

Assessment by gas chromatography–mass spectrometry of hexenes emitted to air from petrol

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ABSTRACT

Hexenes and cyclohexenes in vapours of conventional petrol were separated by gas chromatography on an aluminium oxide column. All hexenes appear in a favourable chromatographic position between hexanes and heptanes. The seventeen isomeric acyclic hexenes were identified by mass spectra and single-ion monitoring on an ion-trap mass spectrometer. The rapidly photooxidant-forming isomers with a non-terminal double bond constitute 70% of the total amount of acyclic hexenes. The proportions of isomers in petrol vapour are similar to those in urban air and in exhaust from petrol-fuelled vehicles.

INTRODUCTION

Alkenes contribute rapidly and efficiently to the formation of photooxidants in air [1,2]. They are therefore given the highest priority in efforts to prevent environmental photooxidant-related problems by decreasing hydrocarbon emissions. The reactivity of alkenes in air increases with the number of carbon atoms. Pentenes and hexenes are emitted mainly as petrol vapours and as unburnt petrol components in vehicle exhaust.

Alkenes in air polluted with petrol hydrocarbons can be favourably assessed by adsorption sampling and gas chromatographic separation on aluminium oxide columns [3]. Concentrations and proportions of pentenes in petrol vapours have been reported for refuelling of cars with and without vapour recovery [4] and for refuelling with conventional and reformulated petrol [5]. The purpose of the present study was

to separate, identify and determine the proportions of the hexenes emitted to air from conventional petrol.

EXPERIMENTAL

The aluminium oxide–5% potassium chloride gas–solid chromatographic columns (one new and one used in our laboratory for 10 years) were obtained from Chrompack. Their dimensions are 50 m × 0.32 mm I.D. and they are of the porous-layer open tubular (PLOT) type.

The mass spectrometric studies were performed on a Varian Saturn II ion trap GC–MS instrument. The scan rate was one spectrum per second over the range m/z 35–200. Reconstructed ion chromatograms and spectra were obtained from the data-stored scans. Injected gas samples of 10–20 μ l were taken from a laboratory flask, above the surface of commercial petrol (Statoil, RON 98) conditioned to room temperature. The carrier gas was helium and the linear gas velocity through the aluminium oxide

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column approximately 20 cm s^{-1} . The temperature sequence of the column was $40\text{--}105^\circ\text{C}$ ($20^\circ\text{C min}^{-1}$), 105°C (isothermal, 50 min), $105\text{--}200^\circ\text{C}$ (2°C min^{-1}) and 200°C (isothermal).

Samples of ambient air were taken by adsorbent sampling and analysed by thermal desorption and gas chromatography as previously described [3]. Hexenes were studied for selected samples of urban air polluted with petrol vapour and vehicle exhaust. The temperature sequence was $30\text{--}110^\circ\text{C}$ ($10^\circ\text{C min}^{-1}$), 110°C (isothermal, 14 min), $110\text{--}200^\circ\text{C}$ (4°C min^{-1}) and 200°C (isothermal). The hexenes appear in the temperature range $150\text{--}200^\circ\text{C}$.

RESULTS AND DISCUSSION

Gas chromatographic separation

The chromatograms given in Fig. 1 demonstrate the separation achieved on the GC-MS

system. The structures and chromatographic positions of all seventeen isomeric hexenes are given. In addition, the cyclic hexenes 1-methylcyclopentene and cyclohexene are marked in the total-ion chromatogram. Systematic names, quantitative proportions and relative retentions are given in Table I for all the isomeric non-cyclic hexenes.

On the aluminium oxide–potassium chloride column, the hexenes characteristically appear between the C_6 and C_7 alkanes. The prominent heptanes in the region MU 6.6–7.0 are dimethylcyclopentanes, methylcyclohexane, dimethylpentanes and methylhexanes. Similarly, the $\text{C}_2\text{--C}_5$ alkenes appear between the corresponding alkanes [3]. The aluminium oxide–potassium chloride column is therefore superior to most columns with other stationary phases for the determination of alkenes in the prevalent applications with higher amounts of alkanes.

