CHROM. 4654

Gas chromatographic analysis of γ-irradiated nitrobenzene for biphenyl and nitroaromatic products

In a study of the γ-radiolysis of nitrobenzene, it was necessary to analyze the irradiated nitrobenzene for biphenyl, the three isomeric dinitrobenzenes, the three isomeric nitrobiphenyls, and the six isomeric dinitrobiphenyls (one nitro group per phenyl ring). At the time this investigation was initiated, a search of the literature did not reveal any information on the conditions necessary for the gas chromatographic analysis of the above compounds. Since then, conditions have been described for the gas chromatographic analysis of *o*-, *m*-, and *p*-dinitrobenzene[1]. This note describes gas chromatographic conditions for the analysis of biphenyl and the aromatic nitro compounds listed above.

Experimental

Materials. Biphenyl, *o*-, *m*-, and *p*-dinitrobenzene, 2-, 3-, and 4-nitrobiphenyl, and 2,2′-, 2,4′-, 3,3′, and 4,4′-dinitrobiphenyl were available commercially. The commercial samples were recrystallized if necessary to obtain satisfactory melting points. Samples of 2,3′- and 3,4′-dinitrobiphenyl were prepared and purified as reported[2]. Column coatings and packings were obtained from various gas chromatography suppliers.

Equipment. A Perkin-Elmer Model 900 dual column unit with hydrogen flame ionization detector was used for all analyses.

Column preparation. The packing for a column was prepared by dissolving the coating material in the appropriate solvent and adding this solution with gentle stirring to the Chromosorb which was covered with the solvent. The solvent was slowly evaporated on a steam bath with occasional gentle stirring or with a rotating vacuum evaporator. The packing was then dried in an oven at 110° for 1 h. The columns were packed by applying a vacuum at one end and were vibrated and tapped until filled. The columns before use were conditioned for about 2 h at the maximum recommended temperature. All columns were 1/8 in. O.D. copper tubing.

Samples. Standard dilute solutions of the various nitroaromatic compounds and biphenyl in nitrobenzene were prepared and used for analysis on the different columns.

Results and discussion

In an investigation of the radiation chemistry of nitrobenzene, the three isomeric dinitrobenzenes, the three isomeric nitrobiphenyls, and the six isomeric dinitrobiphenyls (one nitro group per phenyl ring) were considered to be very likely radiolytic products. Gas chromatography offered the best analytical method for analyzing for these compounds, both qualitatively and quantitatively. A number of different column coatings were tried in the effort to find gas chromatographic conditions which would give the desired analyses and are listed in Table I. It was found that biphenyl and the dinitrobenzenes could be analyzed as a group, the nitrobiphenyls as a group, and the dinitrobiphenyls as a group. The best conditions found in this study for the analyses of the different groups are given in Table II and retention times for these conditions

TABLE I

GAS CHROMATOGRAPHIC COATINGS

Coatings	*Compounds*		
	Biphenyl and dinitro benzenes	*Nitrobi-phenyls*	*Dinitrobi-phenyls*
Dow Corning high-vacuum silicone grease (350°)[a]	X[b]	X	X
Dow Corning Silicone 710 (phenyl methyl) (225°)	X	X	—
Versamid 900 (350°)	X	X	X
Silicone UC-W-98 (methyl vinyl) (300°)	X	X	X
Silicone GE-SE52 (methyl phenyl) (300°)	X	X	X
Ucon Oil-LB-550X (polyglycol) (200°)	X	—	—
Silicone OV-22 (65% phenyl, 35% methyl) (350°)	—	—	X
Polyphenyl ether (6 rings) (225°)	X	X	X
Polyphenyl ether (7 rings) (250°)	—	—	X
Poly-*m*-phenoxylene (300°)	—	—	X

[a] Temperature represents maximum recommended temperature.
[b] X indicates coating was tried with this group of compounds.

TABLE II

GAS CHROMATOGRAPHIC CONDITIONS

Nitrogen carrier gas was used at a flow rate of 30 ml/min for all analyses.

