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# A DTA STUDY OF PHENOLS
## II. Methyl-, methoxy- and methyl, halo-phenols

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**A comprehensive DTA study is reported of eight methyl-phenols, 4-methoxy-phenol and four methyl-halo-phenols and of the corresponding *p*-nitrobenzoylchloride, 3,5-dinitrobenzoylchloride and *p*-phenylazobenzoylchloride derivatives, prepared 'in situ' by heating intimate mixtures of phenol and acid chloride in a DTA system. The thermal analysis data, in particular, the derivative formation temperatures, are interpreted in terms of the inductive, mesomeric 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. The DTA data collectively, provide a comprehensive data base for the identification and characterisation of these phenols via DTA.**

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 was extensively tested and reported as Part 1 of a detailed DTA study [2] of phenols - a series of halo-phenols were characterised via a DTA study of the individual phenols together with the 'in-situ' formation of the corresponding *p*-nitrobenzoylchloride (*p*-NBC), 3,5-dinitrobenzoylchloride (3,5-dNBC) and *p*-phenylazobenzoylchloride (*p*-PABC) derivatives.

The second part of this comprehensive study is reported here as a DTA study of eight methyl-phenols, 4-methoxy-phenol and four methyl-halo-phenols and of the corresponding *p*-NBC, 3,5-dNBC and *p*-PABC derivatives. The thermal analysis data, and in particular, the derivative formation

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temperatures ($T_D$), are interpreted in terms of phenol acidity, steric 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 [2]. The Hot Stage Microscopy system, used to confirm derivative melting points, has also been described [2].

## Results and discussion

The DTA profile analysis data for eight methyl-phenols and 4-methoxy phenol and the corresponding *p*-PABC, *p*-NBC and 3,5-dNBC derivatives are recorded in Table 1. Similar data for four methyl-halo-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 methyl-phenols and methyl-halo-phenols and of the corresponding *p*-PABC, *p*-NBC and 3,5-dNBC derivatives are summarised in Tables 3 and 4 respectively.

Interpretation of the various peaks in the DTA profiles of these phenols is generally in accordance with the sequence: *mp* of phenol, *mp* of acid chloride, derivative formation ($T_D$), derivative *mp* and derivative decomposition [2]. Such an interpretation was facilitated in all cases, by confirmation of derivative *mp* by Thermal Optical Analysis.

Such a sequence of events is illustrated by the DTA peak definition temperature data for the *p*-NBC derivative of 3,4-dimethyl-phenol, as given in Table 4. Depressed melting points of the phenol and acid chloride occur at 43° and 50° respectively, followed by derivative formation at 76° ($T_D$), derivative melting at 123° and derivative endothermic decomposition at 182°. In some cases, the individual melting points of the components are not identifiable, as for example, for the 2,4,6-trimethylphenol-*p*NBC derivative.

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

| Phenol | | Peak definition temperatures, °C | | |
|---|---|---|---|---|
| | | onset | peak | offset |
| 2,6-dimethyl- | parent | 44 | 49 | 62 |
| | | 83 | 157 | 167 |
| | p-PABC | - | - | - |
| | p-NBC | - | - | - |
| | 3,5-dNBC | 31 | 42 | 46 |
| | | 46 | 50 | 56 |
| | | 95 | 120sh | |
| | | | *161 | 168 |
| | | 168 | 179 | 194 |
| 3,4-dimethyl- | parent | 54 | 63 | 69 |
| | | 99 | 152 | 168 |
| | p-PABC | 51 | 55sh | |
| | | | 62 | 70 |
| | | 70 | 86 | 90 |
| | | 94 | *106 | 120 |
| | | 130 | 171 | 211 |
| | p-NBC | 34 | 43 | 45 |
| | | 45 | 50 | 62 |
| | | 62 | 76 | 88 |
| | | 115 | *123 | 135 |
| | | 148 | 182 | 198 |
| | 3,5-dNBC | 40 | 42 | 45 |
| | | 45 | 56 | 67 |
| | | 80 | 98 | 106 |
| | | 170 | *186 | 195 |
| | | 209 | 263 | 289 |
| 3,5-dimethyl- | parent | 56 | 64 | 72 |
| | | 100 | 177 | 195 |
| | p-PABC | 52 | 57sh | |
| | | | 64 | 71 |
| | | 71 | 81 | 92 |
| | | 92 | *109 | 125 |
| | | 125 | 163 | 189 |
| | | 194 | 284 | 311 |
| | p-NBC | 36 | 44 | 46 |
| | | 46 | 53 | |
| | | | sh66 | 71 |
| | | 86 | 113sh | |
| | | | 139 | 159 |
| | 3,5-dNBC | 50 | 54sh | |