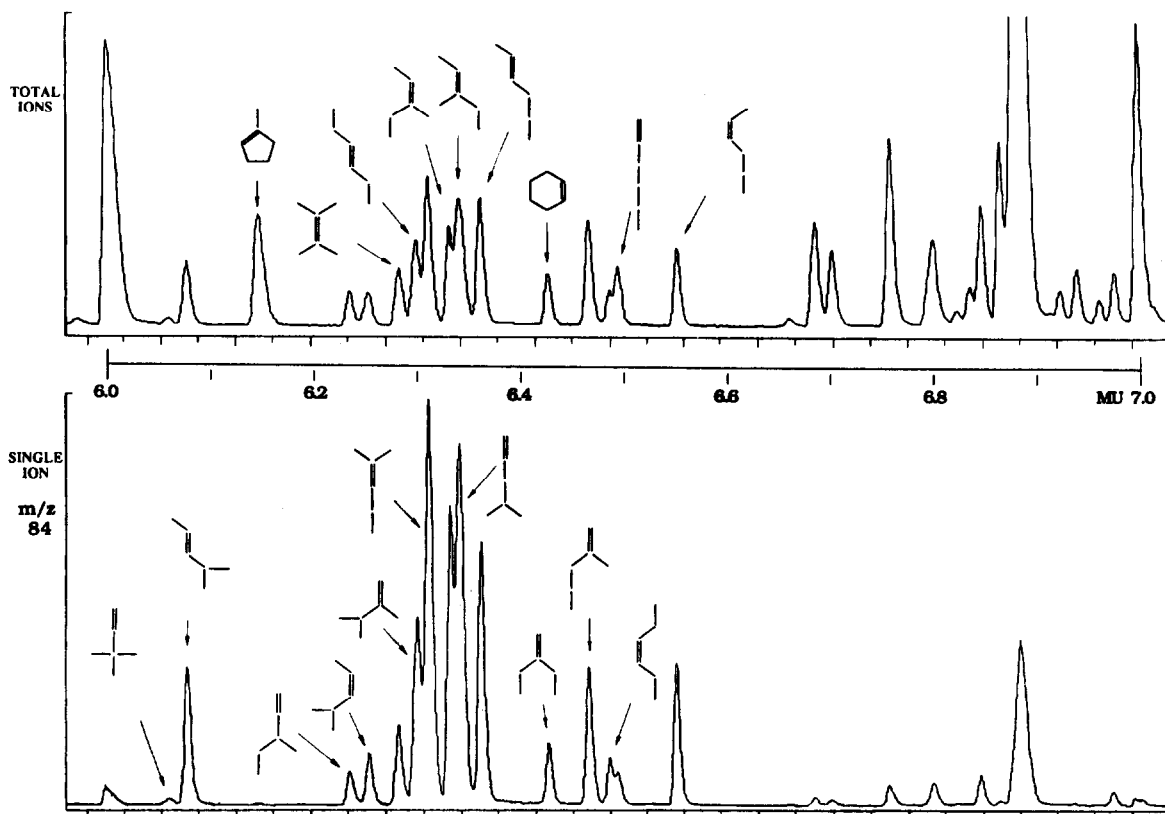


Fig. 1. Chromatographic separation of hexenes in vapours of conventional petrol. Total-ion (above) and single-ion (m/z 84, below) reconstructed GC-MS chromatograms. A methylene unit (MU) retention scale between hexane (6.00) and heptane (7.00) is incorporated.

TABLE I

QUANTITATIVE PROPORTIONS AND PHYSICAL DATA OF THE SEVENTEEN ISOMERIC ACYCLIC HEXENES IN VAPOURS OF CONVENTIONAL PETROL

Relative retentions are given for the aluminium oxide column as methylene units, obtained by linear interpolation between hexane (6.00) and heptane (7.00). The boiling points are physical reference data, and the reaction rate ratios are adapted from literature data [1].

