BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Série des sciences chimiques
Volume X, No. 11-12, 1962

ORGANIC CHEMISTRY

Gas-liquid Chromatography of the C_1—C_4 Nitroparaffins

by

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Presented by T. URBAŃSKI on August 28, 1962

Papers concerning the gas chromatography of nitroparaffins are suprisingly scarce, as compared with the rapid development of that technique the last few years. This may be explained by the difficulties encountered when experimenting with such highly reactive compounds as nitroparaffins which can react with certain column packings. Only two papers have been published on gas chromatography of nitroparaffins. Bethea and Wheelock [1], [2] chromatographed the C_1—C_4 nitroparaffins using as stationary phases Apiezon *T*, Labriseal stopcock grease and Wemco C transformer oil. These authors established also, that dibutyl tartrate, N-methyldiphenylamine, 2,2-diaminoethylamine, tributyl phosphate and tricresyl phosphate used as stationary phases gave negative results in the case of nitroparaffins. Judging from the attached chromatograms, the authors had to do with the problem of the asymmetry of peaks.

Being much interested in the analysis of nitroparaffins, we have also undertaken work on the gas—liquid chromatography of the C_1—C_4 nitroparaffins using column packings differing from those applied by Bethea and Wheelock.

Experimental

Apparatus. The experiments were carried out on the Aerograph A-110-C chromatograph produced by Wilkens Instrument Research Inc., (Walnut Creek, Calif., USA), with coiled, air thermostated steel column of 4.0 mm I.D., 152.4 cm or 304.8 cm in length. The detection was secured by a thermal conductivity cell (katharometer). The recorder Honeywell-Brown of 1 mV span was used. The recorder chart speed was maintained constant in all experiments and was 42 cm/hour.

Nitrogen was used as carrier gas. It was obtained from a high-pressure cylinder and passed through a silica gel container for drying. The inlet pressure of the carrier gas was controlled by a mercury manometer. The rate of gas flow was measured by a soap-film flowmeter.

The samples were introduced by means of a 10 μl. syringe, 2 μl. of examined solute being injected at a time.

Column packings. The following column packings were tried:

Carbowax 20 M on C-22 fire brick 0.17—0.25 mm (60/80 mesh) grain size, in ratio 25:75 (w/w) to solid support.

Craig's polyester succinate on C-22 fire brick, grain size and ratio as above.

Silicone Dow 11 on C-22 fire brick, grain size and ratio as above.

The above mentioned column packings were of commercial standard. We also applied the following column packings prepared by us:

Apiezon *M* (15% w/w) on Chromosorb 0.17—0.42 mm (35/80 mesh) grain size.

Apiezon *L* (15% w/w) and palmitic acid (2% w/w) on Chromosorb (grain size as above).

Apiezon *L* (20% w/w) and stearic acid (5% w/w) on Chromosorb (grain size as above).

Chromosorb was treated with dil. HCl (1:4) prior to use, then washed with water (removal of Cl), finally dried at 140°C for 2 hours. The column packing was prepared in the usual manner using CCl_4 as solvent for stationary liquids. After evaporation of the solvent (under atmospheric pressure) the resultant impregnated support was dried at 140°C for 2 hours and then poured into the straight column, the uniformity of packing being secured by a vibrator (made of a laboratory electric stirrer). The column was coiled again and placed in the chromatograph thermostat.

The nitroparaffins. Nitromethane, nitroethane, 2-nitropropane and 1-nitrobutane were of commercial standard. 1-Nitropropane and 2-nitrobutane were prepared in laboratory by the V. Meyer method. All these compounds were additionally purified in the following way: an approriate amount of a nitroparaffin was treated with 3 per cent aqueous KOH solution, a few drops of diethylamine were added and the whole stirred mechanically for 1 hour. Thereupon the undissolved nitroparaffin was extracted with ethyl ether and the aqueous layer neutralized with hydroxylamine hydrochloride solution. The nitroparaffin thus separated was extracted with ethyl ether. The ethereal extract was washed with 1 per cent HCl solution, followed by water, dried with Na_2SO_4 and distilled.

The purity of nitroparaffins so obtained was checked individually by gas chromatography on two different columns, one containing Carbowax 20 M as the stationary phase, and the other Silicone Dow 11. Gas chromatography proved that all nitroparaffins applied on our work were free of contamination.

