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Note

A study of the side-reaction products of phenylhydrazine production by gas chromatography–mass spectrometry

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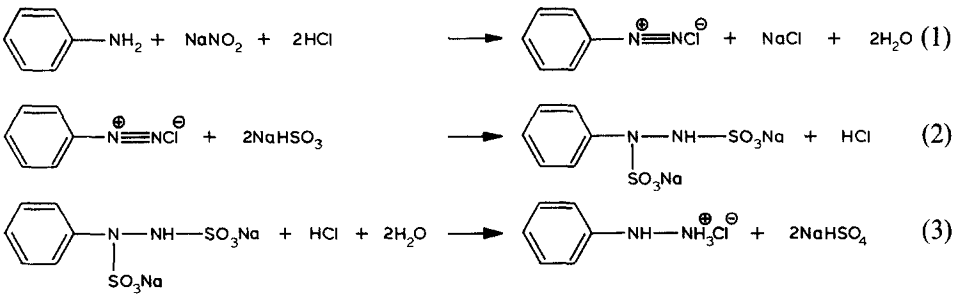
Phenylhydrazine has been produced industrially for more than 100 years. The history of its production is closely connected with that of the origin and/or development of the production technology for organic dyes and pharmaceuticals. At present, phenylhydrazine is widely applied as an important intermediate in the industrial technology of organic compounds, *e.g.*, chloridazone (5-amino-4-chloro-2-phenylpyridazin-3-one), the active ingredient of the selective herbicide Burex®. Its synthesis, starting from aniline, follows the general reaction scheme:



When the technological conditions of the reaction step 2 do not meet the steady-state regime, the formation of a precipitate is observed immediately after the contact of benzenediazonium chloride with sodium hydrogensulphite. This solid waste, which after isolation represented a yield of about 5%, with respect to aniline, was completely soluble in various organic solvents, *e.g.*, methanol, ethanol, diethyl ether. After subjecting the waste sample solutions to gas chromatographic–mass spectrometric (GC–MS) analysis, nine compounds, possible products of side-reactions, were identified. Extracts of the reaction mixtures from the individual reaction steps (see the above scheme) in a model synthesis of phenylhydrazine were analyzed for the compounds of interest. In addition, a sample of the collected gaseous exhaust was also subjected to analysis. Besides the nine substances mentioned, three more compounds were found and identified.

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EXPERIMENTAL

The samples for GC–MS analyses were obtained as follows. A sample of solid waste was recovered by filtration of the precipitate, followed by drying in a thermostatted oven at 70°C. The homogenized sample was diluted in an appropriate solvent and 0.1-μl aliquots were injected onto a capillary column. A sample from the diazotization step (1) was obtained by addition of 277 g of analytical grade toluene, cooled to -2°C, to the reaction mixture, immediately after mixing the reagents. After a simple one-step extraction, the toluene extract was dried over sodium sulphate and 0.1-μl aliquots were subjected to GC–MS analysis. A sample from the reduction step (2) was obtained by addition of the same amount of toluene to the fresh reaction mixture as in step 1, but the toluene temperature was held at 20°C. After mixing for 10 min, the toluene layer was separated, dried over sodium sulphate and subjected to analysis. A sample from reaction step 3 was obtained by addition of 277 g of toluene at 20°C to the reaction mixture heated to 100°C. After cooling of the mixture and partitioning of the layers, the toluene layer was separated, dried over sodium sulphate and subjected to analysis. The samples of condensed gaseous exhaust collected from all three reaction steps were injected directly, without any preliminary treatment.

The GC–MS analyses were performed on an HP-5890 gas chromatograph, connected via the open-split interface to a HP-5970 mass-selective detector (Hewlett-Packard, Avondale, PA, U.S.A.). Sample solutions were injected onto a 12.5 m × 0.2 mm I.D. fused-silica column, coated with a 0.33-μm immobilized film of SE-30 (Hewlett-Packard). Helium was used as a carrier at the linear velocity, $\bar{u}$ = 40 cm/s, the splitting ratio was 20:1. Samples were chromatographed under the programmed temperature conditions, starting from 40°C for 2 min, then increased to 230°C at 10°C/min. The injector port temperature was 230°C and that of the open-split interface was 250°C. Mass spectra were scanned in the mass range of m/z = 29–550, with a scanning ratio of 2.67/s. The photomultiplier voltage was held at 1600 V. For the toluene extracts, the detector was switched off between 2 and 4 min after the start (toluene elution region). The relative abundance of the individual components was quantified as a peak area percentage after the integration of the total ion current (TIC) signal. Benzene and phenol were quantified using the external standard technique. The calibration solution contained 0.8% benzene and 1.1% phenol in toluene respectively.

