AUTOMOBILES
GASOLINE
EXHAUST
VAPOR
1,3-BUTADIENE
ALKENES
SAMPLING
CHROMATOGRAPHY

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# Butenes and butadiene in urban air

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## ABSTRACT

Samples of urban air hydrocarbons were taken on specifically made adsorbent cartridges and analyzed by gas chromatography after thermal desorption.The four isomeric butenes and 1,3-butadiene were favourably resolved and separated from the abundant alkanes on an aluminium oxide PLOT column.

The concentrations of butadiene, reflecting outdoor urban exposure, were in the range of 0.5 - 5 $\mu g/m^3$. An approximate 1:4 ratio was observed between butadiene and propene which both originate predominantly from vehicle exhaust. The four butenes made up ~50 % of the propene concentration in exhaust-polluted air, with methylpropene > 1-butene > *trans*-2-butene > *cis*-2-butene. Petrol vapour contributed less than exhaust but about five times more to the 2-butenes than to methylpropene and 1-butene.

The highest exposure levels of butadiene and butenes were consistently observed in the vicinity of exhaust pipes and petrol-fuelled vehicles.

KEY WORDS: roads, automobiles, exhaust, petrol, alkenes, olefines, gas chromatography, exposure.

## INTRODUCTION

Health hazards attributable to alkenes have recently received attention with regard to the metabolic conversion of these hydrocarbons to genotoxic epoxides. In addition to ethene, propene (Svensson and Osterman-Golkar, 1984) and butadiene (Filser and Bolt, 1984) have been studied. Butadiene has been shown to be a carcinogen (Huff *et al.*, 1985).

Alkenes in urban air are also of concern with respect to health because of their photochemical conversion to genotoxic products in the presence of nitrogen dioxide. Propene has been studied in some detail (Kleindienst *et al.*, 1985) and butadiene appears to be even more potent in this respect (Victorin and Ståhlberg, 1988).

Knowledge of urban ambient concentrations and exposure levels of alkenes is clearly essential for the assessment and prevention of health hazards. Ethene and propene have been extensively measured, while there is very little consistent data on higher alkenes, mainly owing to analytical difficulties. The purpose of the present study is to provide data for butenes and butadiene.

## EXPERIMENTAL

Samples were taken on adsorbent cartridges coupled to personal sampling air pumps. The adsorbents were Tenax TA (60/80 mesh, Chrompack) in the front end, Carbotrap (20/40 mesh, Supelco) in the middle and Carbosieve S-III (60/80 mesh, Supelco) in the back-up end of glass tubes (150 mm x 4 mm i.d.), in approximately equal amounts. The air volumes were in the range of 0.2 - 3 litres per sample. Parallel samples were occasionally taken for quality control with cartridges containing only the well-known adsorbent Tenax TA.

In the laboratory, helium accomplished desorption at 235 °C into a cool trap (liquid nitrogen) in the oven of a Carlo Erba 2900 gas chromatograph. The sample was injected onto a PLOT analytical column (50 m x 0.32 mm i.d.) with KCl-treated aluminium oxide as the stationary phase using electric heating of the trap. The oven temperature was raised 10 °C per minute from 0 °C to 110 °C,was kept constant for 14 minutes at 110 °C, and was finally raised 4 °C per minute to 200 °C. Chromatogram, retention times and quantitative data were obtained from a reporting integrator. Response FID factors for the alkenes were set equal to that determined for *n*-heptane.

Further analytical data were given in a preliminary report (Nordlinder *et al.*,1984) on the performance of the aluminium oxide column obtained from Chrompack. A similar column was used in a study of hydrocarbons, including alkenes, in the air of a French rural area (Kanakidou *et al.*, 1989)

## RESULTS AND DISCUSSION

### *Chromatographic separation*

The chromatogram given in Fig.1 illustrates the separation achieved for propene, butadiene and the four isomeric butenes.The alkenes ($C_n$) appear in a favourable position between the $C_n$ and $C_{n+1}$ alkanes, which are present in much higher concentrations in urban air. With the proper choice of temperature program, butadiene separates from *n*-pentane. The aluminium oxide column also separates the four butenes well. On the commonly used non-polar stationary phases, 1-butene and methylpropene are normally not separated, and alkenes appear in the same region as the corresponding alkanes (Berglund and Petersson, 1990). The alkynes do not interfere with the alkenes, and oxygenated compounds are strongly retained by the aluminium oxide column.

