

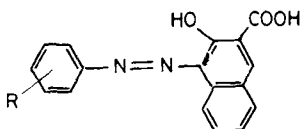
## THERMAL ANALYSIS OF ARYLAZOHYDROXYNAPHTHOIC ACIDS

M. NEČAS and M. HORÁK

*Research Institute for Organic Syntheses, 532 18 Pardubice, ČSSR*

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Arylazohydroxynaphthoic acids of general formula



were subjected to thermal analysis. The decomposition temperatures of the compounds were found to be determined by the resonance and inductive interaction of substituent R with the benzene ring and the azo group of the arylazohydroxynaphthoic acid molecule. The results of DTG analysis correspond with the Hammett  $\sigma_H$  constants. The mechanism of thermal splitting is briefly discussed.

The thermal behaviour of azo compounds has been studied within an evaluation of organic pigments, by investigation of the changes in their application properties with temperature. The thermal stability of an organic pigment is an important factor determining the applicability of the product for special use. Changes occurring in the properties of azo compounds (pigments) as the temperature is elevated have been investigated using electron-microscopy, X-ray spectra, differential thermal analysis and thermogravimetry [1, 2]. Attention has also been paid to the mechanism and kinetics of thermal decomposition of some azo compounds, with the use above all of manometric methods [3–5]. The calculated values of the activation energies have been discussed.

The aim of this paper was to obtain information concerning the thermal stability of arylazohydroxynaphthoic acids, i. e. azo compounds having evident practical importance; they are used as pigments for colouring either directly, or as raw materials for the production of other high-quality products. At present, practice has outrun the level of theoretical knowledge, so it is necessary to compile the currently missing information about the relations between the structures and the physical chemical properties of these compounds, and to use these subsequently in the practical application. We have studied the influence of the substituents on the benzene ring of 4-arylaazo-3-hydroxy-2-naphthoic acids on their thermal stability by means of dynamic thermal analysis.

### Experimental

Substituted arylazohydroxynaphthoic acids prepared by the direct diazotization of the corresponding amine, followed by coupling of the diazonium salt with 3-hydroxy-2-naphthoic acid in alkaline medium. The reaction mixture was acidi-

Table 1  
4-arylaazo-3-hydroxy-2-naphthoic acids

Substituent R		Elemental analysis (calculated/found)				Melting point, °C
		C	H	N	Cl(Br)	
H	C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	69.87 69.86	4.17 4.14	9.70 9.58		239–240
3-CH <sub>3</sub>	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	69.76 70.58	4.68 4.61	9.18 9.14		227–228
4-CH <sub>3</sub>	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	70.81 70.58	4.73 4.61	9.10 9.14		250–253
3,4-diCH <sub>3</sub>	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	71.20 71.24	5.01 5.03	9.00 8.74		259–260
4-CH <sub>3</sub> O	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub>	67.24 67.07	4.46 4.38	8.64 8.69		226–227
2-Cl	C <sub>17</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> Cl	62.38 62.49	3.60 3.39	8.75 8.57	10.98 10.85	265–266
4-Cl	C <sub>17</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> Cl	62.52 62.49	3.57 3.39	8.68 8.57	10.64 10.85	280–281
2,5-diCl	C <sub>17</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	56.56 56.53	2.76 2.79	8.15 7.76	19.65 19.63	271–276
4-Br	C <sub>17</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> Br	55.18 55.01	3.23 2.99	7.75 7.55	21.51 21.53	292–293
2-NO <sub>2</sub>	C <sub>17</sub> H <sub>11</sub> N <sub>3</sub> O <sub>5</sub>	60.57 60.54	3.55 3.29	12.12 12.46		312–314
3-NO <sub>2</sub>	C <sub>17</sub> H <sub>11</sub> N <sub>3</sub> O <sub>5</sub>	60.79 60.54	3.50 3.29	12.36 12.46		308–309
4-NO <sub>2</sub>	C <sub>17</sub> H <sub>11</sub> N <sub>3</sub> O <sub>5</sub>	59.89 60.54	3.39 3.29	12.31 12.46		324–325
2-NO <sub>2</sub> -4-Cl	C <sub>17</sub> H <sub>10</sub> N <sub>3</sub> O <sub>5</sub> Cl	54.22 54.93	2.80 2.71	11.25 11.30	9.62 9.54	289–293
3-COOH	C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> O <sub>5</sub>	64.04 64.29	3.89 3.60	8.41 8.33		302–303

fied, and the product was filtered off, washed with water and dried up to 90°. Elemental analyses of the prepared compounds and the corresponding melting points are given in Table 1.

