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polymer communications

An unexpected mechanism of action of the styrene polymerisation retarder 2,4-dinitro-6-*sec*-butylphenol

Richard J. Bushby[a],*, Nigel Lord[a], Ian McRobbie[b] and Anthony Pryce[b]
[a]*School of Chemistry, The University of Leeds, Leeds LS2 9JT, UK*
[b]*A. H. Marks Co. Ltd, Wyke, Bradford BD12 9EJ, UK*

The reaction of 'DNBP' (2,4-dinitro-6-*sec*-butylphenol) with toluene, ethylbenzene or styrene and *tert*-butylperoxide at 110°C leads to 7-*sec*-butyl-5-nitro-2-phenylbenzoxazole. This benzoxazole was also detected in the residues of an industrial styrene fractionation still in which DNBP was routinely used as the polymerisation retarder. The formation of this product from either ethyl benzene or from styrene involves a carbon–carbon bond cleavage step. © 1998 Elsevier Science Ltd. All rights reserved.

Introduction

*t*ert-Butyl catechol, TBC, is a very satisfactory inhibitor for styrene monomer while it is being stored, but it is only effective in the presence of oxygen [1-3]. Under the conditions of styrene manufacture and purification it is ineffective and a number of specialist retarders and inhibitors have been developed for use in these circumstances. One of the most frequently used is compound **1**, commonly known as DNBP (2,4-dinitro-6-*sec*-butylphenol). Despite its widespread use, the mechanism through which DNBP acts is unknown[4,5]. *A priori* one might suggest that it is acting as a hydrogen atom source, as a one-electron oxidant[6], like a phenol[1-3], or like a nitroaromatic compound[4,7,8]. Indeed, within the complex environment of the manufacturing plant or fractionating still, all of these may be important and it has been argued that the success of DNBP rests on its ability to act in several different ways. However, the present study shows that the main mechanism through which it retards the polymerisation of styrene involves a rather unusual reaction.

Experimental

The reaction between DNBP, toluene and tert-butylperoxide. A mixture of *tert*-butylperoxide (2 mL) and DNBP **1** (3.36 g) in toluene (60 mL) was refluxed at 110°C under nitrogen for 83 h. The excess volatile materials were removed under vacuum to give a viscous brown liquid (2.94 g). A portion of this (750 mg) was dissolved in ether (50 mL) and extracted with 1 M aqueous hydrochloric acid (3 × 50 mL) and 1 M aqueous sodium hydroxide (4 × 50 mL). Basification of the acid extracts and isolation of the amine products by ether extraction gave almost no product (16 mg). Acidification of the sodium hydroxide extract gave a mixture (446 mg) of DNBP and benzaldehyde (roughly equal weights obtained after chromatography). The original ether solution was dried and evaporated in vacuo to give a neutral fraction (252 mg). This was subjected to column chromatography on flash silica eluting with 7:3 chloroform:petrol to give 7-*sec*-butyl-5-nitro-2-phenylbenzoxazole **6** as brown crystals (232 mg, 46% based on DNBP consumed).

M.P. = 81.2–82.4°C (from ethanol); Elemental analysis, C, 68.85; H, 5.05; N, 9.16%; $C_{17}H_{16}N_2O_3$ requires: C, 68.9; H, 5.4; N,9.46%; i.r. (Nujol, ν_{max}) 1510; 1600 cm^{-1}; ^{1}H n.m.r. (300 MHz, CDCl$_3$, δ_H ppm) 0.92 (t, 3H, $J = 7.3$ Hz, $-CH_2CH_3$), 1.47 (d, 3H, $J = 6.8$ Hz, $-CHCH_3$), 1.92 (m, 2H, $-CH_2CHCH_3$), 3.22 (m, 1H, $-CHCH_2CH_3$), 7.63 (m, 3H, Ar–*H*), 8.25 (d, 1H, $J = 1.8$ Hz, H4), 8.29 (dd, 2H, $J = 1.1$ and 8 Hz, *ortho* phenyl H), 8.51 (d, 1H, $J = 1.8$ Hz, H6); Mass Spectrum (EI, *m/z*) 296 (M$^+$, 42%), 281 (M$^+$ − CH$_3$, 6), 267 (M$^+$ − C$_2$H$_5$, 100), 221 (267 − NO$_2$, 17), 118 (16), 105 (C$_7$H$_5$O$^+$, 10), 103 (C$_7$H$_5$N$^+$, 10), 91 (C$_7$H$_7^+$, 30), 90 (11), 89 (16), 77 (C$_6$H$_5^+$, 23), 40 (22).

