

Relative retentions and hydrogen flame detector molar responses of C₁-C₄ nitro compounds*

Relatively little information on the chromatographic behaviour of alkyl nitrites, nitrates and nitroalkanes is available in the literature. FEAR AND BURNET¹ have described GLC analysis of reaction products from the vapour phase nitration of butane and given retention data for several nitroparaffins. HARRISON AND STEVENSON² have reported gas chromatographic separation of methyl, ethyl, and propyl nitrites. A more complete set of data for compounds of this type does not seem to have been reported.

In connection with a study of the photo-oxidation of paraffins by NO₂ we have separated on a 300 ft. dinonyl phthalate capillary column all the C₁-C₄ alkyl nitrites, alkyl nitrates, nitroparaffins and some related oxygenated compounds, and have determined their relative retention times. In most cases the relative molar responses on a hydrogen flame detector have been determined as well. Since some of these compounds are not readily available commercially, the information obtained may be of use to other workers and is reported briefly in the present communication.

Experimental

The capillary column consisted of 300 ft stainless steel tubing 1/16 in. O.D., 0.015 in. I.D., bent in spiral form and coated with dinonyl phthalate. It was maintained at 0° by immersion in an ice bath.

A Perkin Elmer Corp. hydrogen flame detector and amplifier were used, with the oxygen and hydrogen supplied at 20 and 10 p.s.i.g., respectively. The signal from the detector was recorded at a chart speed of 1/2 in. per min on a 1 mV Leeds and Northrup Co. recorder.

Helium was used as the carrier gas at an inlet pressure of 20 p.s.i.g. The helium flow rate at the column inlet was 275 ml per min as measured with a calibrated Brooks rotameter. The helium flow was split before entering the column with the major part of the sample being diverted through a dummy column to the atmosphere. The split ratio was approximately 65:1.

Wherever possible, commercial samples of the nitrocompounds were used. Liquid samples (about 0.1 μl) were injected with a 10 μl Hamilton microsyringe through a selfsealing rubber septum. Gas samples (about 0.1 to 0.5 μmole) were measured manometrically on a vacuum line and transferred into U-traps with greaseless stopcocks. The traps were then connected to the sample input of the chromatograph through a four-way metal valve.

Results

With larger samples the retention times to the peak maximum depended somewhat on the size of the sample, while those to the intersection of the leading edge of the peak with the base line were independent of the sample size. To obtain symmetric peaks the sample size had to be kept as small as possible.

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Benzene was selected as reference. The adjusted relative retention time r , was defined as:

$$r_x = \frac{t'_{rx}}{t'_{rB}} \quad (1)$$

where $t'_r = t_r - t_0$, and t_0 , the retention time of air, was taken to be equal to the retention times of N_2O or CH_4 , which were not retarded in the column; t'_{rx} , t'_{rB} are the adjusted retention times of compound x and benzene respectively.

The relative retention times of the nitrocompounds are given in Table I. The corresponding values for several oxygenated compounds are included, for comparison.

