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Short communication

Liquid chromatographic separation of intermediates of the catalytic hydrogenation of 2,4-dinitrotoluene

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Abstract

An improved HPLC method was developed for the separation and quantification of 2,4-dinitrotoluene and its reduction products. Gradient elution, with a water–acetonitrile mobile phase, was selected for the separation of all components including the 2,4-nitrohydroxyaminotoluene isomers. Provisional identification of the isomer intermediates has been obtained by their UV–Vis spectra.

Keywords: Hydrogenation; 2,4-Dinitrotoluene; 2,4-Nitrohydroxyaminotoluenes

1. Introduction

The catalytic hydrogenation of 2,4-dinitrotoluene (2,4-DNT) is a process used for the production of 2,4-diaminotoluene (2,4-DAT). 2,4-DAT is an intermediate for the manufacture of toluendiisocyanate which is used in the polyurethane industry [1]. In previous papers we have shown that the hydrogenation of 2,4-DNT over Pd/C catalysts involves the formation as relevant intermediates of 4-(hydroxyamino)-2-nitrotoluene (4HA2NT), 2-(hydroxyamino)-4-nitrotoluene (2HA4NT), 4-amino-2-nitrotoluene (4A2NT) and 2-amino-4-nitrotoluene (2A4NT) [2–4]. The arylhydroxylamino intermediates have a great practical importance, due to the large variety of fine chemicals which can be obtained through their rearrangement [5].

Despite the relevant importance of this reaction, no simple and accurate method is so far available for detection and quantification of all intermediates, especially the 2,4-nitrohydroxyaminotoluene isomers. Separation by gas chromatography is unfavorable because some analytes are thermally unstable and they cannot be detected [6]. High-performance liquid chromatography (HPLC) is more suitable [4], however, so far no sufficient separation of the 2,4-nitrohydroxyaminotoluene isomers has been reported by HPLC.

In this work we report a HPLC method for a better separation of the products of 2,4-DNT hydrogenation. By using photodiode array (PDA) detector, the UV–visible spectral characterization of the eluted intermediates has been also carried out.

2. Experimental

The hydrogenation of 2,4-DNT (Aldrich, purity 97%) was carried out in the liquid-phase, in a batch type reactor at 323 K and at pressure of 0.1 MPa

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under H_2 flow, using ethanol as solvent and a 5% palladium on carbon as catalyst. Details of the reaction procedure are reported elsewhere [2–4].

The HPLC analysis was performed on a liquid chromatograph (Waters) equipped with two solvent pumps (Model 510), a pump control module for gradient system, a manual injector (Model U6K) and a PDA detector (Model 996). The Millennium Chromatography Manager System was used for instrument control and data analysis. The separation was carried out on a reversed-phase packed column (Symmetry C_{18}, 250×4.6 mm), using a mixture of solvents (acetonitrile–water). The acetonitrile used in the mobile phase was Fluka HPLC-grade (UV cut-off 190 nm). PDA detection was carried out at a wavelength detection of 254 nm. Peaks were scanned from 200 to 400 nm for compounds characterization. In the gradient elution method employed the acetonitrile concentration was varied from 35 to 80%. The initial concentration (35% acetonitrile) was changed to 50% and 80% after 5 and 10 min, respectively. The concentration of acetonitrile was held at 80% for 18 min, after which the system was re-equilibrated to 35% for 20 min. The mobile phase flow-rate was set at 0.8 ml/min.

Standard samples of 2,4-DNT, 2,4-DAT, 4A2NT and 2A4NT were obtained from Aldrich. The 2,4-nitrohydroxyamino and azoxytoluene isomers were synthesized as reported in previous works [2–4,7].

3. Results and discussion

Fig. 1a,b show typical HPLC analyses obtained from a sample of the reaction mixture taken at a conversion of 2,4-DNT of about 90%. In Fig. 1a, the analysis was performed immediately after sampling. Six major compounds were resolved and identified by comparison with standard samples: 2,4-DAT, 4HA2NT, 2HA4NT, 4A2NT, 2A4NT and 2,4-DNT. Fig. 1b shows the HPLC analysis of the same sample injected after exposure to air for 12 h. In addition to the components observed on the fresh sample, the azoxytoluenes: 4,4′-dinitro-2,2′-azoxytoluene (2,2′-DNAT), 2,4′-dinitro-4,2′-azoxytoluene (4,2′-DNAT) and 2,2′-dinitro-4-4′-azoxytoluene (4,4′-DNAT) were also detected and identified by comparing the spectra and retention times with standards. Their