The reaction between DNBP, ethylbenzene and tert-butylperoxide

In a similar manner a mixture of *t*-butylperoxide (8 mL) and DNBP (3.36 g) in ethylbenzene (60 mL) was heated at 110°C under nitrogen for 83 h. The excess volatile materials were removed under vacuum to give a viscous liquid (3.13 g). A portion (750 mg) was dissolved in ether (50 mL). Separation of components as before gave some acetophenone, DNBP (ca 56 mg) and a neutral fraction (543 mg). Column chromatography gave 7-*sec*-butyl-5-nitro-2-phenylbenzoxazole **6** (230 mg, 23% based on DNBP consumed). Spectroscopic and physical data were identical to those previously detailed.

The reaction of DNBP, styrene and t-butylperoxide

In a similar manner a mixture of *tert*-butylperoxide (2 mL) and DNBP (6 g) in styrene (30 mL) was heated at 110°C under nitrogen for 83 h. The excess volatile materials were removed under vacuum to give a viscous brown liquid (9.99 g). A portion (75 mg) was dissolved in ether (50 mL). Separation of components as before gave DNBP (94 mg) and a neutral fraction (510 mg). Column chromatography gave 7-*sec*-butyl-5-nitro-2-phenylbenzoxazole **6** (302 mg, 53% based on DNBP consumed). Spectroscopic and physical data were identical to those previously detailed.

* To whom correspondence should be addressed. Tel: 0113 2336509; Fax: 0113 2336565; e-mail richardb@chem.leeds.ac.uk
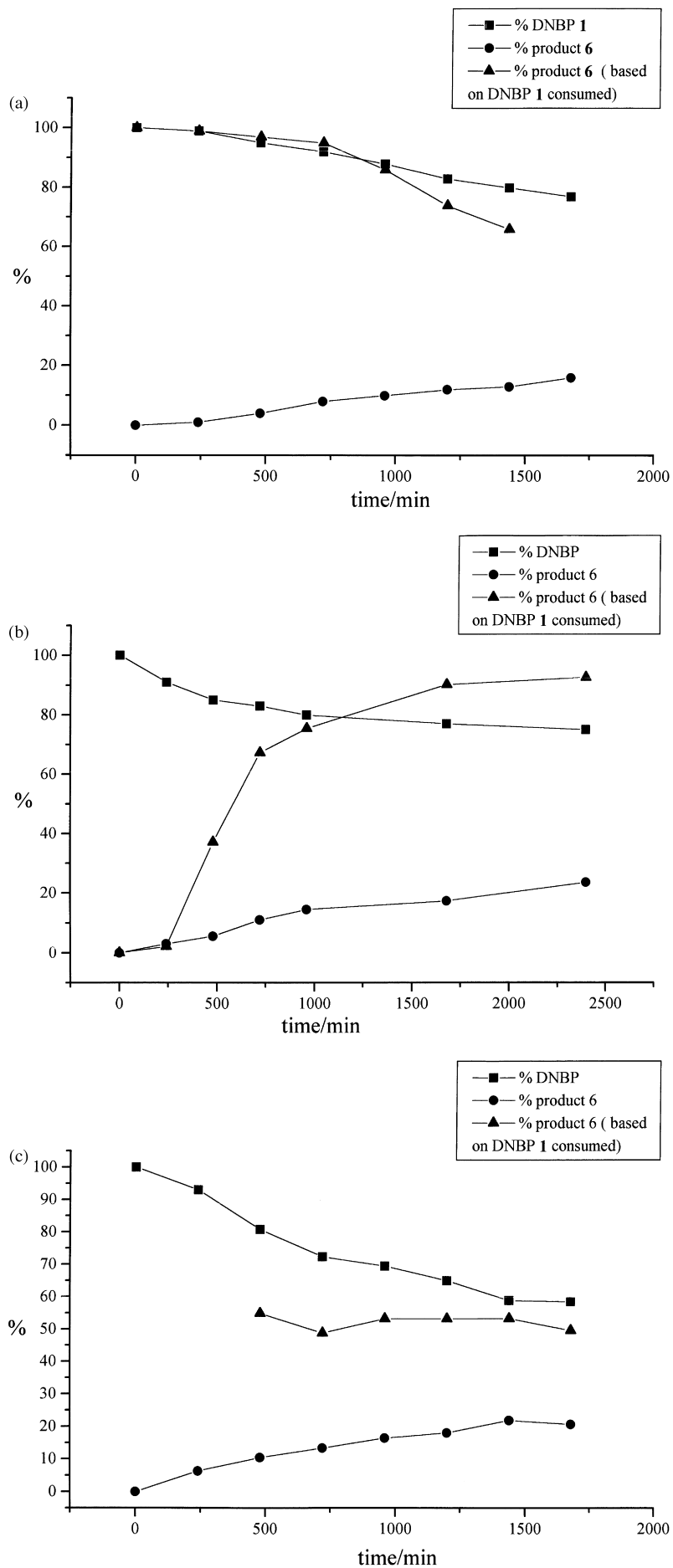
Figure 1 HPLC yields plotted as a function of time (see Experimental section). (a) The reaction between toluene, DNBP **1** and *tert*-butylperoxide at 110°C. (b) The reaction between ethyl benzene, DNBP **1** and *tert*-butylperoxide at 110°C. (c) The reaction between styrene, DNBP **1** and *tert*-butylperoxide at 110°C