TABLE I

RELATIVE RETENTION TIMES AND MOLAR RESPONSES OF C_1 - C_4 NITROALKANES, ALKYL NITRATES AND NITRITES

| Name of compound | Boiling point ³⁻⁴ (1 atm) (°C) | Relative retention time | Relative molar response |
|--------------------------------------|--|-------------------------|-------------------------|
| Benzene | 80.1 | 1.000 | 100 |
| Nitromethane | 100.8 | 1.29 | 8 ^b |
| Nitroethane | 115 | 3.06 | 23 ^b |
| 1-Nitropropane | 131 | 7.89 | 38 |
| 2-Nitropropane | 120 | 4.12 | 32 |
| 1-Nitrobutane | 153 | 26.99 | 49 |
| 2-Nitrobutane | 139 | 11.23 | 53 |
| Nitroisobutane | 140 | 13.38 | — |
| <i>tert.</i> -Nitroisobutane | 127.2 | 5.50 | — |
| Methyl nitrate | 65 | 0.48 | 6 |
| Ethyl nitrate | 88.7 | 1.42 | 20 |
| 1-Propyl nitrate | 110.5 | 4.30 | 32 |
| 2-Propyl nitrate | 101 | 2.51 | 38 ^b |
| 1-Butyl nitrate | 135 | 14.98 | 38 |
| Isobutyl nitrate | 123 | 7.72 | — |
| <i>tert.</i> -Butyl nitrate | 23-24 (at 4.5 mm) | 4.65 | — |
| Methyl nitrite | —12 | 0.016 | — |
| Ethyl nitrite | 17 | 0.050 | — |
| 1-Propyl nitrite | 57 | 0.227 | 38 ^b |
| 2-Propyl nitrite | 45 | 0.147 | 36 |
| 1-Butyl nitrite | 77.8 | 0.747 | — |
| 2-Butyl nitrite | 68 | 0.401 | 58 |
| Isobutyl nitrite | 67 | 0.426 | 48 |
| <i>tert.</i> -Butyl nitrite | 63 | 0.341 | 62 ^b |
| Acetone ^a | 56.2 | 0.240 | 35 |
| <i>n</i> -Butyraldehyde ^a | 75.7 | 0.687 | — |
| Isobutyraldehyde | 62.5 | 0.403 | 46 |
| <i>tert.</i> -Butanol | 82.3 | 0.694 | 65 |
| Isobutylene oxide | 52.0 | 0.264 | 47 |

^a We are grateful to L.C. DOYLE of this laboratory for supplying the data for these compounds.

^b Impure samples of compounds, as explained in the text.

The logarithms of the relative retention times are plotted against the normal boiling points in Figs. 1 and 2. Good linear plots are obtained for the nitroalkanes and alkyl nitrates (Fig. 1). In the case of the nitrites (Fig. 2) a straight line can be drawn through the points for the propyl and butyl nitrites, but methyl and ethyl nitrite deviate from it. The last two compounds were prepared by reacting methyl and ethyl alcohol with *tert.*-butyl nitrite. Although the adjusted retention times of methyl and ethyl nitrite were very small and could not be determined accurately, there appears to be a definite deviation from the straight line drawn through the points for the other nitrites in Fig. 2.

The dependence of the relative retention time (r) on the boiling point (T_b) for the nitroalkanes and alkyl nitrates may be expressed as

$$\log r = aT_b + b \quad (2)$$

The least square values of the parameters a and b are:

| | a | b |
|----------------|--------|--------|
| Nitroalkanes | 0.0260 | -2.509 |
| Alkyl nitrates | 0.0213 | -1.729 |

The empirical equations (2) may be used to predict the retention times of unavailable compounds from their boiling points. For example, nitroisobutane, *tert.*-nitroisobutane