**Table 1** Continued

| Phenol | | Peak definition temperatures, °C | | |
|---|---|---|---|---|
| | | onset | peak | offset |
| | | | 64 | 74 |
| | | 77 | 87 | 103 |
| | | 165 | *197 | 213 |
| | | 245 | 260 | 286 |
| 2,5-dimethyl- | parent | 66 | 75 | 89 |
| | | 107 | 160 | 175 |
| | p-PABC | 51 | 61sh | |
| | | | 73 | |
| | | | sh85 | 91 |
| | | 91 | *99 | 107 |
| | | 107 | 113 | 122 |
| | | 122 | 132 | 183 |
| | p-NBC | 20 | 38 | 47 |
| | | 47 | 53 | |
| | | | sh76 | 80 |
| | | 80 | *91sh | |
| | | | 122 | 141 |
| | 3,5-dNBC | 43 | 44 | 49 |
| | | 56 | 68 | 78 |
| | | 83 | 98 | 119 |
| | | 129 | *140 | 153 |
| | | 180 | 201 | 238 |
| 2,3-dimethyl- | parent | 66 | 75 | 87 |
| | | 107 | 161 | 171 |
| | p-PABC | 56 | 59 | 65 |
| | | 65 | 68 | |
| | | | sh91 | 95 |
| | | 117 | *135 | 151 |
| | | 151 | 163 | 197 |
| | p-NBC | 28 | 43 | |
| | | | sh56 | |
| | | | sh85 | 94 |
| | | 124 | *146 | 150 |
| | | 168 | EXO Drift | |
| | 3,5-dNBC | 43 | 44 | 50 |
| | | 58 | 70 | 80 |
| | | 94 | 107 | 129 |
| | | 157 | *170 | 192 |
| | | 197 | 232 | 251 |
| 2,4,6-trimethyl- | parent | 59 | 69 | 82 |
| | | 99 | 156 | 171 |
| | p-dNBC | 54 | 58 | 63 |

**Table 1** Continued

| Phenol | | Peak definition temperatures, °C | | |
|---|---|---|---|---|
| | | onset | peak | offset |
| | | 63 | 76 | 90 |
| | | 90 | 99 | 107 |
| | | 119 | *139 | 177 |
| | | 192 | 221 | 234 |
| | p-NBC | 44 | 63 | 80 |
| | | 83 | 108 | 120 |
| | | 120 | *148 | 177 |
| | | 177 | EXO Drift | |
| | 3,5-dNBC | 44 | 54 | 64 |
| | | 64 | 73 | 81 |
| | | 87 | 134 | 139 |
| | | 139 | *154 | 173 |
| | | 180 | 194 | 216 |
| 2,3,5-trimethyl- | parent | 85 | 96 | 112 |
| | | 120 | 180 | 198 |
| | p-PABC | 66 | 72sh | |
| | | | 80 | |
| | | | sh92 | 108 |
| | | 120 | *138 | 149 |
| | | 154 | 164 | 198 |
| | p-NBC | 35 | 44 | 57 |
| | | 57 | 65 | 80 |
| | | 80 | 96sh | |
| | | | *145 | 151 |
| | | 170 | 196 | 218 |
| | 3,5-dNBC | 41 | 49 | 58 |
| | | 58 | 66 | 80 |
| | | 100 | 115 | |
| | | | *167 | 176 |
| | | 204 | 234 | 250 |
| 3,4,5-trimethyl- | parent | 99 | 108 | 126 |
| | | 132 | 197 | 215 |
| | p-PABC | 70 | 77sh | |
| | | | 84 | |
| | | | sh86 | 112 |
| | | 112 | *149 | |
| | | | 165 | 191 |
| | | 191 | 210 | 229 |
| | p-NBC | 30 | 43 | 58 |
| | | 58 | 72 | |
| | | | sh74 | 91 |
| | | 139 | *164 | 194 |