HPLC monitoring of the reactions

A mixture of *tert*-butylperoxide (2 mL), and DNBP **1** (3.36 g) in toluene (60 mL) was refluxed at 110°C under nitrogen. At intervals of 240 min, a sample was removed from the reaction mixture and was analysed using the standard HPLC conditions detailed below. The results are shown in *Figure 1*a.

The equivalent results for the reaction between ethylbenzene, DNBP **1** and *tert*-butylperoxide at 110°C are shown in *Figure 1*b and those for the reaction between styrene, DNBP and *tert*-butylperoxide at 110°C in *Figure 1*c.

HPLC analysis conditions

The internal standard (DNPC, dinitrophenylcatechol, 45 mg) was weighed accurately (four figure balance) dissolved in toluene (1 mL) and the sample to be analysed added (1 mL, pipette). A portion of the resulting mixture (20 μL) was injected onto an S5W HPLC column under the following conditions: *Pump*, Varian 5000LC; *Detector*, HP1050; *Integrator*, HP3396 series II; *Flow rate*, 1.0 mL min^{-1}; *Detection*, 285 nm (u.v.), *Mobile Phase*, 99% hexane / 1% tetrahydrofuran / 0.1% trifluoroacetic acid. Typical retention times of the main components were: DNBP **1** (6.7 min); 7-*sec*-butyl-5-nitro-2-phenylbenzoxazole **6** (10.8 min); DNPC (22.5 min). The integrated peak areas were converted to weight ratios and hence used to calculate the amount of DNBP **1** and 7-*sec*-butyl-5-nitro-2-phenylbenzoxazole **6** using calibration

curves produced from samples of known weight mixtures of DNPC with DNBP **1**, and of DNPC with 7-*sec*-butyl-5-nitro-2-phenylbenzoxazole **6** under identical HPLC conditions.

