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THERMOANALYTICAL STUDY OF ACTIVATED CARBON REGENERATION. III. *o*-, *m*-, *p*-NITROANILINE DESORPTION*

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ABSTRACT

The thermal behaviour of granular activated carbon loaded with *o*-, *m*- and *p*-nitroaniline up to 950°C in a N_2 atmosphere is described. Partial release is obtained for all compounds under these conditions, with about 90% of the desorption occurring before 500°C with a complex, exothermic pattern. Energies associated with DTA effects are evaluated.

INTRODUCTION

A thermoanalytical study has been carried out to evaluate the desorption energies of some common pollutants during thermal regeneration of granular activated carbon (AC).

Pyrolysis and related effects have been shown to control desorption of phenol and aniline[1], while simpler patterns have been found when a nitro-group is introduced into a phenolic ring[2].

In this paper the thermal behaviour of AC loaded with each of the three nitroaniline, *o*-, *m*- and *p*-isomers (ONA, MNA, PNA), is described.

EXPERIMENTAL

About 100 mg of 16–25 (US) mesh dry AC (Filtrasorb 400 from Calgon Corp., Pittsburg, Pa.) were equilibrated with 100 cc of aqueous solution containing 300 p.p.m. of the nitro-isomer. The adsorbed amount was determined spectrophotometrically by analysis of the aqueous phase at the wavelength of maximum absorption (i.e., 234, 224 and 380 nm for ONA, MNA and PNA, respectively).

The samples were vacuum filtered and then heated up to 950°C in a dynamic

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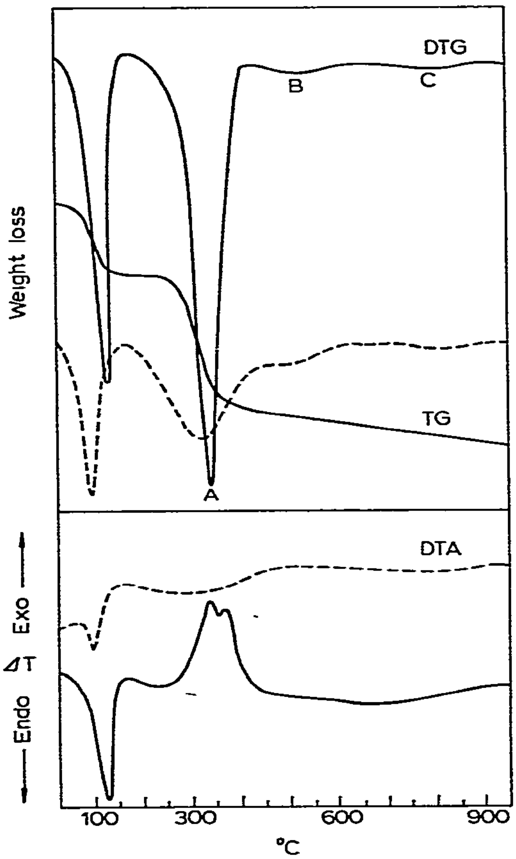
nitrogen atmosphere. Operating details and thermoanalytical procedure have been described previously[1].

RESULTS AND DISCUSSION

Typical thermoanalytical curves for the three isomers are reported in Figs. 1–3. Mass balances show that only water is released before 150°C. From the related endothermic peak, however, a consistently high energy requirement results (−10.7, −12.0 and −11.4 kcal mole^{-1}) for the ONA- MNA and PNA, compared with −9.0 kcal mole^{-1} obtained for aniline loaded AC under the same conditions[1] and with heat evaporation of water[3], −10.0 kcal mole^{-1}.

According to Saxena et al.[4], and Braun and Drost-Hansen[5], this should indicate the presence of an appreciable fraction of "tightly bound" water related to the $-NO_2$ group in this system, as suggested also by data scattering previously found in the nitro-phenol series[2].