**Table 1** Continued

| Phenol | | Peak definition temperatures, °C | | |
|---|---|---|---|---|
| | | onset | peak | offset |
| | | 226 | 291 | 306 |
| 3,4,5-trimethyl- | 3,5-dNBC | 53 | 61 | 72 |
| | | 76 | 87 | 90 |
| | | 90 | 93 | 106 |
| | | 123 | *145 | 154 |
| | | 171 | 213 | 264 |
| 4-methoxy- | parent | 50 | 56 | 75 |
| | | 115 | 194 | 212 |
| | p-PABC | 47 | 58 | 65 |
| | | 73 | 76sh | |
| | | | 80 | 102 |
| | | 110 | *125 | 134 |
| | | 134 | 149 | 160 |
| | p-NBC | 41 | 55 | |
| | | | sh61 | 73 |
| | | 149 | *171 | 191 |
| | | 215 | 286 | 302 |
| | 3,5-dNBC | 36 | 57 | 71 |
| | | 71 | 84 | 104 |
| | | 125 | *146 | |
| | | | 164 | 179 |

sh shoulder

*Derivative melting point (confirmed by Hot Stage Microscopy)

Additionally, in this case, the final decomposition process is not well defined.

The peak definition temperature data (Tables 1 and 2) relating to the decomposition of the parent phenols, give an indication of the relative thermal stability of these systems. For the methyl-phenols, it is apparent that as the number of methyl substituents on the phenol increases, the thermal stability of the phenol increases. For example, 3,4,5-trimethyl-phenol decomposes at 197° whereas 3,4-dimethyl-phenol decomposes at 152°. A single methoxy group enhances thermal stability, since 4-methoxy-phenol decomposes at the relatively high temperature of 194°. Thus, it appears that as a general trend, the thermal stability of a phenol is enhanced by electron donor ring substituent groups.

In the general context of the interpretation of DTA data for phenols, Salman *et al.* [3, 4] have revealed an interesting correlation between fusion and decomposition enthalpies of orthosubstituted phenols, as derived by DTA,

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

| Phenol | | Peak definition temperatures, °C | | |
|---|---|---|---|---|
| | | onset | peak | offset |
| 4-chloro-2-methyl- | parent | 26 | 45 | 59 |
| | | 78 | 167 | 193 |
| | p-PBC | 32 | 45 | 60 |
| | | 70 | 84 | 93 |
| | | 107 | 120 | |
| | | | *145 | 161 |
| | | 198 | 213 | 226 |
| | p-NBC | - | - | - |
| | 3,5-dNBC | 31 | 42 | 49 |
| | | 49 | 58 | 69 |
| | | 102 | 146sh | |
| | | | *162 | 201 |
| | | 201 | 227 | 249 |
| 4-chloro-3-methyl | parent | 59 | 65 | 80 |
| | | 165 | 208 | 221 |
| | p-PABC | 44 | 56 | |
| | | | sh70 | 80 |
| | EXO Drift to | 87.94 | 120 | 132 |
| | | 132 | *158 | 181 |
| | | 251 | 282 | 311 |
| | p-NBC | 20 | 45 | 64 |
| | | 98 | 138 | 145 |
| | | 145 | *166 | 172 |
| | | 172 | 187 | 210 |
| | 3,5-dNBC | 31 | 42 | 49 |
| | | 49 | 58 | 69 |
| | | 112 | 154sh | |
| | | | *173 | 191 |
| | | 201 | 227 | 249 |
| 4-bromo-3,5-dimethyl- | parent | 101 | 113 | 127 |
| | | 137 | 201 | 224 |
| | p-PABC | 67 | 76 | 80 |
| | | 80 | 90 | 106 |
| | | 107 | 123 | 138 |
| | | 138 | *162 | 174 |
| | | 214 | 292 | 304 |
| | p-NBC | 34 | 45 | 51 |
| | | 51 | 53 | 66 |
| | | 120 | 140sh | |
| | | | *177 | 198 |