RESULTS AND DISCUSSION

Solid waste corresponding to about 5%, with respect to aniline, was recovered from the final raw reaction product of technical phenylhydrazine, obtained at elevated temperature and prolonged reaction time. After complete dissolution in the organic solvent and subsequent GC–MS analysis, this waste was found to be a mixture of benzene, phenol, thiophenol, phenylazide, 1,1′-biphenyul, azobenzene (*trans*), diphenyl sulphide, the phenyl ester of benzenesulphonic acid and the S-phenyl ester of benzenesulphinothioic acid. The main component was the S-phenyl ester of benzenesulphinothioic acid, comprising about 50% of the total peak area sum.

In a more detailed study aimed at the elucidation of the possible origins of the

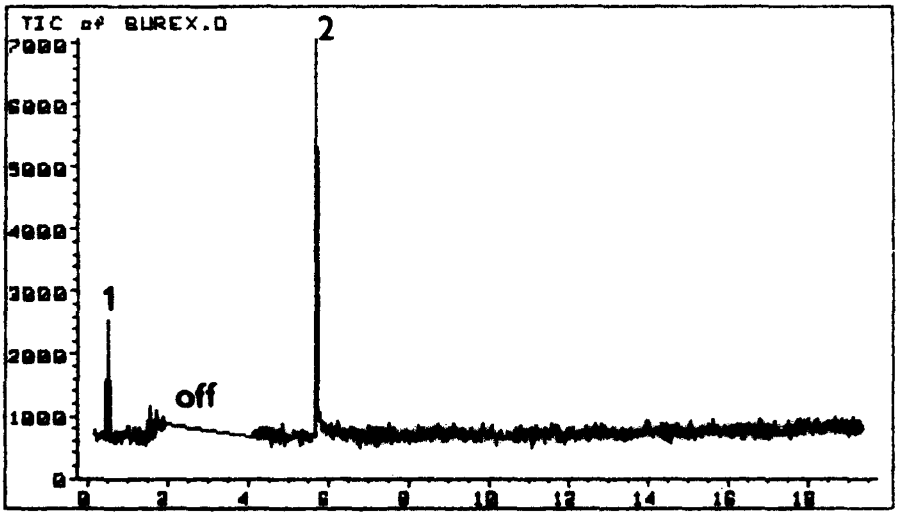

Fig. 1. Chromatogram of diazotization by-products. Peaks: 1 = benzene; 2 = phenol, "off" indicates the period when the detector was switched off. Time scale in min.

side-reaction products, the individual steps 1–3 of the reaction scheme were separately analyzed according to the procedures described in the Experimental.

Fig. 2 shows the TIC of the by-product mixture from the first reaction step (diazotization). The only by-products found were benzene and phenol, at levels of 0.08 and 0.6% respectively. The phenol could arise from decomposition of the diazonium salt in water, and a parallel homolytic decomposition of the salt could give rise to the benzene, the limiting factor being the temperature[1]. Another possible by-products, chlorobenzene, could not be found in the mixture possibly due to the fact that under the described conditions it would have been eluted in the time when detector was switched off. With regard to the amounts of the by-products, the first reaction step does not contribute substantially to their formation, though both compounds could be important from a toxicological point of view.

A chromatogram of the sample from the second reaction step is shown in Fig. 2. In addition to sulphur dioxide, the sample contains benzene, phenol (0.12 and 1.2% with respect to aniline), phenyl azide, 1,1'-biphenyl, diphenyl sulphide, diphenyl disulphide and the S-phenyl ester of benzenesulphinothioic acid. The relative sum of these compounds, without sulphur dioxide, is 2% with respect to aniline.

The chromatogram in Fig. 3 shows the sample from the third reaction step. Besides the compounds found in the samples from previous steps, this sample contains the phenyl ester of benzenesulphonic acid. The whole yield is about 10%, with respect to aniline. Fig. 4 shows a chromatogram of the sample from step 3, except that the reduction was accomplished with zinc. Compared with Fig. 3, there is a substantial decreasse in both the amount and presence of the by-products. The sample contains only phenol, thiophenol, diphenyl disulphide, cyclo-octasulphur and the S-phenyl ester of benzenesulphinothioic acid. The total content of by-products decreased to about 1%, with respect to aniline. The sample of gaseous exhaust was also analyzed. The resulting chromatogram is presented in Fig. 5. Phenyl azide and chlorobenzene were found to be the main components. The following compounds repre-