As expected, partial release of adsorbate between 150 and 950°C occurs under



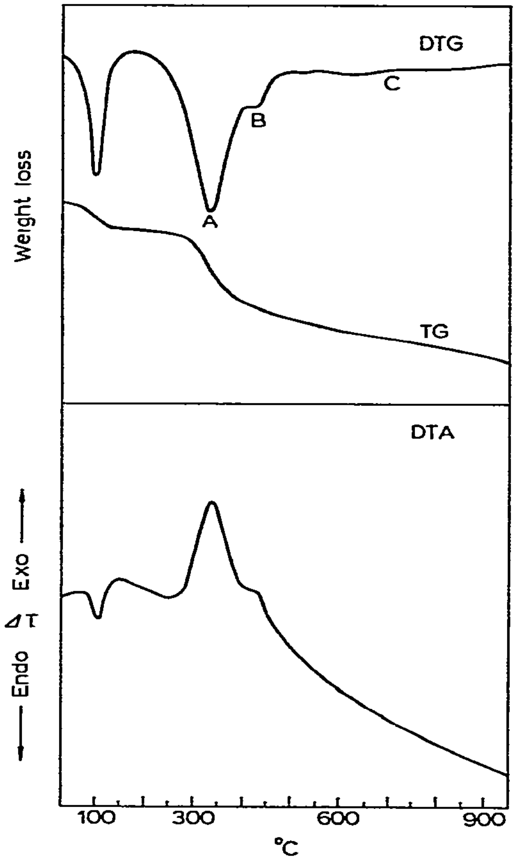


Fig. 1. TG, DTG and DTA curves for *o*-nitroaniline loaded activated carbon. Broken lines refer to aniline.

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

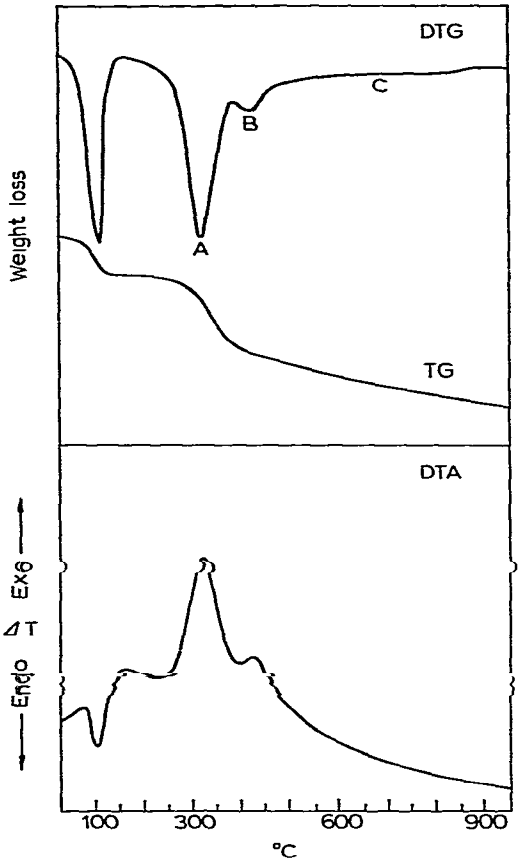


Fig. 3. TG, DTG and DTA curves for *p*-nitroaniline loaded activated carbon.

these conditions. A lower desorption is obtained with MNA and PNA (about 45%) compared with aniline loaded AC (54% overall weight loss at 950°C), in agreement with higher adsorption affinities shown by these products[6].

Maximum desorption, however, (60%), is unexpectedly obtained with ONA, which showed the highest adsorptivity[6]. The same anomalous pattern for the *o*-isomer has been previously found for the phenol nitro-derivatives series[2].

Considering this is the preferred adsorbate among the three nitro-derivatives, the H-bridge formation between $-NO_2$ and $-NH_2$ ($-OH$) is clearly to be accounted for with the *o*-isomer.

The approximately biphenilic configuration accordingly occurring, indeed, allows one to expect higher adsorptive interactions between AC and the larger planar surface of the *o*-compound; at the same time, such a more rigid configuration should be eventually responsible for its simplified release pattern during heating.

In every case, about 90% of desorption occurs before 500°C, mainly during step A (peak tip temperature 320°C) for ONA, with appreciable release also in step B (420°C) for MNA and PNA (see DTG curves).

Only pyrolytic fragments retained by the porous matrix of AC are released at higher temperatures (step C)[7], where no relevant energetic effects are evidenced in the adopted experimental conditions.

Compared to the endothermic peak measured for aniline desorption (−15 kcal mole^{-1})[1] (dotted DTA curve in Fig. 1) the strong oxidative effects associate with the nitro-group are strikingly evident from the exothermic peaks obtained, from which positive overall values of +65, +113 and +117 kcal mole^{-1} are obtained by referring weight losses to nitroaniline molecular weight.

The higher surface temperatures, locally associated with these exothermic effects, could help to explain the anticipated release before 500 °C. As in the nitrophenol series, desorption characteristics seem to be markedly influenced by the presence and position of the $-NO_2$ group. Step B occurs at an appreciably lower temperature in the *m*- and *p*-isomers compared to the non-substituted substrate, while it almost disappears in the *o*-derivative (see DTG curves).

CONCLUSIONS

Lower furnace temperatures than those expected from their higher adsorptivities are required to desorb nitro-derivatives than for the non-substituted aniline.

As in the case of the phenol-derivatives series, a simpler pattern for thermodesorption can be associated with the introduction of a nitro-group in the aniline series.

Further investigations are planned to clarify how the reduced adsorbent–adsorbate interactions favoured by a substituent like $-NO_2$ can produce an effective simplication in the thermodesorption mechanism.

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