**Table 2 Continued**

| Phenol | | Peak definition temperatures, °C | | |
|---|---|---|---|---|
| | | onset | peak | offset |
| | | 198 | 241 | 265 |
| | 3,5-dNBC | 46 | 57 | 66 |
| | | 81 | 90 | 98 |
| | | 135 | 156 | 164 |
| | | 164 | *180 | 189 |
| | | 205 | 243 | 291 |
| 4-chloro-3,5-dimethyl- | parent | 101 | 114 | 130 |
| | | 140 | 205 | 220 |
| | p-PABC | 71 | 86sh | |
| | | | 95 | 107 |
| | | 119 | 121 | 129 |
| | | 154 | *167 | 182 |
| | | 184 | 200 | 214 |
| | p-NBC | 38 | 48 | 54 |
| | | 54 | 56 | 69 |
| | | 111 | 138 | |
| | | | *179 | 201 |
| | | 258 | 287 | 299 |
| | 3,5-dNBC | 55 | 60 | 67 |
| | | 82 | 90 | 103 |
| | | 122 | 154 | 160 |
| | | 166 | *186 | 198 |
| | | 211 | 261 | 302 |

sh shoulder

*Derivative mp confirmed by Hot-stage Microscopy

with the degree of intramolecular hydrogen bonding in these systems. Since hydrogen bonding effects associated with phenols directly influence the acidity of these systems, such a quantitative correlation is of importance in the rationalisation of DTA data related to phenol derivatives.

As a preliminary to a detailed interpretation of the $T_D$ data (Tables 1, 2) for the various phenol derivatives studied, it is relevant to briefly discuss the chemistry of these systems in terms of the intramolecular electronic effects operating [5].

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 acid chloride and phenoxide ion respectively. Thus, derivative formation is directly favoured by electron releasing ring substituents of the phenol and electron withdrawing ring substituents of the acid chloride. This primary interaction is impeded by steric effects of ring substituents in the 2 and 6 positions of each moiety. Also, intra- and intermolecular hydrogen-bonding effects associated with the phenol and intermolecular phenol/acid chloride hydrogen-bonding impede derivative formation.

**Table 3** Melting points of methyl- and methoxy- phenols and of the corresponding derivatives

| Phenol | Melting point, °C | | | |
|---|---|---|---|---|
| | Parent | p-PABC | p-NBC | 3,5-dNBC |
| 2,4-dimethyl- | 27 | $111^a$ | $102^b$ | $164^b$ |
| 2,6-dimethyl- | 49 | | | 161 |
| | | | | $159^b$ |
| 3,4-dimethyl- | 62.5 | 106 | 123 | 186 |
| | | $104^a$ | | $182^b$ |
| 3,5-dimethyl- | 64 | 109 | 113 | 197 |
| | | $105^a$ | $109^b$ | $195^b$ |
| 2,5-dimethhyl | 74.5 | 99 | 91 | 140 |
| | | $96^a$ | $87^b$ | $137^b$ |
| 2,3-dimethyl- | 75 | 135 | 146 | 170 |
| 2,4,6-trimethyl | 69 | 139 | 148 | 154 |
| 2,3,5-trimethyl- | 96 | 138 | 145 | 167 |
| 3,4,5-trimethyl- | 108 | 149 | 164 | 145 |
| 4-methoxy- | 56 | 125 | 171 | 146 |