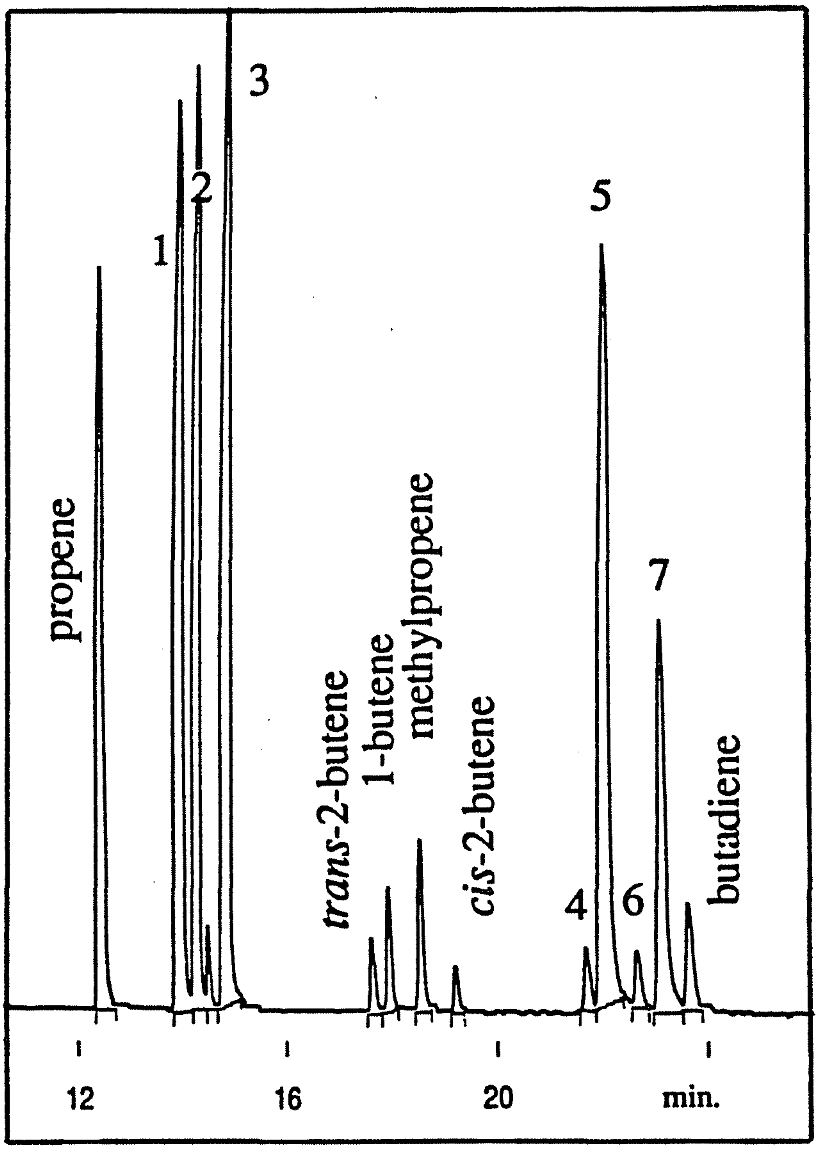

Fig. 1. Gas chromatographic analysis of $C_3$ and $C_4$ alkenes in urban air near a major road (**1** ethyne, **2** methylpropane, **3** butane, **4** cyclopentane, **5** methylbutane, **6** propyne, **7** pentane).

### *Concentration levels*

The results given in Table 1 were selected as representative from a considerable number of urban air samples. The concentration levels and the concentration ratios between the hydrocarbons were checked by duplicate samples. Results for propene and butanes (methylpropane + *n*-butane) are included to permit comparisons with other studies reporting on these hydrocarbons.

The seven reported samples represent widely differing circumstances with respect to emissions, locality and meteorology. The urban background sample indicates low concentrations far from motor vehicles. The second sample from the parade street of Göteborg reflects near-average urban outdoor exposure. The third sample represents unfavourable winter inversion conditions near slow traffic and the fourth sample unfavourable summer conditions at the same, fairly typical, intersection. The fifth (Fig. 1) and sixth samples reflect ordinary winter and summer concentrations near to fast road traffic.The last sample represents intermediate indoor levels of a parking garage. Much higher concentrations were recorded under unfavourable conditions in large parking garages.

It is seen that the concentration of butadiene is 20 - 30 % as compared with that of propene, and is similar to that of methylpropene. Among the four isomeric butenes, methylpropene is the most abundant and *cis*-2-butene the least abundant.

