

ANALYSIS OF ALKENE MIXTURES BY COMBINED CAPILLARY GAS CHROMATOGRAPHY - CHEMICAL IONIZATION MASS SPECTROMETRY.

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The combination of a gas chromatograph (GC) with a mass spectrometer (MS) especially adapted for 'chemical ionization' (CI) has been described in recent reports.^{1 to 4} This new variety of GC/MS instrumentation (GC/CIMS)¹ shows considerable promise of becoming a valuable tool for the analysis of complex mixtures of such compounds of which information regarding molecular size is difficult to obtain by other methods, including electron impact ionization mass spectrometry (EIMS). Packed or SCOT GC columns were employed in direct coupling with quadrupole or time-of-flight mass spectrometers, allowing the use of a single gas, i.e. methane, simultaneously functioning as a carrier (GC) and as a reactant (CI). The resulting technical convenience has the disadvantage, however, that the scope of the method is limited, particularly when high efficiency open tubular columns are to be employed. Shortcomings arise from the fact that, compared with the customary use of helium or hydrogen gas in such applications, use of methane (or heavier gases) as carrier has an adverse effect on the gas chromatographic resolution of the system. For the same reason, reactants other than methane (e.g. isobutane, ammonia, water etc.), possibly meeting the CI requirements of the particular problem to a higher degree, cannot be utilized.

In an attempt to allow for flexibility in the choice of optimal parameters in both GC and CIMS, we explored the feasibility of admixing a different CI reactant gas, e.g. methane, with the effluent of a GC capillary column, in our case helium, prior to its admission to the CI source, i.e. after effecting separation of the components under favorable conditions. Since low flow rates of carrier gas (1 to 4 ml/min), yet high ones of reactant, are typical of such a system, high CH₄/He ratios can build up in the mass spectrometer source and approximate ideal CI conditions to a much greater extent than with the use of different gases as carrier and reactant on packed columns with much higher gas flow, resulting in undue dilution of the latter

The GC/CIMS system employed in our laboratory consisted of a FINNIGAN 1015/012 mass spectrometer (direct inlet for GC capillary columns), and a VARIAN model 1400 gas chromatograph (dual

injector assembly with modifications to accommodate a CARLO ERBA inlet split). One injector was supplied with helium as carrier gas (3, Fig. 1) and used for sample injection upon an open tubular glass column (1, Fig. 1, SF-96, 50m x 0.35mm), while the other served as inlet for the reactant gas (2, Fig. 1). Both lines were connected with the capillary inlet of the spectrometer directly at the ion source and could be operated independently by means of needle valves (5 and 6, Fig. 1).

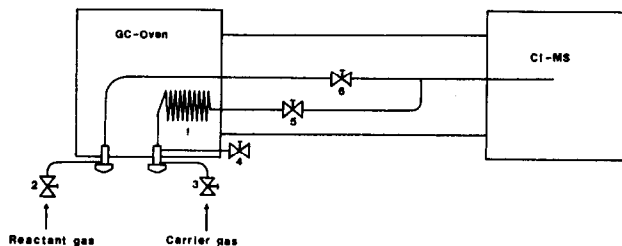
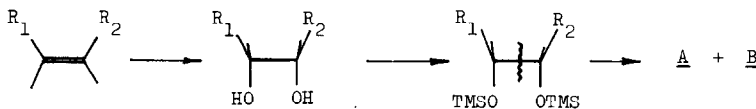


Fig. 1: Gas Chromatograph/Chemical Ionization Mass Spectrometer System.

The potential usefulness of such a system in a combined GC/CIMS and GC/EIMS application can be illustrated, e.g., in the case of analysis of a mixture of branched and unbranched monoalkenes. While molecular weights (yielding the number of double bonds or their equivalents) could, in principle, be obtained by GC/EIMS of the mixture of original alkenes, determination of double bond positions generally requires chemical pretreatment of the samples to form special derivatives. In absence of suitable fragmentation of the unfunctionalized molecules, the objective is to induce extensive cleavage to a pair of 'diagnostic' fragments A and B, from which the site of the original unsaturation can be deduced. In practice, stereospecific hydroxylation of the double bonds to vic-diols (OsO_4) and conversion of these to di-trimethylsilyl (TMS) derivatives (silylating agents) have shown promising results on single, pure compounds: 5,6



Owing to the usual absence or low abundance of molecular ions M (or of other fragments that could serve as substitutes), simultaneous recognition of the molecular size from these derivatives is, however, difficult except when it is assumed that A + B = M. In the case of mixtures GC/EIMS analysis of the original alkenes, and of the di-TMS diols for obtaining M and characteristic A/B pairs in two successive, independent steps is likewise bound to fail because of different orders of elution of the components for the two types of compounds involved. The arising correlation problem is obviously avoided if both kinds of required information can

be derived from just one type of derivative, e.g. the di-TMS diols (i.e. di-TMSO alkanes) by GC/CIMS analysis for molecular size, and subsequent (or preceding) GC/EIMS analysis, preferably on the same system by merely changing the mode of operation of the ion source, for double bond localization.