[a] From Ref. [6]

[b] From Refs [7-9]

**Table 4** Melting points of methyl, halo-phenols and of the corresponding derivatives

| Phenol | Melting point,°C | | | |
|---|---|---|---|---|
| | Parent | p-PABC | p-NBC | 3,5-dNBC |
| 4-chloro-2-methyl- | 45 | 145 | - | 162 |
| 4-chloro-3-methyl- | 65 | 158 | 166 | 173 |
| 4-bromo-3,5-dimethyl- | 113 | 162 | 177 | 180 |
| 4-chloro-3,5-dimethyl- | 114 | 167 | 179 | 186 |

With respect to a particular methyl-phenol or to 4-methoxy-phenol, the general trend in corresponding derivative formation temperatures ($T_D$), (Table 1), is: *p*-NBC<*p*-PABC<3,5-dNBC. The corresponding trend for methyl-halo-phenol derivative formation temperatures (Table 2) is *p*-PAB<*p*-NBC< 3,5-dNBC. These trends are simply a reflection primarily of the cumulative electron withdrawing ability of the acid chloride based upon the nature of the ring substituents and their associated steric effect.

With respect to the derivative formation ability of methyl-phenols, the associated methyl ring substituents primarily reduce the acidity of the phenol, and those phenols with methyl ring substituents at the 2 and 6 positions exert an additional steric effect. For example, the overall decreased acidity effect is shown by $T_D = 76^\circ$ for the 3,4-dimethyl-phenol-*p*NBC derivative and $T_D = 66^\circ$ for the 3,5-dimethylphenol-*p*NBC derivative. The effect is sufficiently refined to reveal that a methyl substituent in the 4 position is more effective in reducing phenol acidity than one in the 5 position. Further, a methoxy group is more effective in reducing phenol acidity than a methyl group, as shown by $T_D$ of 80° and 86° for the 4-methoxy-phenol and 3,4-dimethyl-phenol-*p*PABC derivatives respectively. However, a halo ring substituent coupled with a methyl ring substituent appears also to give a net reduction in phenol acidity, which is explained in terms of the halo ring substituent preferentially promoting phenol intermolecular hydrogen bonding. This effect is revealed by the $T_D$ data (Table 2) for 3,4-dimethylphenol and 4-chloro-3-methyl-phenol-*p*NBC derivatives ($T_D = 76^\circ$ and 120° respectively).

**Table 5** p$K_a$ data for methyl- and methoxy- phenols and $T_D$ data for the corresponding derivatives

| Phenol | a | Derivative formation temperature $T_D$, °C | | |
|---|---|---|---|---|
| | p$K_a$ | p-PABC | p-NBC | 3,5-dNBC |
| 3,5-dimethyl- | 10.20 | 81 | 66 | 87 |
| 4-methoxy- | 10.21 | 80 | 61 | 84 |
| 3,4,5-trimethyl- | 10.25 | 84 | 74 | 93 |
| 3,4-dimethyl- | 10.36 | 86 | 76 | 98 |
| 2,5-dimethyl- | 10.41 | 85 | 76 | 98 |
| 2,3-dimethyl- | 10.54 | 91 | 85 | 107 |
| 2,3,5-trimethyl- | 10.59 | 92 | 96 | 115 |
| 2,4,6-trimethyl- | 10.89 | 99 | 108 | 134 |

[a] From Refs [10-12]

Although the electronic and steric effects associated with the phenol and acid chloride produce a net sinergistic effect, it appears that phenol acidity is the dominant effect on derivative formation and this is qualitatively revealed by the $pK_a/T_D$, relationships shown in Figs 1 and 2. Essentially, as phenol acidity decreases, $T_D$ increases. However, those phenols which exhibit a pronounced primary steric effect, are not in conformity with the trend, as revealed by the *p*Ka/*T*D data (Table 5) for 3,4,5-trimethyl-phenol and 2, 4, 6-trimethylphenol and the corresponding *p*NBC derivatives.