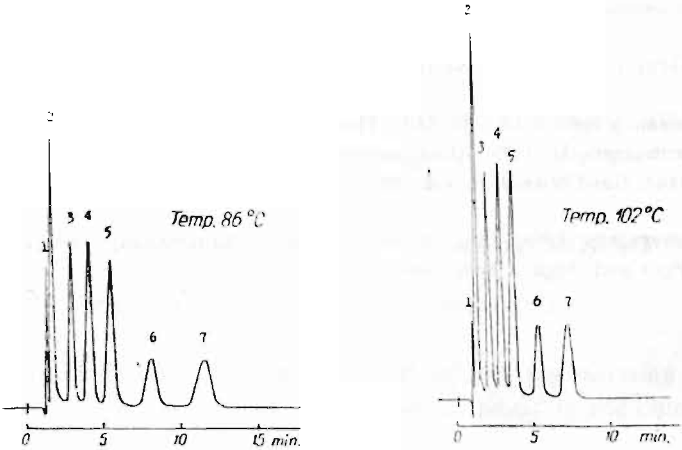
Discussion and results

The initial experiments have shown the difficulties encountered in the gas—liquid chromatography of nitroparaffins. The separation of those compounds effected on Carbowax was unsuccessful due to the failure in separation of nitromethane from nitroethane. The separation carried out on polyester succinate gave no better result. The application of stationary liquid of non polar character, Silicone Dow 11, gave full separation of the nitroparaffins. However, the resulting peaks on the chromatogram were asymmetric, and a very distinct deviation of the chromatogram base line was also observed. The asymmetry of peaks was caused by the tailing effect.

The tailing effect very often occurs in the chromatography of polar compounds on a stationary phase of low polarity. It is caused by the adsorptivity of the support for the solute components of higher polarity [3]. Scott recommended "silver plating" of the supporting solid by treating it with $AgNO_3$ soln. and a reducing agent [4], [5]. According to Janák tailing is caused by the presence of sorption centres existing on the surface of the support. The sorption centres can be blocked by a sorbing substance, liquid or solid [6], [7]. Kaiser recommended the blocking of the sorption centres by adding to the stationary liquid such relatively nonvolatile substances as polyethylene glycol, fatty acids or their alkali metals salts [8].

In our case the application of Apiezon *M* or Apiezon *L* as the stationary phases gave no better results as in the case of Silicone Dow 11. The addition of palmitic acid to the stationary liquid improved the symmetry of peaks to some extent. The application of the stationary phase composed of: Apiezon *L* (20% w/w) and stearic acid (5% w/w) on Chromosorb finally gave the satisfactory symmetry of peaks and complete stability of the chromatogram base line.

The typical chromatograms for two temperatures: 86° and 102° are presented below.



Separation of the C_1—C_4 nitroparaffins. 1. Solvent — ethyl ether. 2. Nitromethane. 3. Nitroethane. 4. 2-Nitropropane. 5. 1-Nitropropane. 6. 2-Nitrobutane. 7. 1-Nitrobutane
Column packing: Apiezon *L* (20% w/w) and stearic acid (5% w/w) on Chromosorb 0.17—0.42 mm (35/80 mesh) grain size; column length: 152.4 cm; nitrogen inlet pressure 176 mm Hg; nitrogen flow (exit): 40 ml/min (at 20°C); detector: thermal conductivity cell; sample size: 2 μl

Relative retentions (r_{12}) of the C_1—C_4 nitroparaffins are given in the Table.

TABLE

Substance	Relative retention at:	
	86°C	102°C
benzene	1.0	1.0
nitromethane	0.09	0.10
nitroethane	0.59	0.52
2-nitropropane	0.91	0.86
1-nitropropane	1.35	1.28
2-nitrobutan	2.21	2.07
1-nitropropane	1.35	1.28
2-nitrobutan	2.21	2.07
1-nitrobutan	3.30	3.03

Note: The relative retentions are given according to the "Preliminary recommendation on nomenclature and presentation of data in gas chromatography" [9]. Relative retentions were calculated from the adjusted retention volumes (V'_R). V'_R values taken for calculations were based upon triplicate analyses.

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