*-NBC derivatives of: a) 2-aminophenol, b) 3-aminophenol, c) 4-aminophenol

For the amino-phenols studied, the relative thermal stability of these compounds can also be determined from the DTA data given in Table 2. 2-Aminophenol, 3-aminophenol and 4-aminophenol decompose at 195°, 228° and 216° respectively and hence within this series, 2-aminophenol is the least thermally stable. Aminonaphthols exhibit enhanced thermal stability: 3-amino-2-naphthol and 8-amino-2-naphthol decompose at the relatively high temperatures of 236° and 276° respectively. It is apparent that methyl ring substituents on the phenol reduce thermal stability: 2-aminophenol and 6-amino-2,4-dimethyl-phenol decompose at 195° and 193° respectively.

The general interpretation of peaks in the DTA profiles of aminophenols is similar to that discussed for nitrophenols and may be illustrated by reference to the DTA profiles for the *p*-NBC derivatives of 2-aminophenol, 3-aminophenol and 4-aminophenol, shown in Fig. 2. For the 3-aminophenol/*p*-NBC system, depressed *p*-NBC and phenol melting points appear at 75° and 106° respectively, followed by derivative formation at 170° derivative melting at 195° and, derivative decomposition at 259°.

In order to rationalise T_D data for aminophenol derivatives, it is necessary to note that derivative formation involves the preferential acylation of the amino ring substituent on the phenol [6, 7] as shown for the interaction of 2-aminophenol and *p*-NBC to form 2'-hydroxy-4-nitrobenzanilide [8].



Hence, the electronic effects of the hydroxyl ring substituent on the phenol have to be taken into consideration in the interpretation of T_D data for aminophenol derivatives.

There is some evidence for a steric effect of an ortho hydroxyl group of the aminophenol influencing derivative formation: T_D for the *p*-NBC derivatives 2-aminophenol and 3-aminophenol are 186° and 170° respectively. This is unlikely to be an intramolecular hydrogen-bonding effect associated with 2-aminophenol, since such bonding has been discounted previously [9]. Such a steric effect is also apparent with the aminonaphthols: T_D for the *p*-NBC derivatives of 3-amino-2-naphthol and 8-amino-2-naphthol are 216° and 205° respectively.

The -I inductive effect of chloro and nitro ring substituents on the phenol is revealed in the T_D data for the *p*-PABC derivatives of 2-aminophenol, 2-amino-4-chlorophenol and 2-amino-4-nitrophenol: 167°, 173° and 179° respectively. These substituents reduce the basicity of the aminophenol and thereby inhibit derivative formation. The opposite trend is exhibited by methyl ring substituents of the aminophenol. T_D data for the *p*-NBC derivatives of 2-aminophenol and 6-amino-2,4-dimethylphenol are 186° and 165° respectively. Such methyl substituents increase the basicity of the aminophenol and thereby enhance derivative formation. The cumulative electronic, steric and second-order effects associated with aminophenol derivative formation result in the ease of derivative formation for a given aminophenol being in the order: 3,5-dNBC < *p*-PABC ≃ *p*-NBC.

Table 4 Melting point of amino-phenols and of the corresponding derivatives

Phenol	Melting point, °C			
	Parent	*p*-PABC	*p*-NBC	3,5-dNBC
2-amino-	174	193 188^a	208 209^b	226
3-amino-	124	236 234^a	195	204
4-amino-	188	277 274^a	276 273^b	258
2-amino-4-chloro-	134	211	192	204
2-amino-4-nitro-	146	225	204	200
6-amino-2,4-dimethyl-	135	189	217	187
3-amino-2-naphthol	225	241	244	229
8-amino-2-naphthol	207	223	248	218

^{a}From Ref. 10, ^{b}From Ref. 11

Thus, in summary, it is apparent that the T_D data for the derivatives of nitrophenols and aminophenols can be rationalised in terms of primary electronic effects and secondary steric effects and hydrogen-bonding interactions associated with the phenol and derivative forming agent. It is a significant feature of the DTA method, that these effects at the molecular level are revealed.

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Zusammenfassung — Dies ist eine umfassende DTA-Untersuchung von acht Nitrophenolen und acht Aminophenolen 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 DTA-Gerät hergestellt wurden. Die bei der Thermoanalyse erhaltenen Angaben, insbesondere die Bildungstemperatur der Derivate wurde bezüglich des elektronischen und sterischen Effektes der Substituenten an 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.