	Quantitative proportions (%)	Relative retention (MU)	Boiling point (°C)	Ions from allylic MS cleavage (<i>m/z</i>)	Relative rate for reaction with ozone in air
3,3-Dimethyl-1-butene	1	6.06	41.2	69	1
<i>E</i> -4-Methyl-2-pentene	6	6.07	58.6	69	20
3-Methyl-1-pentene	3	6.23	54.2	55 and 69	1
<i>Z</i> -4-Methyl-2-pentene	2	6.25	56.4	69	10
2,3-Dimethyl-2-butene	3	6.28	73.2	—	100
2,3-Dimethyl-1-butene	3	6.29	55.6	69	1
<i>E</i> -3-Hexene	4	6.29	67.1	69	20
2-Methyl-2-pentene	15	6.31	67.3	69	50
<i>Z</i> -3-Methyl-2-pentene	9	6.33	67.7	69	50
<i>E</i> -3-Methyl-2-pentene	11	6.34	70.4	69	50
4-Methyl-1-pentene	3	6.35	53.9	41	1
<i>E</i> -2-Hexene	13	6.36	67.9	55	20
2-Ethyl-1-butene	2	6.43	64.7	69	1
2-Methyl-1-pentene	10	6.47	62.1	55	1
<i>Z</i> -3-Hexene	2	6.49	66.4	69	10
1-Hexene	6	6.50	63.5	41	1
<i>Z</i> -2-Hexene	7	6.56	68.9	55	10

The hexenes elute after the hexanes because of the induced polar interactions between the double bond and the aluminium oxide stationary phase. The MU increment is 0.5 for 1-hexene as compared with hexane. Two alkyl groups in the *Z* (*cis*) or *E* (*trans*) positions at the double bond sterically increase (*Z*) and decrease (*E*) the availability of the π electrons for interactions. An MU difference of 0.2 is observed. Alkyl branching at the double bond results in counteracting steric and inductive effects, whereas the unbalanced steric effect of β -branching evidently decreases retention (3-methyl-1-pentene, 4-methyl-2-pentenes). There is also a general retention-decreasing effect of alkyl branching because of the decreased non-polar interactions of compact molecules.

The relative retentions of the hexenes normally deviated less than 0.01 MU from the tabulated values with the particular temperature programme applied. With different temperature programmes, the MU values still accurately give the retention order of the hexenes, although

absolute MU scale shifts of up to 0.05 MU were observed. The MU values for a new aluminium oxide column and one routinely used for about 10 years were very similar. Comparisons with MU values given in a study of alkenes in synthetic mixtures [6] agree well for 1-hexene and the unbranched 2-hexenes. Comparisons also reveal that several other hexenes were incorrectly identified in that study.

On non-polar columns, the hexenes elute essentially in the order of increasing boiling points (Table I), *i.e.* very differently from the aluminium oxide column. Retention data on non-polar stationary phases have been given for most of the hexenes [7,8]. Because of the absence of polar interactions, many hexenes elute unfavourably in the same region as the hexanes on these commonly used phases. On the other hand, complementary separation on a non-polar methylsilicone column was useful for ascertaining the proportions of the hexenes that were not completely resolved on the aluminium oxide column.

Mass spectrometric identification

As illustrated in Fig. 1, an abundant molecular ion (m/z 84) permits specific single-ion monitoring of the acyclic hexenes. The heptanes are traced because they give rise to fragment ions of m/z 84 in low abundance. The relative abundance of the m/z 84 molecular ions varies to some extent between the isomeric hexenes. It is low for 1-hexene as illustrated by the relatively larger peak in the total ion chromatogram. The cyclohexenes are not present in the m/z 84 record but were specifically monitored from their abundant m/z 82 molecular ions. The only other hydrocarbons observed in the hexene region were small amounts of pentadienes. These were traced from their mass-specific and very abundant molecular ions of m/z 68. Isoprene elutes near to hexane and the 1,3-pentadienes in the MU 6.20–6.35 region.

Mass spectra were recorded and interpreted for all chromatographic peaks observed in the hexene region. Comparisons with library spectra were made automatically on the MS system. The spectra permit an unambiguous identification of hexenes as a group, whereas the spectral differences between most of the isomers are small. The spectra of *cis* (*Z*) and *trans* (*E*) isomers are almost identical.