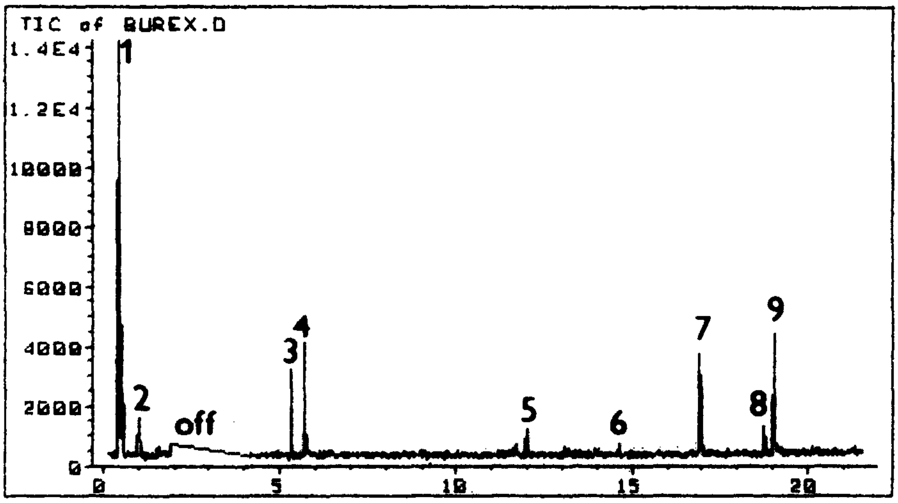

Fig. 2. Chromatogram of by-products from reaction step 2. Peaks: 1 = sulphur dioxide; 2 = benzene; 3 = phenyl azide; 4 = phenol; 5 = 1,1'-biphenyl; 6 = diphenyl sulphide; 7 = diphenyl disulphide; 8 = unknown; 9 = S-phenyl ester of benzenesulphinothioic acid.

sented the main part of the by-products: benzene, chlorobenzene, thiophenol, phenyl azide, phenol, 1,1'-biphenyl, azobenzene, diphenyl sulphide, diphenyl disulphide, cyclo–octasulphur, the phenyl ester of benzenesulphonic acid and the S-phenyl ester of benzenesulphinothioic acid. Their identities were confirmed either by chromatographing appropriate standards or by chromatographing reactions mixtures prepared according to the literature[2,3].

The origin and mechanism of formation of the by-products in the first step of phenylhydrazine synthesis, *i.e.*, diazotization was found to be rather sample and

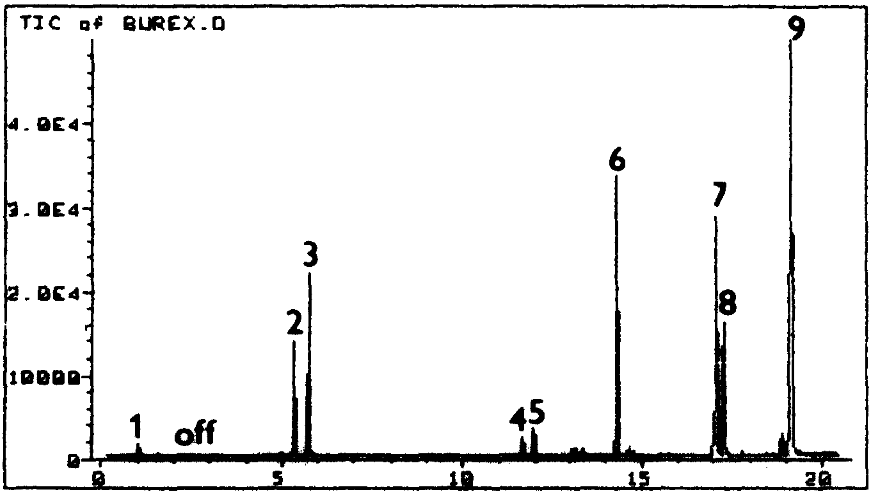

Fig. 3. Chromatogram of by-products from reaction step 3. Peaks: 1 = benzene; 2 = phenyl azide; 3 = phenol; 4 = unknown; 5 = 1,1'-diphenyl; 6 = diphenyl sulphide; 7 = diphenyl disulphide; 8 = phenyl ester of benzenesulphonic acid; 9 = S-phenyl ester of benzenesulphinothioic acid.