Results and discussion

Almost forty years ago, Jackson and Waters showed that benzyl radicals (generated by heating *tert*-butylperoxide in toluene) reduce nitroaromatics to the corresponding amines by the mechanism shown in outline in *Scheme 1*[8]. This redox process involves the transfer of an oxygen atom from the nitro group to the benzylic site and is believed to be essentially the mechanism through which nitroaromatic compounds inhibit or retard the polymerisation of styrene. In our initial investigation of the retarder DNBP we chose to duplicate the Jackson and Waters reaction conditions and, as in their original experiments, to use the benzyl radical **2a** as the model for the growing polystyrene chain **2c**[8]. A solution of DNBP **1** in toluene containing *tert*-butylperoxide was refluxed for 83 h. The crude product was found to contain the expected benzaldehyde but, unexpectedly, the major product was found to be 7-*sec*-butyl-5-nitro-2-phenylbenzoxazole **6** (46%). In the early stages, these were the only detectable reaction products (^{1}H n.m.r., t.l.c., h.p.l.c) but as the reaction progressed the yield of the benzoxazole **6** slowly fell. The results of quantitatively monitoring the reaction by HPLC are shown in *Figure 1*a. After 3 h 5% of the DNBP had been consumed and the 'normalised' HPLC yield of **6** (based on the weight of DNBP consumed) was
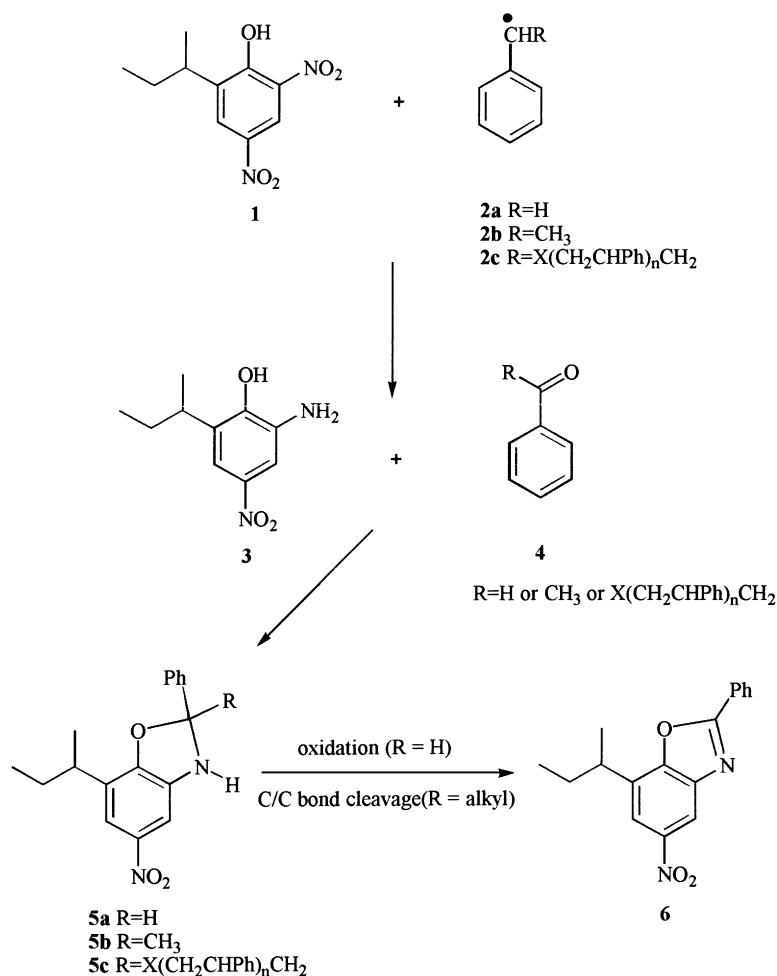
Overall Reaction