The thermal analyses were carried out using an OD-102 derivatograph (Paulik, Paulik, Erdely), in an atmosphere of air, in the temperature range 20–700°, at a heating rate of 7.0°/min.

## Results and discussion

The course of the changes occurring during the dynamic thermal analysis of 4-phenylazo-3-hydroxy-2-naphthoic acid is given in Fig. 1. The other compounds studied behaved in a similar way. Their thermoanalytical parameters (endo- and exo-peaks from DTA curves and DTG peak positions) are given in Table 2. It can be seen from Fig. 1 and Table 2 that three exothermic and two endothermic reactions occur during the dynamic heating of arylazohydroxynaphthoic acids. In all cases, immediately following the endothermic phase change (melting of the sample), vigorous exothermic decomposition starts. This reaction proceeds very quickly and results in a mass loss of 25–44%. On subsequent heating, the mass loss slows down (ca. 15–20%) and endothermic peaks appear in the DTA curve. At around 400° the mass-loss rate increases and in the very strongly exothermic oxidation reaction two peaks can usually be distinguished in the DTA or DTG curves.

The temperature ( $T_D$ ) corresponding to the top of the DTG peak of the first exothermic decomposition reaction was used as a measure of the thermal stability of the investigated compounds. The strong influence of the substituents R on the

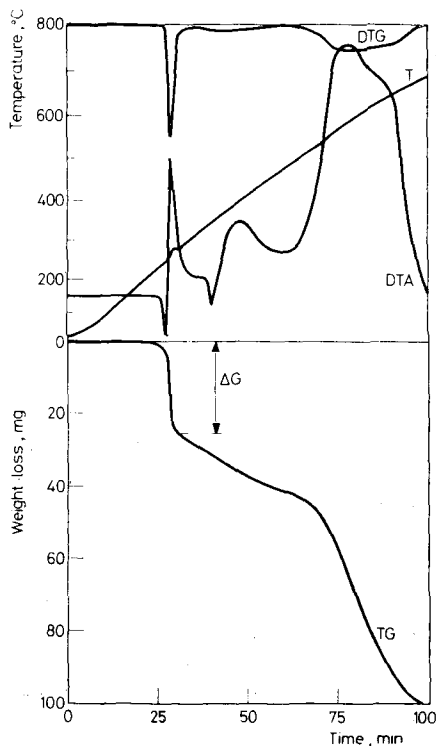


Fig. 1. Simultaneous TG/DTG/DTA of 4-phenylazo-3-hydroxy-2-naphthoic acid



The qualitative explanation of the stabilization or destabilization of the arylazo-hydroxynaphthoic acid molecule via the influence of the substituent on the benzene ring was confirmed experimentally by a study of the behaviour of the acids using dynamic thermal analysis. The good correlation of the thermal stability values ( $T_D$ ) with the Hammett  $\sigma_H$  constant (see ref. [8]) was found, reflecting the influence of substituents in the meta or para positions in the azo group. The dependence of parameter  $T_D$  on the Hammett constant was found to be described by the function

$$T_D = A \cdot \sigma_H + B$$

where  $A$  and  $B$  are the constants of linear regression (see Fig. 2). The results of dynamic thermal analysis are thus in full agreement with considerations concerning the electronic structures of the investigated compounds.

The mass loss in the first thermal decomposition reaction of the arylazohydroxynaphthoic acids ( $\Delta G$  in Fig. 1) corresponds approximately to the mass of the substituted aryl group (Table 3). This means that the basis of the reaction is the heterolytic splitting of the bond between the aryl and the azo-bound nitrogen; the resulting substituted aryl, having a lower molecular weight than the rest of the molecule, will evaporate from the sample under investigation. It is interesting to note that the found values of the mass loss are greater than the calculated  $\Delta G$  only for the 2-Cl, 2-NO<sub>2</sub> and 2-NO<sub>2</sub>-4-Cl derivatives, i. e. those compounds where we can assume a partial hydrogen-bond to the chlorine or nitro group in the ortho position to the azo-bond, in addition to the hydrogen-bond N-H...O discussed above. Anyway, the differences between the  $\Delta G$  calculated and found values indicate that the discussed reaction is more complicated. Thus, the mechanism cannot be expressed by the simple reaction equation, and several other reactions besides the heterolytic splitting take place within the decomposition of the acids.

