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SEPARATION AND IDENTIFICATION OF 2-NITROALKANOL-1 COMPOUNDS BY GAS CHROMATOGRAPHY

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SUMMARY

A satisfactory gas chromatographic separation of nitroethanol, 2-nitropropanol-1, 2-methyl-2-nitropropanol-1, 2-nitrobutanol-1, 3-methyl-2-nitrobutanol-1, 2-methyl-2-nitrobutanol-1 and 2-nitropentanol-1 was achieved in about 40 min on Carbowax 20M .Reproducible retention times were obtained; a correlation between them and molecular weight, boiling point and structural parameters was found and on this basis a regression equation was established.

INTRODUCTION

Nitroalkanols of the type $R-\underset{\underset{NO_2}{|}}{CH}-CH_2-OH$ could be easily prepared by the reaction

$$R-CH_2-NO_2 + HCHO \rightarrow R-\underset{\underset{NO_2}{|}}{CH}-CH_2-OH$$

Their analysis, however, has been little investigated. Individual nitroalkanols were determined by potentiometric titration and polarography[1]. In their synthesis, however, a mixture is usually obtained and gas chromatography (GC) would seem to be a better method. A GC method is described in this paper.

EXPERIMENTAL

Apparatus

A Tswett Model 104 (U.S.S.R.) gas chromatograph equipped with a flame-ionization detector was used. The recorder used was a Kutesz (Budapest, Hungary),

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Type 175, with 10 mV full-scale at a chart speed of 250 mm/h. Injections were made with a Hamilton 7005 5-μl syringe. Columns of length 0.5, 1.0, 1.5 and 2.0 m were used, packed with 1, 2, 3 and 5% SF-96 silicone oil or Carbowax 20M on silanized Chromosorb G and 2, 5 and 10% of the same stationary phases on silanized Chromosorb W. The column temperatures were 343, 353, 363, 373 and 383°K and that of the injector was 523°K. The flow-rate of the carrier gas (nitrogen) was optimized.

The preparative mode of a Fractovap 2407T chromatograph (Carlo Erba, Milan, Italy) with a thermal conductivity detector (TCD) was used to obtain the pure sample substances. IR, NMR and mass spectroscopy (MS) and physico-chemical determinations were used for identification purposes.

Materials

The supports (Chromosorb W and Chromosorb G, both 80–100 mesh, both silanized) and the stationary phases (Carbowax 20M and SF-96) were obtained from Carlo Erba.

Mixtures of 2-nitroalkanol-1 compounds were prepared in the Higher Chemical Technological Institute, Burgas, Bulgaria. Pure nitroethanol was obtained from Aldrich (Milwaukee, WI, U.S.A.).

RESULT AND DISCUSSION

Separation

The following parameters were optimized using silanized Chromosorb G and W supports: length of the column, L; analysis temperature, T; mobile phase flow-rate; and percentage of the stationary phase. It was found that Carbowax 20M gives more peaks on the chromatogram and that a 1-m column is an acceptable compromise between separation and analysis time. Using the simplex optimization technique[2], it was found that the best results were obtained with 1–3% of stationary phase on Chromosorb G or 2–5% on Chromosorb W. Regardless of the higher number of theoretical plates of the former column, only six peaks could be distinguished, whereas the column with 2% Carbowax 20M on Chromosorb W gave an additional shoulder on the second peak. A more detailed study of the separation according to the 2^4 experimental design did not lead to a better separation.

Because of the better symmetry of the peaks on the 1% Carbowax 20M on Chromosorb G column, we adopted it for further investigations. The design experiment with this column gave the following optimal separation parameters: temperature, 343 $\pm$ 2°K; mobile phase flow-rate, 8 cm/sec; 1% Carbowax 20M on silanized Chromosorb G; and column length, 1 m. The analysis time under these conditions was 245 min. A decrease in the analysis time to 40 min by increasing the temperature to 373°K diminished the worst separation from 0.71 to 0.61 R (resolution factor).

The chromatogram obtained under these conditions is given in Fig. 1 and the relative retentions, $r_{1,2}$, and resolution factors (R) of all peaks are given in Table I. It was established that the temperature dependence of the retention times of all peaks is almost constant and no change in the positions of the peaks takes place. Differences in dt_R/dT exist, however, and this could be helpful information for identification purposes.

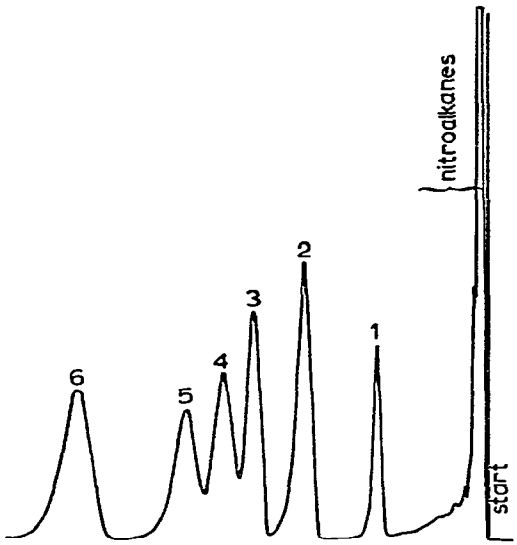

Fig. 1. Chromatogram of nitroalkanol mixtures on 1% Carbowax 20M on Chromosorb G at 373°K. Peaks: 1 = 2-methyl-2-nitropropanol-1; 2 = 2-nitropropanol-1+2-methyl-2-nitrobutanol-1; 3 = ntiroethanol; 4 = 2-nitrobutanol-1; 5 = 3-methyl-2-nitrobutanol-1; 6 = 2-nitropentanol-1.