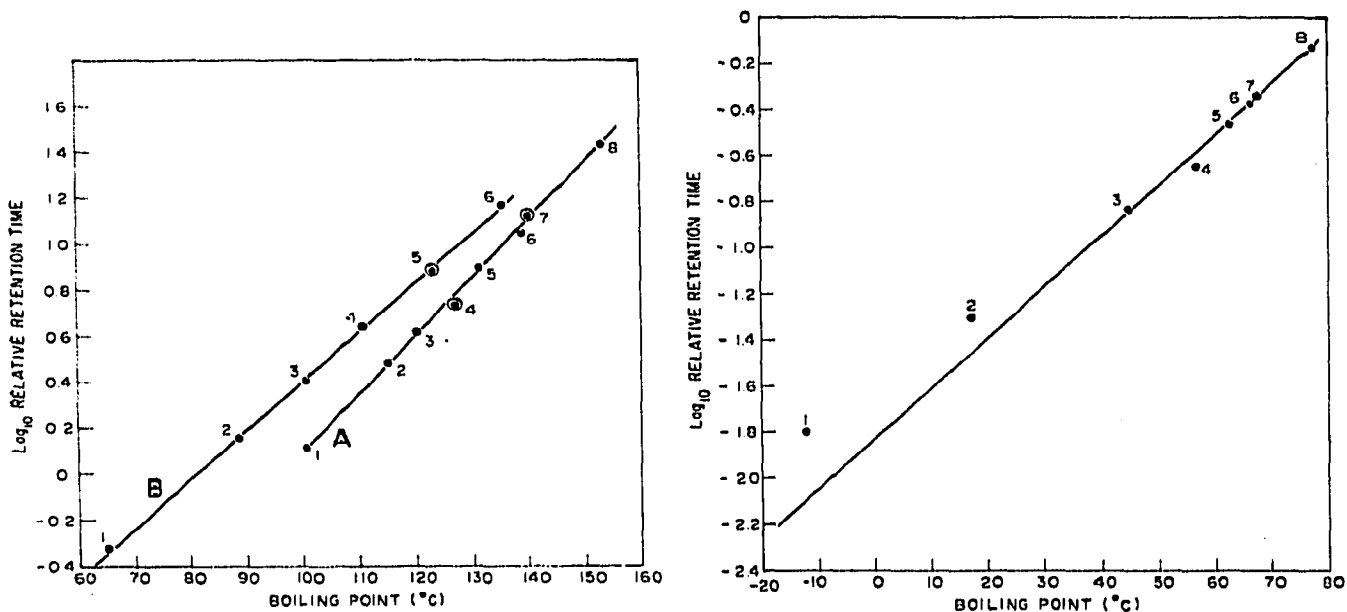


Fig. 1. Boiling point plot of the logarithm of relative retention times. Line A, nitroalkanes: 1 = nitromethane; 2 = nitroethane; 3 = 2-nitropropane; 4 = *tert.*-nitroisobutane; 5 = 1-nitropropane; 6 = 2-nitrobutane; 7 = nitroisobutane; 8 = 1-nitrobutane. Line B, alkyl nitrates: 1 = methyl nitrate; 2 = ethyl nitrate; 3 = 2-propyl nitrate; 4 = 1-propyl nitrate; 5 = isobutyl nitrate; 6 = 1-butyl nitrate.

Fig. 2. Boiling point plot of the logarithm of relative retention times for alkyl nitrites. 1 = Methyl nitrite; 2 = ethyl nitrite; 3 = 2-propyl nitrite; 4 = 1-propyl nitrite; 5 = *tert.*-butyl nitrite; 6 = isobutyl nitrite; 7 = 2-butyl nitrite; 8 = 1-butyl nitrite.

and iso- and *tert.*-butyl nitrates were identified as the products of the photo-oxidation of isobutane by NO_2 from peak assignments based on the plots of Fig. 1. Commercial samples of these compounds were not available. The points based on the relative retention times of the peaks identified in this manner as nitroisobutane, *tert.*-nitroisobutane and isobutyl nitrate are encircled in Fig. 1. The boiling point of *tert.*-butyl nitrate is known only at reduced pressure ($23\text{--}24^\circ/4\text{--}5$ mm Hg) since the compound is unstable at higher temperatures. This compound was therefore identified by seeding with the products from the thermal reaction of *tert.*-butanol with NO_2 . In this reaction *tert.*-butyl nitrite is the major product and *tert.*-butyl nitrate the expected byproduct. Analogous products are obtained in the reaction of isobutanol and NO_2 , and the retention time of the byproduct is consistent with that of the compound identified as isobutyl nitrate from the boiling point plot of Fig. 1. From the observed retention time and the plot in Fig. 1 it appears that the normal boiling point of *tert.*-butyl nitrate would be close to 112° if the compound were stable at this temperature.

The molar responses (relative to benzene) of the compounds available in pure form were determined from the peak areas of known mixtures of these compounds and benzene. The results are given in Table I. The average error of the measurements has been between 1 and 4%. The data with superscript b in Table I belong to compounds which contained impurities and although corrections were applied for the impurities, the accuracy of the relative molar responses for these compounds is not better than about 10%.

It may be seen that the molar responses of the nitrates are generally somewhat lower than those of the corresponding nitrites and nitroalkanes. There appears also to be a definite variation in the responses of the isomers with the molecular structure. However, no definite trend could be established that would eliminate the necessity for individual calibrations.

*Division of Applied Chemistry,
National Research Council,
Ottawa (Canada)*

G. PARASKEVOPOULOS*
R. J. CVETANOVIC

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* National Research Council of Canada Postdoctorate Fellow.