Compound group	*Coating*	*Inert packing*	*Coating (%)*	*Column length (ft.)*	*Temperature (°C)*
Biphenyl and dinitrobenzenes	Versamid 900	Chromosorb W, AW/DMCS, 80/100 mesh	5	10	150° for 10 min; programmed to 165° at 10°/min
Nitrobiphenyls	Polyphenyl ether (6 rings)	Chromosorb P, AW/DMCS, 80/100 mesh	5	7.5	220°
Dinitrobiphenyls	Polyphenyl ether (6 rings)	Chromosorb P, AW/DMCS, 80/100 mesh	3	5	235°

are listed in Table III. Chromatograms which represent analyses of the standard nitrobenzene solutions are given in: Fig. 1, biphenyl and dinitrobenzenes; Fig. 2, nitrobiphenyls; and Fig. 3, dinitrobiphenyls. In the analysis of the dinitrobiphenyls, the polyphenyl ether column was used at 235°, which is 10° above the maximum recommended temperature. The column deteriorated faster at this temperature, but a column could be utilized for about 20 to 25 analyses. The higher temperature was used so that better peaks could be obtained for the 3,3′-, 3,4′-, and 4,4′-dinitrobiphenyls and the analysis time would be reduced. For the column coatings tested for the analysis of biphenyl and the dinitrobenzenes, the one that offered the next best possible analysis was Dow Corning Silicone 710. With the Dow Corning Silicone 710 columns tested, the dinitrobenzenes had some tailing and there was some overlap of the *meta* and *para* isomers. Additional work with Dow Corning Silicone 710 would be required to determine the necessary gas chromatographic conditions to give satisfactory analysis for biphenyl and the dinitrobenzenes. For the nitrobiphenyls, a 10-ft. column

TABLE III

RETENTION TIMES

Compound	*Retention time*[a] *(min)*
Biphenyl	7.3
p-Dinitrobenzene	15.6
m-Dinitrobenzene	17.1
o-Dinitrobenzene	20.7
2-Nitrobiphenyl	14.1
3-Nitrobiphenyl	25.3
4-Nitrobiphenyl	30.3
2,2'-Dinitrobiphenyl	6.9
2,3'-Dinitrobiphenyl	9.7
2,4'-Dinitrobiphenyl	11.3
3,3'-Dinitrobiphenyl	19.5
3,4'-Dinitrobiphenyl	23.2
4,4'-Dinitrobiphenyl	26.9

[a] These retention times are those obtained for conditions listed in Table II.

packed with 5 % poly-*m*-phenoxylene on 80/100 mesh Chromosorb P (AW/DMCS) gave excellent results at 230° for the standard nitrobenzene solution with complete resolution of the three isomers. For the dinitrobiphenyls, a 7.5-ft. column packed with 3 % poly-*m*-phenoxylene on 80/100 mesh Chromosorb P (AW/DMCS) gave excellent results at 260° for the standard nitrobenzene solution with complete resolution of the six isomers. However, neither of these poly-*m*-phenoxylene columns gave satisfactory results when they were used to analyze irradiated nitrobenzene for the

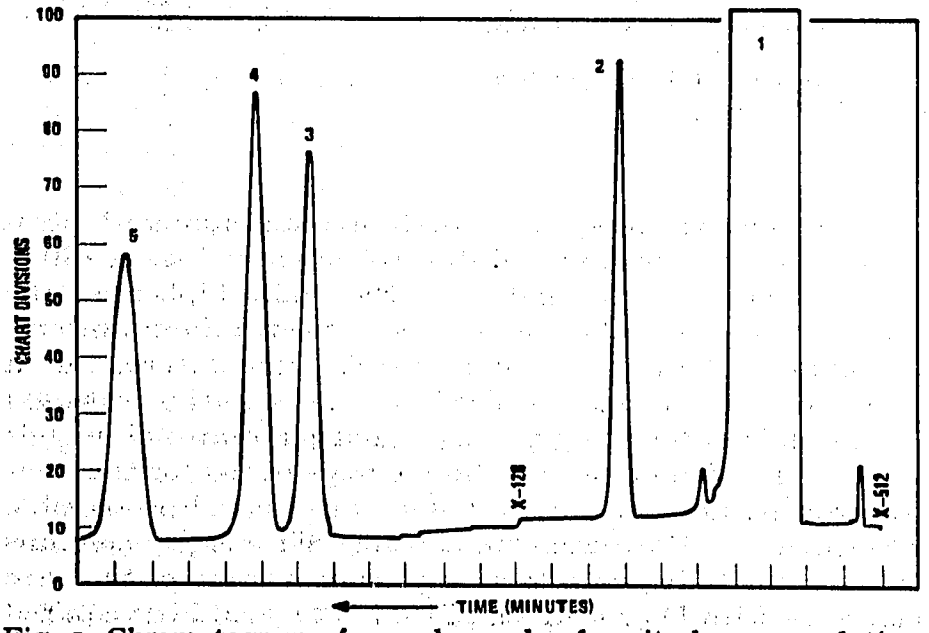

Fig. 1. Chromatogram of a 3-μl sample of a nitrobenzene solution of biphenyl and the dinitrobenzenes. Peaks: (1) nitrobenzene; (2) biphenyl; (3) *p*-dinitrobenzene; (4) *m*-di-nitrobenzene; (5) *o*-dinitrobenzene.