TABLE I

RELATIVE RETENTIONS ($r_{1,2}$) AND RESOLUTION FACTORS (R) FOR THE CHROMATOGRAM SHOWN IN FIG. 1

Peak No.	$r_{1,2}$	R	*Peak No.*	$r_{1,2}$	R
1	0.47		4	1.13	
		2.51			0.61
2	0.80		5	1.30	
		1.33			1.48
3	1.00		6	1.76	
		0.66			

Identification

GC retention data can also be used for identification purposes. The present theory of solutions is successful only for qualitative or semi-qualitative purposes, and the different chromatographic relationships are limited in their application. It is our opinion that the use of only GC data for identification purposes has both theoretical and practical importance. On this basis, an attempt to use known chromatographic methods for correct identification with only chromatographic data is made here.

By means of preparative GC, peaks 1 and 6 (Fig. 1) were isolated and their IR spectra were obtained. By comparison with spectra in the Aldrich Library of IR Spectra, it was found that peak 1 is 2-methyl-2-nitropropanol-1 (Spectrum No. 209E).

The IR spectrum of peak 6 and its molecular mass indicates that it is a nitropentanol, but only by considering NMR data was it confirmed as 2-nitropentanol-1. Pure 2-nitropropanol-1 and 2-nitrobutanol-1 were obtained from pure nitroethane

and nitropropane-1 after preparative GC purification of the reaction mixtures. Their identities were confirmed by their molecular masses and IR spectra. It was found that peaks 2 and 4 are 2-nitropropanol-1 and 2-nitrobutanol-1, respectively. The IR spectrum of the isolated peak 2 showed, however, that it is an overlapped peak. A combined GC–MS confirmed the identity of all peaks and indicated that peak 5 is 3-methyl-2-nitrobutanol-1 and that the impurity in peak 2 could be 2-methyl-2-nitrobutanol-1. Isolation of 2-nitrobutanol-1 from the nitroparaffin mixture, followed by condensation with formaldehyde and preparative GC purification of the basic compound gave a product with the same retention time.

As can be seen, the identifications made require many data obtained by different non-chromatographic methods. We then tried to identify the same peaks using mostly GC data. Let us consider only three pure substances: nitroethanol from Aldrich and 2-methyl-2-nitropropanol-1 and 2-nitropentanol-1 (isolated peaks 1 and 6). To discover the identities of the other peaks, the temperature dependence of their retention times was studied first. The linear relationship

$$\log t = A + B/T \tag{1}$$

was checked at five temperatures and the results given in Table II were obtained.

TABLE II

VALUES OF CONSTANTS A AND B IN EQN. 1

Peak No.	*A*	*B*	*Peak No.*	*A*	*B*
1	−5.887	3235.1	4	−6.509	3608.0
7	−6.155	3418.2	5	−6.410	3594.0
3	−6.375	3539.4	6	−6.712	3766.6

We expect that only the members of one homologous series will lie on the curve: $B = B_1 + B_2 n_C$, where n_C is the number of C atoms and B_1 and B_2 are constants.

Peak 6 is 2-nitropentanol-1 and we started with the identification of the peaks of 2-nitroalkanol-1 compounds. If peak 5 is 2-nitrobutanol-1, the value of B_2 is obtained from the equations

$$3766 = B_1 + 5B_2$$
$$3594 = B_1 + 4B_2$$

Thus $B_2 = 172$. By subtracting 172 from 3594 the number 3422 is obtained, which is nearly equal to 3418.2. Hence, the first combination of 2-nitroalkanol-1 peaks could be 6–5–2. If peak 5 is 2-nitrobutanol-1, $B_2 = 158$, the value 3450 is obtained, and again the B value of peak 2 is the nearest. Hence, a second combination is possible: peaks 6–4–2. Let us now check these two combinations according to the equation

$$\log t = a + bn_C \tag{2}$$

The criterion will be the variances (s^2) obtained between the experimental and calculated values. The calculations show that the variance of the curve 6–5–2 is