Table 1. Representative concentrations of alkenes (μg/m$^3$) reflecting human exposure in different environments.

| | 1; park off-traffic 7/25-90 | 2; street esplanade 7/25-90 | 3; street crossing 11/30-89 | 4; street crossing 5/07-90 | 5; road plume 11/17-89 | 6; motorway roadside 5/09-90 | 7; garage exit 5/23-90 |
|---|---|---|---|---|---|---|---|
| Propene | 0.26 | - | 27 | 12 | 6.5 | 4.3 | 24 |
| Methylpropene | 0.09 | 0.7 | 7.7 | 3.2 | 1.5 | 0.7 | 7.5 |
| 1-Butene | 0.07 | 0.4 | 5.2 | 2.4 | 1.0 | 0.5 | 4.7 |
| *trans*-2-Butene | 0.03 | 0.4 | 3.7 | 2.3 | 0.7 | 0.3 | 4.7 |
| *cis*-2-Butene | 0.03 | 0.3 | 3.1 | 1.8 | 0.5 | 0.2 | 3.7 |
| Butadiene | - | 0.6 | 6.1 | 2.9 | 1.6 | 0.9 | 7.4 |
| Butanes ($C_4$) | 2.2 | 26 | 160 | 85 | 21 | 8.8 | 155 |

**1**- The Slottskogen park 2 km downwind central Göteborg and 500 m downwind traffic, 20 °C. **2**- Walking along the Avenue of Göteborg, 20 °C. **3**- Near intersection with traffic lights, 0 °C, inversion. **4**- Same intersection, morning rush hour, calm and sunny, 20 °C. **5**- Bridge 5 m above motorway approach to Göteborg, 0 °C. **6**- E6 (90 km/h) 10 km south of Göteborg, 10 °C. **7**- Inside parking garage near cars leaving in the morning, 15 °C.

### *Sources of butenes and butadiene*

In urban outdoor air, the hydrocarbons assessed here originate predominantly from petrol vapours and exhaust from petrol-fuelled vehicles. As illustrated in Table 2, the composition is very different for exhaust and vapours. The figures are based on the results of exhaust samples and on previous studies of petrol vapours (Berglund and Petersson, 1990). An Australian study reports similar differences in the composition of the four butenes (Nelson *et al.*, 1983).
From Table 1, it is evident that petrol exhaust is the major source of alkenes throughout. The increased proportion of butenes, particularly 2-butenes, for the fourth sample is attributed to an increased proportion of vapours at high ambient temperatures. The similar composition for the garage sample may be explained by the higher emissions of unburnt petrol from cold engines. The increased proportion of alkenes, particularly propene, as compared with butanes for the road samples is explained by the increased proportion of lower alkenes in exhaust at elevated speeds (Bailey *et al.*, 1990).

It is concluded that petrol vapours and exhaust are sources of a similar magnitude for the 2-butenes in urban air. For methylpropene and 1-butene, the proportion from vapour is ~10 %. For both butadiene and propene, the contribution from petrol vapour is negligible as compared with exhaust. In hotter climates, the proportion of butenes from petrol vapours is greater (Nelson *et al.*, 1983).

Table 2. Representative percentual composition of $C_3$ -$C_4$ alkenes in petrol exhaust and vapour.

| | Exhaust | Vapour |
|---|---|---|
| Propene | 60 | 0 |
| Methylpropene | 12 | 20 |
| 1-Butene | 8 | 15 |
| *trans*-2-Butene | 4 | 35 |
| *cis*-2-Butene | 3 | 30 |
| Butadiene | 13 | 0 |

### *Human exposure*

Health hazards with respect to metabolic formation of genotoxic epoxides should be directly related to the exposure levels of the alkenes. Particular attention should be paid to the carcinogenic butadiene from vehicle exhaust. High exposure levels in situations where many people are exposed should be of special concern.

The reported samples focus on the comparatively high concentrations in the vicinity of petrol-fuelled vehicles. At the time of this study about 20 % of these vehicles were equipped with catalytic converters in Sweden. With increasing distance from exhaust-emitting vehicles, more than a tenfold decrease of the concentrations of exhaust hydrocarbons were recorded. Motorists are exposed at least to the roadside levels but also to irregular additional contributions from their own cars. These findings conform with previous exposure-related studies of $C_5$ - $C_{10}$ exhaust hydrocarbons using a similar analytical technique (Mattsson and Petersson, 1982).

When indoor exposure is considered, it is important to include environmental tobacco smoke. High levels of butadiene as well as propene are reported from this source (Löfroth *et al.*, 1989).

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