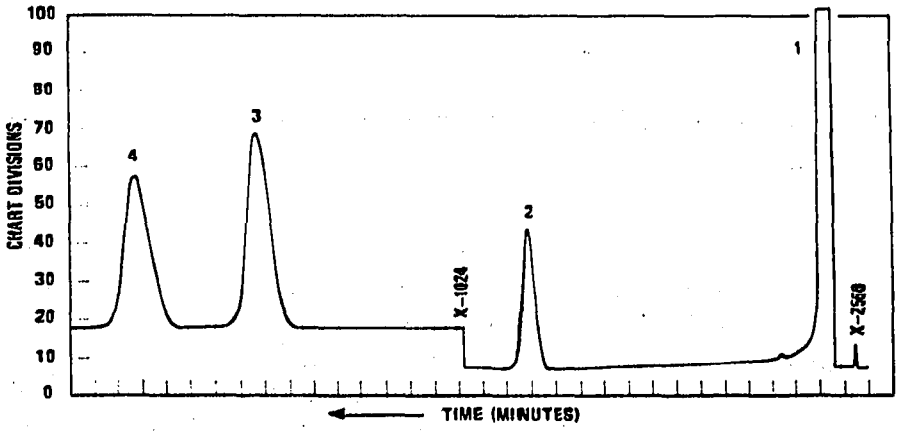

Fig. 2. Chromatogram of a 3-μl sample of a nitrobenzene solution of the nitrobiphenyls. Peaks: (1) nitrobenzene; (2) 2-nitrobiphenyl; (3) 3-nitrobiphenyl; (4) 4-nitrobiphenyl.

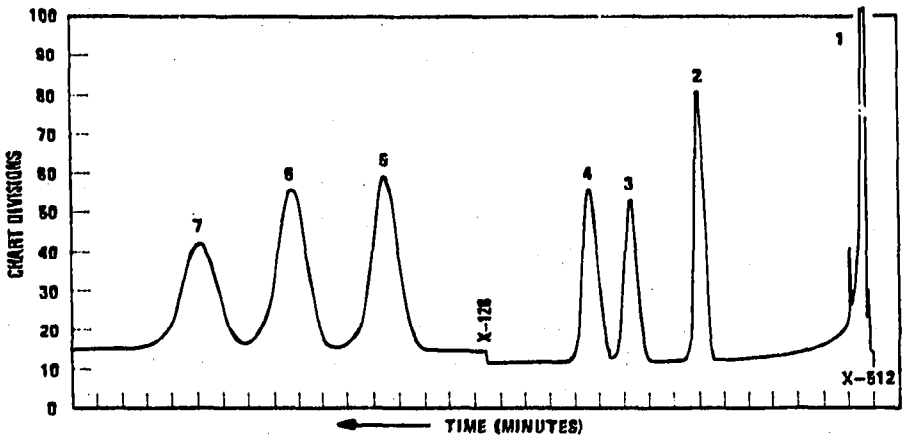

Fig. 3. Chromatogram of a 3-μl sample of a nitrobenzene solution of the dinitrobiphenyls. Peaks: (1) nitrobenzene; (2) 2,2'-dinitrobiphenyl; (3) 2,3'-dinitrobiphenyl; (4) 2,4'-dinitrobiphenyl; (5) 3,3'-dinitrobiphenyl; (6) 3,4'-dinitrobiphenyl; (7) 4,4'-dinitrobiphenyl.

nitrobiphenyls and the dinitrobiphenyls. The reason for this could be due to the presence of a radiolytic product in the irradiated nitrobenzene which had a deleterious effect. The 7-ring polyphenyl ether, which has a higher temperature limit than the 6-ring polyphenyl ether, was tried only for the analysis of the dinitrobiphenyls. The 7-ring material, however, did not give quite as good resolution as the 6-ring material for the dinitrobiphenyls. Of the nitroaromatic compounds in this study, the 3,3'-, 3,4'-, and 4,4'-isomers of the dinitrobiphenyls presented the greatest difficulty in finding conditions which gave satisfactory analyses.

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1 S. YOSHIHITO, N. YOSHIKURI AND F. TAKEUCHI, *Kogyo Kagaku Zasshi*, 71 (1968) 1841.
2 F. H. CASE AND A. IDELSON, *J. Org. Chem.*, 27 (1962) 4651.

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