

CHROM. 13,776

Note

Antioxidants and stabilizers

LXXXVI*. Use of chromatography in the investigation of the mechanism of action of amine antidegradants

JITKA ROTŠCHOVÁ* and JAN POSPÍŠIL

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6 (Czechoslovakia)

(Received February 26th, 1981)

Rubbers are protected against atmospheric ageing mainly by additives of the 1,4-phenylenediamine (1,4-PD) type, which possess antioxidant and/or antiozonant properties. In order to understand the mechanism of their action, one ought to have a knowledge of changes in the composition of the additives during ageing and the properties of the reaction products. The identification and determination of the original amines and especially of their transformation products directly in the polymers or in extracts of aged polymers are very difficult. The analysis of rubbers, which contain, in addition to amine stabilizers, other processing and vulcanizing additives, is particularly difficult. Basically, these compounds impede the total analysis of mixtures in rubbers, and thus the obtaining of data needed for the determination of the mechanism of action of amines under specific ageing conditions. Chromatographic methods are to be preferred to other methods for the solution of these problems, which are important from both theoretical and technical points of view^{1,2}.

One of these problems consisted in developing analytical methods for amine additives and their transformation products under model conditions. We investigated the thermal oxidation, photo-oxidation and ozonization of low-molecular-weight liquid hydrocarbons³ and examined possibilities for the determination of changes in the composition of the additives during these processes by using thin-layer (TLC) and liquid chromatographic (LC) methods.

EXPERIMENTAL

Chemicals

The following compounds were used for the stabilization of hydrocarbons: N,N'-diphenyl-1,4-phenylenediamine (DPPD) (Altofane DIP; S.A. Française des Matières Colorantes, St. Denis, France), N-isopropyl-N'-phenyl-1,4-phenylenediamine (IPPD) (Santoflex IP; Monsanto, St. Louis, MO, U.S.A.) and N-cyclohexyl-N'-phenyl-1,4-phenylenediamine (CHPPD) (ASM 4010; Bayer, Leverkusen, G.F.R.).

* Part LXXXV: ref. 3.

Pure compounds were obtained by repeated crystallization of commercial samples. For the 1,4-benzoquinonediimines (BQDI), the symbols denoting substitution in the N,N'-positions are the same as those used for derivatives of 1,4-PD; they were prepared by the oxidation of diamines with potassium hexacyanoferrate(III)⁴ or silver oxide⁵.

Methods

Solutions of purified tetralin, cyclohexene, squalane and squalene in chlorobenzene and pure oxygen were used in the oxidation experiments. Thermal oxidation was initiated with azobisisobutyronitrile (AIBN) at 60°C, and photo-oxidation was examined at 35°C with irradiation with light of wavelength 300–400 nm. A chlorobenzene solution of squalene was used at 25°C for ozonization with oxygen–ozone mixtures with a rate of ozone generation of 1 g/h. Atmospheric ageing of diamines and BQDI was carried out in chlorobenzene solution and in the solid phase at 25°C. Samples for analyses were taken during the oxidation processes.

Chromatographic analyses

TLC was carried out using Silufol UV 254 silica gel sheets (Kavalier. Votice, Czechoslovakia) and detection with hexacyanoferrate(III) reagent, acidic potassium permanganate solution and a UV lamp. The elution systems were S₁ = benzene–acetone–26% aqueous ammonia solution (95:5:0.1) and S₂ = light petroleum–diethyl ether–triethylamine (50:60:0.1).

LC was carried out using an LC Chrom 50 chromatograph (Laboratory Instruments, Prague, Czechoslovakia) with a 300 × 4 mm I.D. glass column packed with SG-10 silica gel (Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia) at a flow-rate of 33–64 ml/h and a pressure of 1–1.5 MPa; detection was effected with a differential flow UV analyser at 254 nm. The elution systems were mixtures of isopropanol and *n*-hexane in various proportions containing 0.1% of triethylamine.

RESULTS AND DISCUSSION

The results showed that the individual derivatives of 1,4-PD and BQDI could be adequately determined by using either TLC or LC (Table I). BQDI derivatives prepared independently as standards by the oxidation of 1,4-PD form in solution a