In order to explore such an approach, a synthetic mixture of six known C-9 monoalkenes, 1-nonene (I), trans-2-nonene (II), trans-3-nonene (III), trans-4-nonene (IV), 2,6-dimethyl-1-heptene (V) and 2,3-dimethyl-2-heptene (VI), was analyzed in this fashion after conversion to the vic-diols and silyl derivatives (threo-configuration in the case of the trans-isomers) in batch. All six components could be separated and appeared well resolved in the gas chromatograms obtained by monitoring total ion current (TIC) in either mode of operation, CI (electronic integration of the multiplier signals m/e 57 \rightarrow 400, Fig. 2), or EI (m/e 32 \rightarrow 400). Switching from CI to EI was performed by stopping the reactant gas flow (needle valve 6, Fig. 1, closed) in CI operation, or - less conveniently - by exchanging ion sources. When using the CI source in the EI mode, a small loss of separation efficiency was observed in the corresponding EI-TIC gas chromatograms.

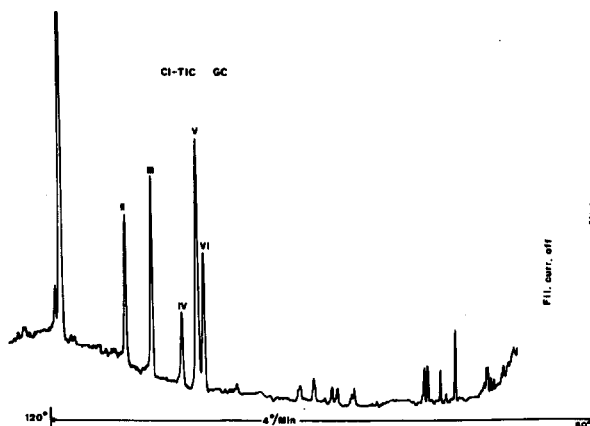


Fig. 2: CI-TIC gas chromatogram of the vic-di-TMSO alkane mixture

In all cases, the CI mass spectra permitted the facile recognition of the molecular size ($M = 304$, $C_{15}H_{36}Si_2O_2$) from 'quasimolecular ions' ($M + H$) and ($M - H$), m/e 305 and 303, respectively, and even more so from pre-eminent ($M - CH_3$) fragments (base peaks in the spectra) chiefly arising from loss of methyl from one of the TMS substituents. Confirmatory evidence for correct assignments as to the molecular ion region is, in addition, obtainable from ($M - TMSO$) ions of considerable prominence (m/e 215), which are likely to originate from ($M + H$) ions by loss of TMS-OH. In Fig. 3 the CI spectrum of a typical representative of this series, the di-TMS derivative of the diol of VI, is shown together with its EI spectrum for reference. As expected, the latter is dominated by the cleavage products A and B (m/e 131 and 173, respectively) to such an extent as to fail to furnish information on molecular size at all. Besides these ions, m/e 147 fragments ($Me_3SiO^+SiMe_2$) are pronounced in all members of this series and represent

products of functional group interaction.⁷

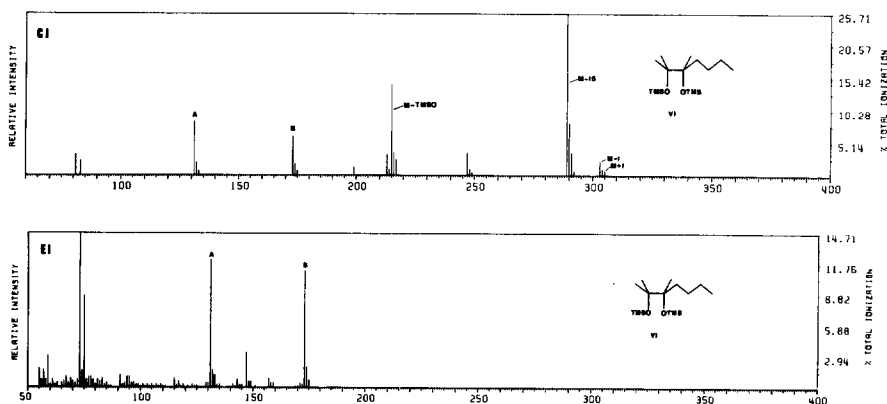


Fig. 3: CI and EI mass spectra of 2,3-di-trimethylsilyloxy-2,3-dimethylheptane (di-TMS derivative of the diol of VI).

These pairs of A and B ions, which are also (though in a more moderate abundance) present in the CI spectra, allow prompt deduction of double bond positions and thus identification of all six components emerging from the capillary column in the sequence indicated in Fig. 2. These assignments were verified in each case by separate analysis of the derivatives prepared from the single alkenes.

In view of the unexcelled separation potential of capillary GC and the unique advantage of combined EIMS and CIMS (particularly after optimizing CI conditions through variation of the reactant gas, as is possible in the system described) it is hoped that such techniques can be elaborated to a degree sufficiently high to secure their applicability to multi-component mixtures of higher structural complexity than represented by this series of model compounds. Extension of these experiments in this direction is being currently attempted in our laboratory.

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