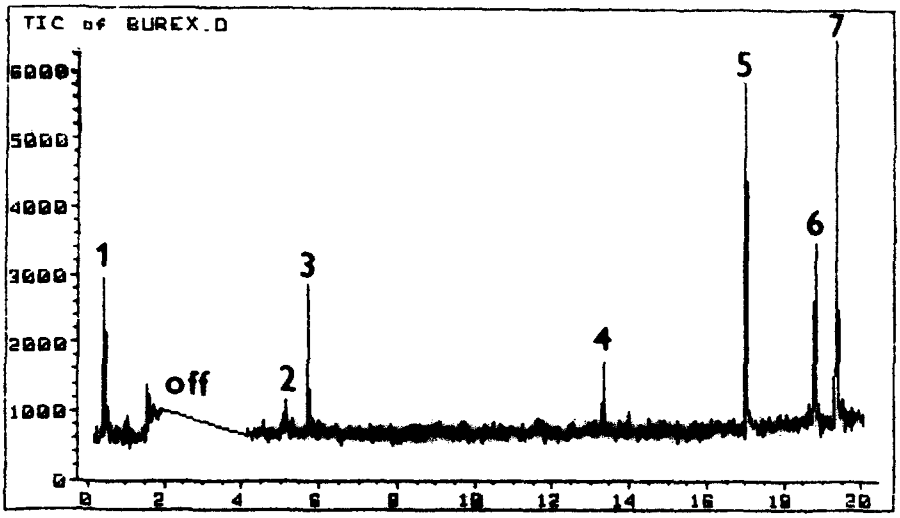

Fig. 4. Chromatogram of by-products from reaction step 3, using for the reduction. Peaks: 1 = sulphur dioxide; 2 = thiophenol; 3 = phenol; 4 = unknown; 5 = diphenyl disulphide; 6 = cyclo-octasulphur; 7 = S-phenyl ester of benzenesulphinothioic acid.

unequivocal. However, the situation is more complicated in the subsequent reaction steps. In the second step, there is a possibility of formation of by-products during the reaction, either via decomposition of the diazobenzene chloride (benzene, phenol), or via a competing reaction taking place in parallel with the formation of sodium phenylhydrazino sulphonate (phenyl azide), respectively, via decomposition of the sodium phenylhydrazino sulphonate itself. In the third step, by-products may be

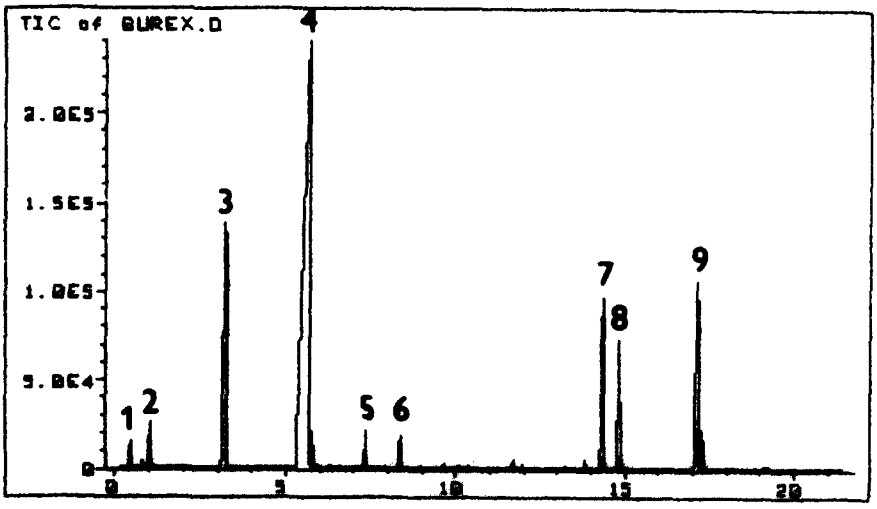

Fig. 5. Chromatogram of the condensed gaseous exhaust. Peaks: 1 = sulphur dioxide; 2 = benzene; 3 = chlorobenzene; 4 = phenyl azide; 5,6 = unknown; 7 = diphenyl sulphide; 8 = azobenzene; 9 = diphenyl disulphide.

found as a result of the decomposition of phenylhydrazine. Information on the formation of most of the compounds mentioned can be found in the basic chemical manuals. The origin and preparation of benzene, thiophenol, diphenol, diphenyl sulphide, diphenyl disulphide, phenol, azobenzene and biphenyl are described in ref. 2, and the formation of phenylazide in ref. 3.

The influence of sulphur dioxide and sulphites on phenylhydrazine promoted by heat gives rise to N-sulphono acids[2]. At elevated temperature, these may rearrange, resulting in the formation of sulpho acids, which can subsequently react with phenol or thiophenol, both present in the reaction mixture. The corresponding esters of sulpho acids are the final reaction products. Ester formation represents the major competing reaction to the phenylhydrazine synthesis according to the reaction schemes 1–3.

Despite the worldwide industrial production of phenylhydrazine and the use of a general procedure, practically identical to the reaction scheme 1–3 for over 100 years, and that the conditions for the formation of the various compounds originating from benzenediazonium chloride or phenylhydrazine are well known[1–3], there is still a need for a complete analytical study of the synthesis of phenylhydrazine. The present paper was aimed at elucidating the possible risk and environmental impact of phenylhydrazine production, especially in the case of breakdown, or deviation, from the steady-state conditions. The results obtained indicate that even a simple and well known process can be a source of undesirable side-reaction by-products, some of which may present serious hazards for man and his environment (benzene, phenol, biphenyl).

ACKNOWLEDGEMENT

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