TABLE I

R_F VALUES OF DERIVATIVES OF 1,4-PD AND BQDI IN SYSTEMS S₁, S₂

Compound	R _F	
	S ₁	S ₂
N-Isopropyl-N'-phenyl-1,4-phenylenediamine (IPPD)	0.47	0.47
N-Isopropyl-N'-phenyl-1,4-benzoquinonediimine (IPBQDI)	0.15 + 0.30	0.28 + 0.45
N,N'-Diphenyl-1,4-phenylenediamine (DPPD)	0.51	0.49
N,N'-Diphenyl-1,4-benzoquinonediimine (DPBQDI)	0.22 + 0.31	0.38 + 0.46
N-Cyclohexyl-N'-phenyl-1,4-phenylenediamine (CHPPD)	0.54	0.50
N-Cyclohexyl-N'-phenyl-1,4-benzoquinonediimine (CHPBQDI)	0.18 + 0.29	0.30 + 0.37

mixture of *syn*- and *anti*-stereoisomers⁶; in LC, they form two peaks with similar elution times (Fig. 1), and in TLC they yield two spots with similar R_F values. This finding complicates the investigation of transformations of 1,4-PD in rubber extracts.

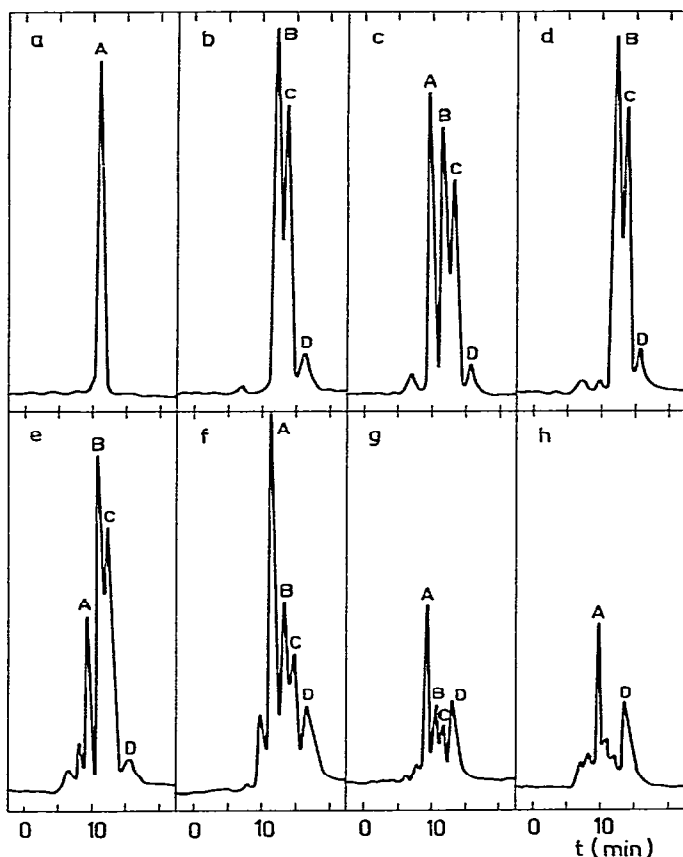


Fig. 1. Liquid chromatograms of transformation products of IPBQDI after long-term ageing. Eluent, 15% isopropanol in *n*-hexane + 0.1% triethylamine; UV detection (254 nm). Peaks: A, IPPD; B, C, isomers of IPBQDI; D, acetone. (a) Recrystallized IPPD; (b) recrystallized IPBQDI; (c) freshly prepared mixture of IPPD + IPBQDI. Ageing of IPBQDI: (d) 3 days; (e) 14 days; (f) 60 days; (g) 151 days; (h) 203 days.

In the long-term atmospheric ageing (1 year) of IPPD, DPPD and CHPPD in solution, chemical changes occurred in which a mixture of several compounds with lower V_c or R_F values than those of the initial amine and a small amount of the corresponding BQDI were formed. In the solid state, 1,4-PD derivatives are more stable. A perceptible change takes place only in crystalline IPPD (change in colour; a small spot at the start appears in TLC). On the other hand, CHPPD and DPPD were stable. Interesting data were provided by an investigation of the long-term ageing of pure BQDI. DPBQDI was very stable; no visible changes occurred during the investigation. CHPBQDI changed very slowly to a corresponding amine (which appeared in the mixture after 80–100 days). IPBQDI was transformed very quickly into IPPD and a mixture of other amine compounds with a lower V_c or R_F values (Fig. 1).

After 342 days, IPBQDI completely disappeared from the reaction mixture. With respect to the mechanism of action of these additives, this result suggests an important role played by the character of the *N,N*-disubstitution of 1,4-PD. Data on the composition of the mixture of products thus obtained cannot be generalized for the various derivatives of 1,4-PD because of the different reactivities of the derivatives of BQDI, which are an important primary transformation product of 1,4-PD.

