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THERMOANALYTICAL STUDY OF ACTIVATED CARBON REGENERATION. II. *o*-, *m*-, *p*-NITROPHENOL DESORPTION*

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ABSTRACT

Partial adsorbate release (63, 50 and 53% for *o*-, *m*-, and *p*-derivatives, respectively) occurs when a commercial activated carbon loaded with each nitrophenol isomer is heated between 25 and 950°C in a dynamic N_2 atmosphere. After the endothermic process of water removal below 150°C, three definite steps are associated with adsorbate release. Evaluation of the related energies is presented.

INTRODUCTION

A thermoanalytical investigation of the desorption of various pollutants from a granular activated carbon (AC) has been systematically undertaken.

Release patterns and energy requirements when phenol or aniline saturated AC are heated, presented in Part I of this study[1], suggested that other energetic processes (pyrolysis, readsorption, etc.) are superimposed upon the desorption step, thus making the thermodesorption mechanism of single pollutants difficult to evaluate.

In this paper the investigation is extended to mono-nitro-derivatives (*o*-, *m*-, *p*-isomers) of phenol to examine the modifications of thermoanalytical behaviour associated with the introduction of the $-NO_2$ group.

EXPERIMENTAL

Various samples (about 100 dry mg each) of 16–25 (US) mesh granular carbon (Filtrasorb 400 from Calgon Corp., Pittsburg, Pa.) were equilibrated at room temperature with 100 ml aqueous solution at 300 p.p.m. of each *o*-, *m*- and *p*-nitrophenol (ONF, MNF, PNF). Prior to thermal analysis, all samples were vacuum filtered to variable residual moisture, to ascertain possible ternary AC–H_2O– adsorbate inter-

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actions. This made for an overall number of 10 × 3 = 30 samples to be processed.

Quantitative determinations on the liquid phase were performed spectrophotometrically at wavelengths of maximum absorption, namely 280, 230, 314 nm for ONF, MNF and PNF, respectively.

Thermal analyses between 25 and 950 °C were accomplished with a thermoanalyzer (TA 1 from Mettler AG, Zürich, Switzerland) in a dynamic nitrogen atmosphere.

Further details on apparatus and operating procedure are described in a previous paper[1], where reference should also be made to the "matrix blank" evaluation during mass balances.

RESULTS AND DISCUSSION

As shown by Figs. 1–3 (TG and DTG curves), weight losses continuously occur up to 950 °C for all three nitro-derivatives, with major releases associated with three specific temperature intervals. When provisions for weight loss of carbonaceous matrix are made[1], mass balances show that water is almost completely released before 150 °C, quite independently of residual moisture content of the sample. The different DTG peak areas in this temperature range, hence, refer to different

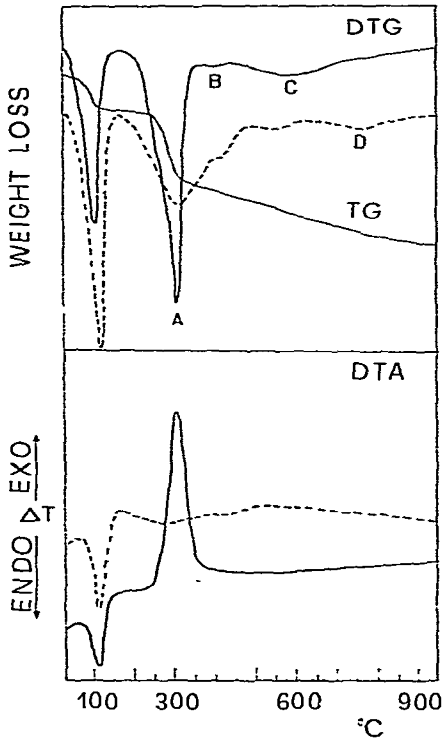

Fig. 1. TG, DTG and DTA curves for *o*-nitrophenol loaded activated carbon. Broken lines refer to phenol.

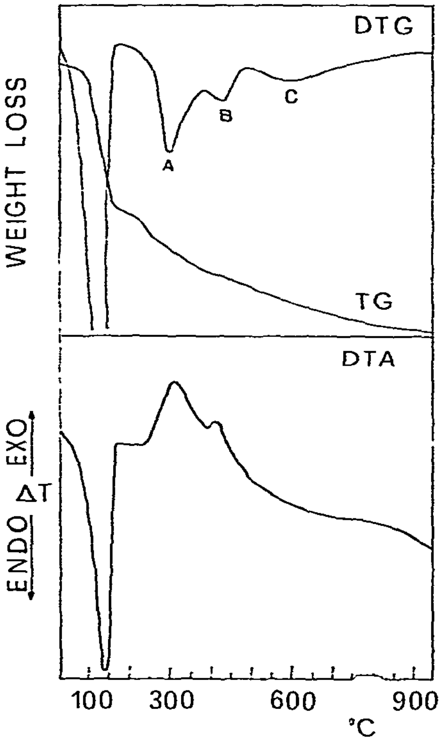

Fig. 2. TG, DTG and DTA curves for *m*-nitrophenol loaded activated carbon.