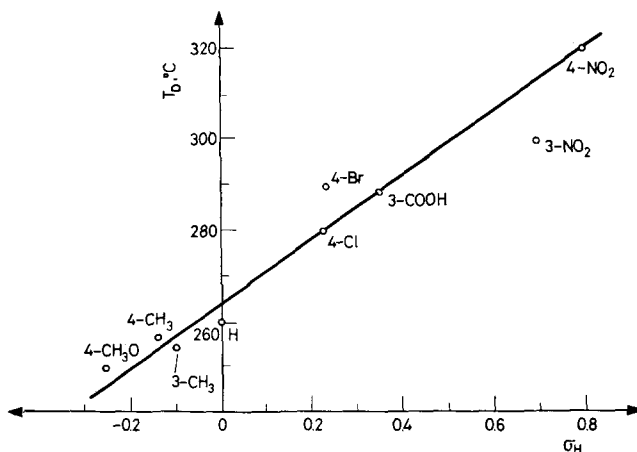


Fig. 2. Correlation of thermal stabilities of arylazohydroxynaphthoic acids with the Hammett constants

Table 3

Mass loss in the first decomposition reaction

R	Mass loss $\Delta G$ , wt. %	
	calculated	found
H	26	26
3-CH <sub>3</sub>	30	29
4-CH <sub>3</sub>	30	28
3,4-diCH <sub>3</sub>	33	29
4-CH <sub>3</sub> O	33	30
2-Cl	34	37
4-Cl	34	28
2,5-diCl	40	39
4-Br	42	30
2-NO <sub>2</sub>	36	41
3-NO <sub>2</sub>	36	31
4-NO <sub>2</sub>	36	33
2-NO <sub>2</sub> -4-Cl	42	45
3-COOH	36	26

### Conclusion

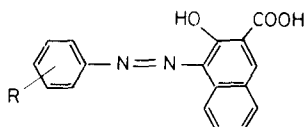
A study of substituted 4-aryloxy-3-hydroxy-2-naphthoic acids using dynamic thermal analysis has proved that the thermal stability of the acid is determined by the substituent on the phenyl ring of the molecule. The decomposition temperatures of the compounds were found to be determined by the resonance and inductive interaction of substituent R with the benzene ring and the azo group of the arylazo-hydroxynaphthoic acid. The results of dynamic thermal analysis are in full agreement with considerations concerning the electronic structures of the molecules. The experimentally found values of the thermal stabilities correlate with the Hammett  $\sigma_H$  constants. The mechanism of the thermal decomposition is complicated, but basically consists in the heterolytic splitting of the bond between the substituted benzene ring and the azo-bound nitrogen. The thermal stability of the arylazo-hydroxynaphthoic acid can be influenced in a large temperature range by the choice of substituent R.

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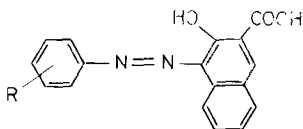
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ZUSAMMENFASSUNG — Die Thermoanalyse wurde zur Untersuchung der thermischen Zersetzung substituierter 4-Arylazo-3-hydroxy-2-Naphtoesäuren



eingesetzt. Es zeigte sich, daß die Zersetzungstemperaturen der Verbindungen durch die Resonanz und induktiven Wechselwirkungen der Substituenten R mit dem Benzenring und den Azogruppen der Arylazohydroxy-naphtoesäure bestimmt wird. Zwischen den Versuchsergebnissen der Thermostabilität und den Hammettschen  $\sigma_H$ -Konstanten besteht eine Korrelation. Der Zersetzungsmechanismus wird kurz diskutiert.

Резюме — В процессе изучения термических свойств замещенных 4-арилазо-3-окси-2-нафтойных кислот



методом динамического термического анализа установлено, что термоустойчивость их определяется типом заместителя в фенильном кольце. Экспериментально найденные значения термоустойчивости коррелируются с константами Гаммета  $\sigma_H$ . Обсужден механизм термического разложения.