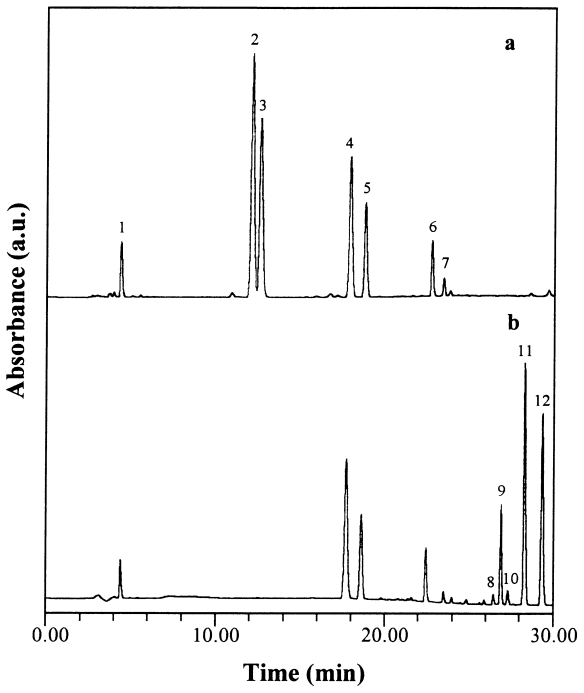

Fig. 1. HPLC analysis of reaction mixture (a) immediately after sapling; (b) after 12 h. 1=2,4-DAT; 2=4HA2NT; 3=2HA4NT; 4=4A2NT; 5=2A4NT; 6=2,4-DNT; 7, 8, 10=impurities; 9=2,2′-DNAT; 11=4,2′-DNAT; 12=4,4′-DNAT.

formation is due to the fast oxidation of the arylhydroxylamines after exposure to air of the reaction mixture [7]. Azoxytoluenes are undesired by-products, because they can act as poisons for the catalyst. The monitoring of these compounds is therefore of great importance in order to enhance the life of the catalyst.

The retention times of all the detected intermediates are given in Table 1. The components were eluted on the basis of their polarity. The more polar 2,4-DAT was eluted first, whereas the less polar azoxytoluene isomers show the highest retention times. Moreover, the compounds with the amino (or hydroxylamino) group in *para* to the methyl group show a lower retention time with respect to their isomers having these groups in the *ortho* position. It is likely that steric effects decrease the polarity of the molecules when these polar groups are in close proximity to the methyl group. The azoxytoluenes have a very complex molecular structure and it is not easy to estimate the molecule polarity. However, a

Table 1
Retention times of 2,4-DNT and its reduction products

Compound	Retention time (min)
2,4-DAT	4.41
4HA2NT	11.96
2HA4NT	12.46
4A2NT	17.65
2A4NT	18.55
2,4-DNT	22.43
2,2′-DNAT	26.88
4,2′-DNAT	28.25
4,4′-DNAT	29.28

correlation can be observed between the elution order and the molecular structure of these compounds. On the basis of their retention times, the compound 2,2′-DNAT is the most polar product. The higher polarity of 2,2′-DNAT with respect to 4,4′-DNAT can be ascribed to the presence of methyl groups in *ortho* to the azoxy group which alters the planar configuration of the molecule.

The analytical method reported in this communication allows a separation of all compounds and by using a PDA detector it is also possible to identify the different isomers during elution. It should be noted that the identification of the complex mixture of isomers deriving from 2,4-DNT hydrogenation is not easy because tedious and time consuming column on thin-layer chromatographic separation are generally employed. The UV–Vis spectra obtained for the 2,4-nitrohydroxyaminotoluene isomers and the 2,4-nitroaminotoluene isomers are shown in Figs. 2 and 3, respectively. The 4HA2NT and 4A2NT compounds, having the functional group (–NHOH or $–NH_2$) in *para* to the methyl group and the nitro group in the *ortho* position, present a strong absorption peak at about 233 nm. Their isomers 2HA4NT and 2A4NT show a more complex pattern. The lower wavelength absorption band is split into two peaks; moreover a band of medium intensity in the 280–300 nm region is also present. This latter absorption is attributed to a conjugate effect present when an electron-donating group and an electron-withdrawing group, in *para* to each other, are present in the aromatic ring [8]. When these groups are in *ortho* to each other, such as in the 4HA2NT and 4A2NT isomers, the planarity necessary for conjugation of these groups and the aromatic ring is lost, due