Reaction mixtures were analysed in detail during the oxidation of tetralin, cyclohexene, squalane and squalene stabilized with derivatives of 1,4-PD. LC demonstrated in all instances that during the induction period the content of 1,4-PD gradually decreased, while the content of derivatives of BQDI increased. During the induction period (determined kinetically by oxygen absorption measurements) and in the oxidation stages after the induction period the reaction mixture contained only derivatives of BQDI in all instances, the original amine having disappeared. The chromatograms in Fig. 2 provide an example: they represent the composition of products after the oxidation of squalene. On the one hand, this result confirms the transformation of 1,4-PD as a consequence of the role played by its chain-breaking properties during the autoxidation, and on the other, it is one of the pieces of evidence for retardation of the oxidation stages after the induction period.

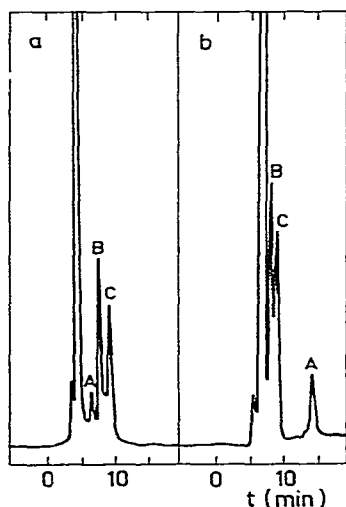


Fig. 2. Liquid chromatograms of the reaction mixture in the induction period range in the inhibited oxidation of squalane. Eluent, 4% isopropanol in *n*-hexane + 0.1% triethylamine; UV detection. Content of 1,4-PD derivatives: (a) $5 \cdot 10^{-3}$ mol/l IPPD; (b) $5 \cdot 10^{-3}$ mol/l DPPD. Peaks as in Fig. 1.

The investigation of changes in the derivatives of 1,4-PD during the photooxidation of various hydrocarbons revealed differences in the rate of formation of BQDI arising in systems during the induction period. No other transformation products of amines could be detected. The chromatograms were more complicated, because the transformation products of the substrate were present in much higher numbers and amounts than in the thermal oxidation.

The results of analyses of the samples after ozonization differed considerably from those obtained in earlier investigations, where oxygen or RO_2 radicals and

hydroperoxides derived from the hydrocarbon substrate were the oxidizing agents. Ozonation yielded a varied mixture of products both from the substrate and from the additives. According to chromatograms and colour tests, the original amines disappeared and no corresponding BQDI derivatives were formed. The V_e or R_F values did not correspond to any of the model products of the oxidation transformations of derivatives of 1,4-PD prepared so far and having the structures of substituted amino derivatives of 1,4-PD, BQDI, benzoquinonemonoimine or phenazine⁷. The presence of 8–10 compounds was observed on the chromatograms of ozonized amines in an inert solvent. Ozonation of mixtures of squalene with amines gave rise to even more complicated mixtures. This finding of differences in the reaction products between diamines and ozone or squalene ozonide arising in the ozonization of the mixture indicates the complicated character of the chemical transformations that ought to be considered in rubbers (squalene is a model of polyisoprene). At the same time, it was found that chromatograms of freshly ozonized samples and those of older samples differ from each other, which causes difficulties in the interpretation of data.

The results obtained in this study demonstrate the character of primary transformations that an amine stabilizer undergoes under defined conditions of oxidation ageing of hydrocarbons. Derivatives of BQDI, which are the cause of the retarded oxidation of hydrocarbons, are formed in the thermal or photo-initiated oxidation³. The absence of BQDI from the mixture arising after the ozonolysis of hydrocarbons indicates a completely different mechanism of the process. The methods used have also proved to be useful in extensive studies of the mechanism of the stabilizing action of diamines that are in progress and also involve syntheses and identifications of unknown transformation products.

REFERENCES

- 1 J. Pospíšil and J. Rotschová, *Rev. Gén. Caout. Plast.*, 54 (1977) No. 567, 72; No. 568, 73; and No. 569, 131.
- 2 J. Rotschová and J. Pospíšil, *Syntet. Kaučuk*, 31 (1980) 1, 86 and 64; *Report Edition Macro*, Revue R-3, IMC, Prague, 1980.
- 3 J. Rotschová and J. Pospíšil, *Chem. Ind. (London)*, in press.
- 4 M. E. Cain, I. R. Gelling, G. T. Knight and P. M. Lewis, *Rubber Ind.*, 9, No. 6 (1975) 216, 221, 223 and 226.
- 5 J. Honzl and M. Metalová, *Tetrahedron*, 25 (1969) 3641.
- 6 L. Taimr, J. Rotschová and J. Pospíšil, *Chem. Ind. (London)*, (1979) 413.
- 7 L. Taimr and J. Pospíšil, *Angew. Makromol. Chem.*, 92 (1980) 53.