**Table 6** p*K*a data for methyl, halo-phenols and *T*D data for the corresponding derivatives

| Phenol | *a* | Derivative formation temperature *T*D, °C | | |
|---|---|---|---|---|
| | p*K*a | p-PABC | p-NBC | 3,5-dNBC |
| 4-chloro-3-methyl- | 9.55 | 120 | 138 | 154 |
| 4-chloro-3,5-dimethyl- | 9.70 | 119 | 133 | 151 |
| 4-chloro-2-methyl- | 9.71 | 120 | - | 146 |

[a] From Refs [10-12]

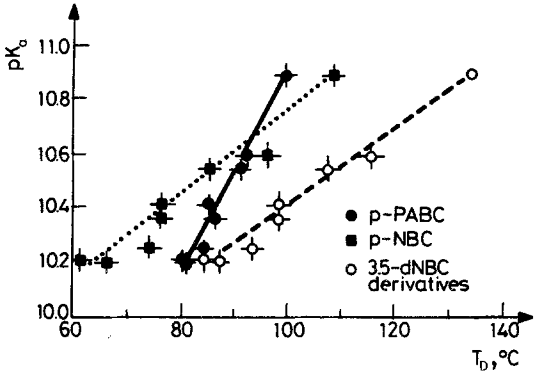

**Fig. 1** *p*Ka/*T*D relationships for methyl- and methoxy-phenol systems

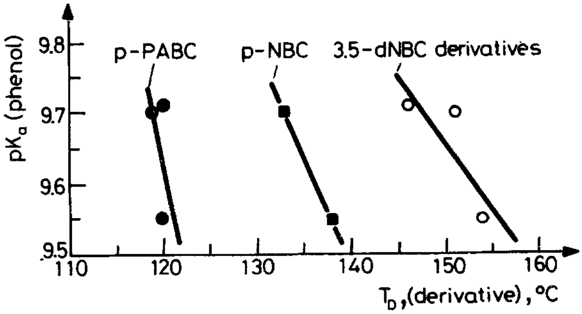

**Fig. 2** *p*Ka/*T*D relationships for methyl, halo-phenol systems

Thus, in summary, it is apparent that the cumulative peak definition temperature data (Tables 1, 2) relating to these phenols and the corresponding derivatives, can be adequately rationalised in terms of the inductive, mesomeric and steric effects inherent in these systems.

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**Zusammenfassung** — An durch Erhitzen inniger Mischungen aus Phenol und Säurechloriden in einem DTA-System hergestellten acht Methylphenolen, an 4-Methoxyphenol, an vier Methylhalophenolen und an den entsprechenden *p*-Nitrobenzoylchlorid-, 3,5-Dinitrobenzoylchlorid- und *p*-Phenylazobenzoylchloridderivaten wurden ausführliche DTA-Untersuchungen durchgeführt. Thermoanalytische Ergebnisse, insbesondere die Bildungstemperatur der Derivate wurden als Ausdruck des induktiven, mesomeren und sterischen Effektes bezüglich der Substituenten am Phenolring und des Säurechlorides sowie des Ausmaßes der in diesem System existierenden inter- und intramolekularen Wasserstoffbrückenbindungen gewertet. Die Gesamtheit der DTA-Daten ist gleichzeitig eine ausführliche Datenreferenz zur Identifizierung und Charakterisierung dieser Phenole mittels DTA.