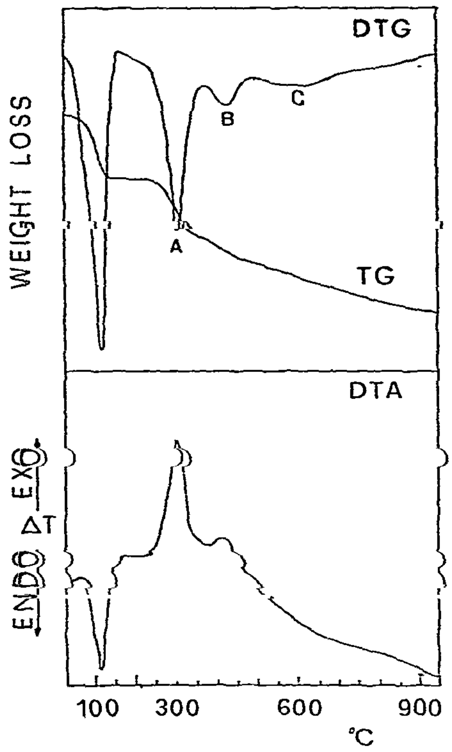

Fig. 3. TG, DTG and DTA curves for *o*-nitrophenol loaded activated carbon.

humidities of the sample. Three definite steps, with an almost constant value for peak tip temperatures (300, 420 and 630°C for steps A, B and C) invariably appear for the three isomers. At each step, however, different weight losses and peak heights occur for each isomer, making an overall desorption of about 63, 50 and 53% of adsorbed amount for the *o*-, *m*- and *p*-isomer, respectively. As previously found for phenol loaded AC[1], partial desorption up to 950°C in these conditions is in agreement with backing performances in an inert atmosphere. As in the case of phenol, however, the greatest percentage release occurs below 500°C (up to 70% of desorption associated with step A for the *o*-isomer).

By comparison with thermal behaviour of phenol loaded AC (dotted DTG curve in Fig. 1), a slightly simplified thermogravimetric pattern (step D disappears for all isomers), with a modified ratio between steps A and B, is obtained with the nitro-derivatives. This should be clearly related to the electron-drawing character of the $-NO_2$ group, which facilitates the interactions of the adsorbate benzenic ring with the π-electron system of the graphitic surface of AC[2]. While step A markedly predominates over the remaining steps in *o*-nitrophenol, the comparable extension of steps A, B and C for *m*- and *p*-nitrophenols points to the nitro-group, rather than hydroxyl, as the major contributor to AC–adsorbate interactions, in agreement with conclusions of Mattson and Mark[3], based on coincidence of adsorption isotherms of the two isomers.

As for DTA curves, it should be noticed that only steps A and B, other than the weight loss below 150 °C, can be associated with quite distinct DTA peaks (Figs. 1–3). By relating energetic effects to corresponding weight losses, a value of about -10.0, -11.8, -9.5 kcal mole^{-1} for the endothermic peak below 150 °C is obtained for ONF, MNF and PNF, respectively.

It is quite interesting to observe that exothermic DTA effects are invariably associated with thermal treatment beyond 150 °C for all three isomers, confirming that other, exothermic reactions are simultaneously occurring during desorption, an intrinsically endothermic process[4].

If one neglects to evaluate separately energetic effects of steps A and B for MNF and PNF, referring mass decrease to the molecular weight of nitrophenol, an overall heat release of about $+114$, $+134$ and $+105$ kcal mole^{-1} can be associated with DTA effects for ONF, MNF and PNF in that order. As already found by Nwankwo and Turk[5] during the thermal analysis of AC loaded with various oxygenated organic solvents, accounting for the moderate endothermic DTA effect shown by phenol in the same interval (about -25 kcal mole^{-1}, see Fig. 1), an approximately six-fold energy release is clearly to be associated with oxidation side reactions induced by the $-NO_2$ group (main oxidation within step A, with remaining material gradually removed in step B). The recovery of this consistent energy release could be eventually utilised for a self-maintaining AC thermal regeneration in these systems.

CONCLUSIONS

The explosive content of the $-NO_2$ group produces exothermic peaks during the heating of *o*-, *m*- and *p*-nitrophenols, of possible significance for an energy conservation approach to thermal regeneration of AC. No resolution has been evidenced, under the adopted experimental conditions, between oxidation reactions and the adsorbate desorption process.

An easier release pattern, however, can be observed for the three $-NO_2$ isomers, compared to the desorption of phenol.

As already anticipated for the parent material (phenol), for all three isomers experimental evidence shows that side processes, not desorption, lead to their energetic behaviour during thermal treatment.

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