statistically greater than those of the curve 6–4–2: $s^2_{6-5-2} = 1.077 \cdot 10^{-3}$, $F^{exp} = 8.286$; $s^2_{6-4-2} = 0.130 \cdot 10^{-3}$, $F^{0.9}_{3,3} = 5.39$. Hence, with confidence we could say that peak 4 is 2-nitrobutanol-1 and peak 2 is 2-nitropropanol-1. Now, a plot of B *versus* n_C could be constructed (Fig. 2). As nitroethanol has no other homologous members its point remains separated. The points of peaks 6, 4 and 2 are connected and the curve representing 2-nitroalkanol-1 compounds is produced. Two other peaks still have to be identified: peak 5 and the impurity in peak 2. The possible compounds left are 2-methyl-2-nitrobutanol-1 and 3-methyl-2-nitrobutanol-1, both with $n_C = 5$. The position of the other part of the overlapped peak could be easily found: this is the cross-point of $n_C = 5$ and B of peak 2. Hence a new point, 2^a is located in the plot. One of these two points (2^a or 5) belongs to 2-methyl-2-nitrobutanol-1 which is a homologue of 2-methyl-2-nitropropanol-1 (point 1). If we connect point 1 with point 5 a curve with a slope of 0.434 is obtained. On connecting points 1 and 2^a the slope is 0.262. The curve 2–4–6 has a slope of 0.22. As no great differences in the enthalpy changes could be expected for the dissolution of the different homologous series studied we assume that the overlapped peak consist of 2-nitropropanol-1 and 2-methyl-2-nitrobutanol-1 while peak 5 is 3-methyl-2-nitrobutanol-1.

This identification is as accurate as those made by the combination of spectral and synthetic methods. It is less time consuming purely chromatographic and has the additional advantage that the curves in Fig. 2 show a promising situation namely that the position of the normal carbon chain lies above the location of the curve for 2-nitroalkanol-1 compounds, and the latter above the curve for 2-methyl-2-nitroalkanols.

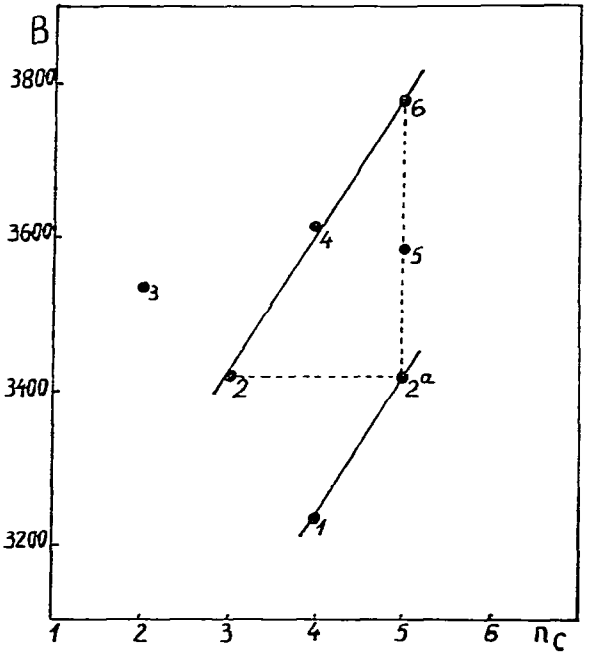

Fig. 2. Investigation of the dependence of slope B in eqn. 1 on the number of carbon atoms, n_C. For peak numbers, see Fig. 1. 2^a is a 2-methyl-2-nitroalkanol.

As a first approach, similar to that for isoalkanes, the following rule could be postulated: the more branched the molecular structure, the worse is the retention. From this, and taking into acount the fact that the retention times are constant under the optimal separation conditions (the variances, s^2, of $r_{1,2}$ are 0.05) we decided to search for a linear regression between the relative retentions and some molecular properties of the nitroalkanols studied. The boiling point (T), molecular weight (M_w) and the topological invariant (W, Wiener number)[3,4] were chosen as parameters. The analysis shows that a fourth parameter, the extent of $-NO_2$ hindrance (h_{NO_2}), should also be involved. We succeeded in simplifying the final equation representing the regression to a biparametric form:

$$r_{1,2} = -9.70 + 0.044T + 0.493M_w/(W + h_{NO_2})$$

where the coefficient h_{NO_2} has an empirically found value of 20 units for tertiary $-NO_2$ groups and 10 units in all other instances.

The comparison of $r_{1,2}^{calc.}$ with $r_{1,2}^{exp.}$ is shown in Table III.

TABLE III

COMPARISON OF $r^{exp.}$ AND $r^{calc.}$

Compound	$r^{exp.I}$	$r^{exp.II}$	*Difference*	$r^{calc.}$	*Difference*
2-Methyl-2-nitropropanol-1	0.47	0.47	0.00	0.38	+0.09
2-Nitropropanol-1	0.80	0.80	0.00	0.73	+0.07
2-Methyl-2-nitrobutanol-1	0.80	0.80	0.00	0.80	+0.00
Nitroethanol	1.00	1.00	0.00	1.03	−0.03
2-Nitrobutanol-1	1.13	1.14	0.01	1.18	−0.04
3-Methyl-2-nitrobutanol-1	1.30	1.32	0.02	1.42	−0.10
2-Nitropentanol-1	1.76	1.79	0.03	1.93	−0.14

The Fisher criterion shows that the proposed mathematical model is not adequate, but in practice the correlation is satisfactory and using this equation one could corroborate the identification made with GC data only in an independent manner. This equation may also be useful in identifying other nitroalkanols of the type studied.

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