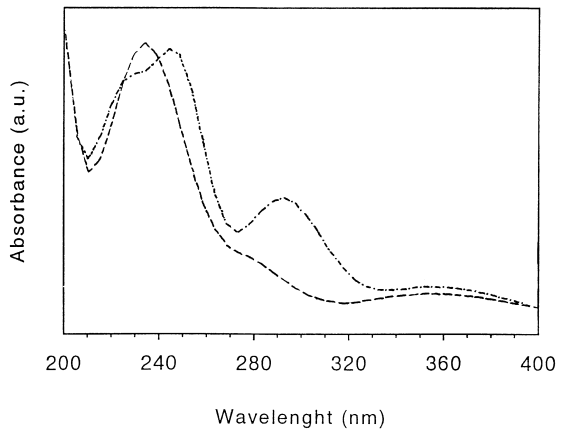

Fig. 2. UV–Vis spectra of 4HA2NT and 2HA4NT isomers acquired by PDA. (- - -) 4HA2NT; (– · –) 2HA4NT.

to a strong steric interaction between the substituents, and the band at 280–300 nm disappears.

Fig. 4 shows the UV–Vis spectra acquired for the azoxytoluene isomers. The presence of the azoxy-chromophore group in conjugation with the aromatic ring leads to two absorption peaks, in the region 240–380 nm. In the spectrum of 4,4′-DNAT the two absorption bands have a similar intensity, whereas on the spectra of 4,2′-DNAT the absorption band at lower wavelengths is the most intense one. In the spectra of third isomer (2,2′-DNAT) the band at higher wavelengths is absent, due to the loss of conjugation between the aromatic ring and the azoxy-chromophore group. Furthermore, it can be

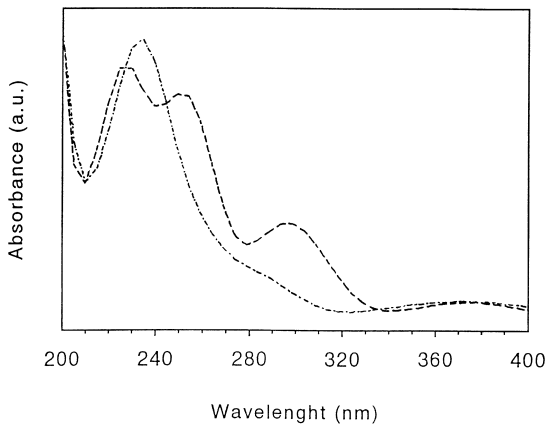

Fig. 3. UV–Vis spectra of 4A2NT and 2A4NT isomers acquired by PDA. (– · –) 4A2NT; (- - -) 2A4NT.

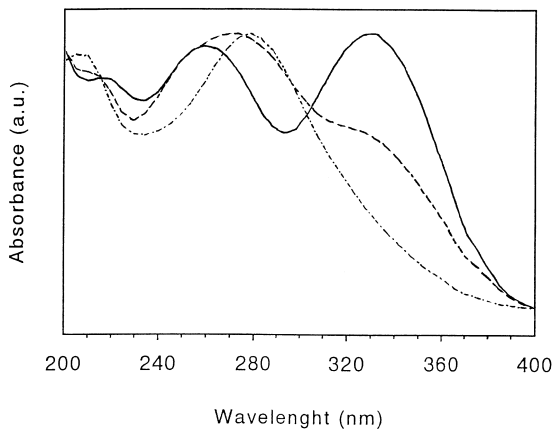

Fig. 4. UV–Vis spectra of azoxytoluene isomers acquired by PDA. (– · –) 2,2′-DNAT; (- - -) 4,2′-DNAT; (—) 4,4′-DNAT.

noted that the 4,2′-DNAT shows the maximum of adsorption at a wavelength which is intermediate between that related to the position of the first band of 4,4′DNAT and that of 2,2′-DNAT, due to a mixed structure.

The differences found in the UV–Vis spectra of these compounds allow therefore a very fast provisional identification of each of the eluted isomer.

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