A favoured fragmentation of the molecular ion of alkenes is allylic cleavage with loss of an alkyl radical. In Table I, the masses of the primary fragment ions to be expected are given. At the conventional high electron impact energy of 70 eV, the structural specificity of these fragment ions is partly lost by non-specific hydrogen rearrangements and secondary fragmentations. The largest (base) peak in the spectra of most hexene isomers is due to m/z 41 ions. Exceptions are *cis*- and *trans*-2-hexene, for which m/z 55 ions from primary allylic cleavage give rise to the base peak.

The final structural assignments as given in Fig. 1 were made from a combination of mass spectra, structure–retention relationships and comparisons with authentic commercial hexenes.

Atmospheric chemistry

In daylight, hydrocarbons are decomposed in air, mainly by reactions with the hydroxyl radical

or with ozone. The tropospheric reactions of hydrocarbons were recently reviewed [1].

As seen from Table I, the 1-alkenes react slowly with ozone. The reaction rate of other alkenes increases sharply with the number of alkyl groups adjacent to the double bond. For reaction with the hydroxyl radical, the rate constants of the hexene isomers differ by less than a factor of 5. As a result, the 1-alkenes normally decompose by reaction with the hydroxyl radical, whereas the 2- and 3-methyl-2-pentenes react mainly with ozone if the ambient ozone levels are not too low. The reaction paths and products for the reaction with ozone should be similar to those recently reported for 2-methyl-2-butene [9].

The lifetime of all hexenes in air is normally less than 1 day, and that of the most reactive isomers less than 1 h in the photooxidant season. As a result, the hexenes contribute more efficiently than lower alkenes to locally elevated photooxidant levels. The most reactive isomers do not necessarily produce ozone very efficiently [2], but they give rise to a wide range of other photooxidants [1] such as peroxides, which may be even more harmful.

Emissions to air

The results reported refer to vapours from commercial petrol with a conventional content of alkenes from catalytic cracking. The composition and chromatographic separation of the whole range of vapour hydrocarbons, emitted from a similar commercial petrol (RON 95) during refuelling, were recently reported [5]. The portion of the acyclic hexenes was 1.7% of the amount of total hydrocarbons. Although these vapour samples were taken on adsorbent cartridges, and although the temperature programme was more rapid, the proportions of the isomeric hexenes are distinctly similar to those reported here. Similar proportions of the hexene isomers are also seen in a published chromatogram of C_2 – C_8 hydrocarbons from exhaust-polluted urban air [10]. Approximately the same proportions were actually observed in a large number of unpublished chromatograms from samples of petrol vapour, petrol exhaust and vehicle-polluted urban air.

The observed uniform composition of hexene isomers in petrol vapours is obviously explained by the output from the catalytic cracking processes, which deliver most of the alkene-rich fractions mixed into petrol. From Table I, it is seen that 1-alkenes account for almost 30% of the total acyclic hexenes. The reactive 2- and 3-methyl-2-hexenes constitute more than one-third of the total. The somewhat more variable content of cyclohexenes was found to be approximately 10% and 2% for methylcyclopentenes and cyclohexene, respectively, as compared with the total amount of acyclic hexenes. The uniform quantitative proportions of the hexenes permit estimates of all isomers even under conditions when only one or a few of them can be determined reliably.

Hexenes in exhaust from petrol-fuelled vehicles are emitted as unburnt petrol hydrocarbons. This explains the observed similar proportions of hexene isomers in petrol vapours and in urban air that is normally polluted mainly with exhaust hydrocarbons. Obviously, however, exhaust differs from equilibrated vapours by having higher proportions of the less volatile isomers. Not only the C_6 but also the C_5 alkenes in vehicle exhaust are predominantly unburnt petrol components,

whereas ethene, propene and a prominent portion of the butenes are combustion products. The total proportion of hexenes, including the cyclic C_6 alkenes, was found to be about the same as that of the pentenes in vehicle-polluted urban air in Sweden. This means approximately 1% of the total amount of C_2 – C_8 hydrocarbons [10].

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