Outline Reaction Mechanism
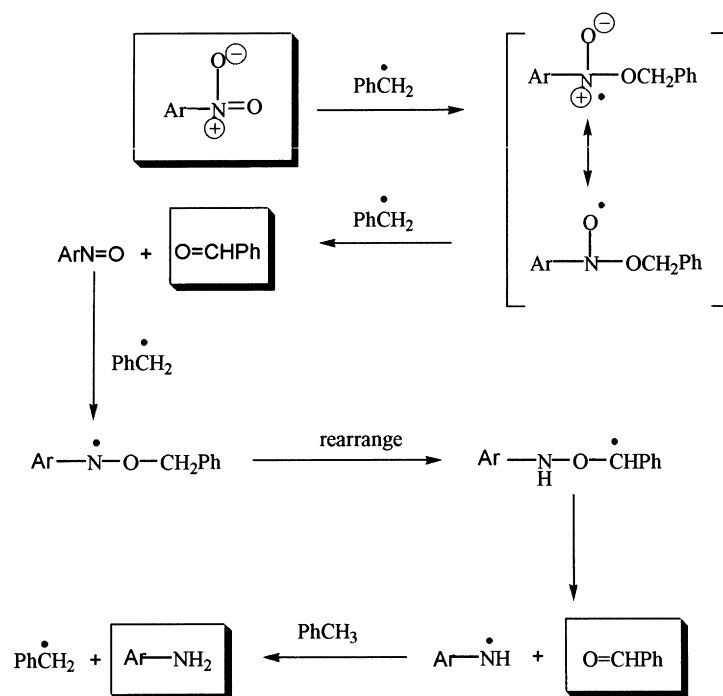
Scheme 1

Scheme 2

95%. After 25 h, 20% of the DNBP had been consumed and the 'normalised' HPLC yield of **6** had fallen to 70% The mechanism by which the benzoxazole **6** is formed can be formulated in several different ways. The simplest (shown in *Scheme 2*) is that, by analogy with other benzyl radical/nitroaromatic reactions[8], benzaldehyde and 2-amino-4-nitro-6-*sec*-butylphenol **3** are formed. A condensation reaction between these two leads to the dihydrobenzoxazole **5a** and oxidation of this gives the observed product **6**

At first sight it appears that this reaction would only be possible for a primary benzylic radical and hence that the benzyl radical **2a** (a primary radical) had been a poor choice as the model for the growing styrene polymer end-chain **2c** (a secondary radical). Hence the reaction was repeated using ethylbenzene as the solvent (a source of a secondary radical **2b**). Surprisingly, the same product **6** was obtained in an isolated yield of 23% after 83 h (110°C). By HPLC it was shown that, after 25 h 20% of the DNBP had been consumed and the 'normalised' HPLC yield of **6** (based on the weight of DNBP consumed) was 85% (*Figure 1*b). The form of this 'normalised yield' curve for the isoxazole suggests that some moderately stable intermediate is involved in the formation of compound **6** (possibly compound **5b**) but attempts to detect and isolate this have not been successful. At some stage in this reaction, presumably at the stage of the intermediate **5b**, a carbon–carbon bond cleavage reaction has occurred. The driving force for this is presumably aromatisation of the ring and there are some precedents for this process in the reactions of 1,2-diaminobenzene derivatives, 2-aminophenol derivatives and 2-aminothiophenol derivatives with ketones[9–11]. However, most of these reactions involve more 'forcing' conditions.

Finally, a mixture of DNBP, styrene and *tert*-butyl peroxide was heated at 110°C for 83 h. Compound **6** was isolated in 53% yield. In a reaction which was monitored by HPLC, after 3 h, 5% of the DNBP had been consumed and the 'normalised' HPLC yield of **6** was 53% (*Figure 1*c). The dihydrobenzoxazole **5c** is the presumed intermediate and, once again, a carbon–carbon bond cleavage must occur.

To show that this reaction occurs 'on-plant' the residues from an industrial styrene fractionation still in which DNBP was routinely used were examined by HPLC. As expected the mixture was highly complex but it was possible to detect 12 000 ppm of DNBP and 850 ppm of compound **6**. The latter was identified on the basis of its HPLC retention time and an MS comparison of the pure compound with that of a small fraction isolated from the still residues by semi-preparative HPLC.

Conclusions

The main mechanism by which DNBP retards styrene polymerisation is shown to be a variant on the normal mechanism for nitroaromatic compounds. The surprising feature is the formation of the heterocycle 7-*sec*-butyl-5-nitro-2-phenylbenzoxazole **6**. To form this a carbon / carbon bond cleavage reaction must occur.

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