Gas-Solid Chromatography of Hydrocarbons on Activated Alumina. II. Alkane, Alkene, Alkyne Separations and Subtractive Adsorption[1]

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Abstract

Various alkanes, -enes and -ynes of molecular weights below C_{10} are rapidly separated by gas-solid adsorption chromatography on untreated activated alumina. Solid silver nitrate coated on alumina removes alkenes and alkynes through oxidative degradation. Silver-nitrate concentration and column temperature markedly affect olefin removal. At about 300C some of the C_8 and higher molecular weight saturated hydrocarbons are destroyed. Conditions for this subtractive chromatography are detailed, and the fate of unsaturated hydrocarbons is explained.

Introduction

ALUMINA GAS-SOLID CHROMATOGRAPHY (GSC) is a valuable tool in analyzing volatile hydrocarbons (4,6,8). Paraffinic, olefinic, cyclic and branched homologues below C_{10} are easily separated on columns of activated alumina at temperatures well within the operating range of most commercial instruments. Any chromatograph equipped with a flame ionization detector and with a connection suitable to use nitrogen or carbon dioxide as a carrier gas (3) can be used to separate and identify various hydrocarbons of carbon number C_{10} or less. Factors influencing retention time and column efficiency in alumina GSC have already been treated (2,3,5).

Figure 1 is a plot of retention time versus carbon number for eight classes of homologous hydrocarbons. It shows how their retention times increase as their molecular volume and degree of unsaturation increases.

Neo-alkanes, iso-alkanes and cyclanes elute before the n-alkanes of equivalent carbon content. The progressive increase in molecular volume of the isomers accounts for this elution order.

As carbon number increases, retention times for

iso-alkanes approaches and then becomes identical to those observed for n-alkanes. This asymptotic merger is probably caused by reduction in the relative contribution toward compactness offered by the 2-methyl substituent as carbon number increases. Degree of unsaturation dramatically affects retention time, as evidenced by the lines representing 1-alkenes, 1,3-dienes and 1-alkynes.

Olefin Adsorber

An olefin adsorber was prepared from Microtek (9) 60/80 mesh F-20 alumina impregnated with 17% $AgNO_3$ as follows: 10 g $AgNO_3$ + 10 cc H_2O + 200 cc acetone were mixed to form a solution. This solution was poured over 50 g alumina contained in a 500 cc flask, foil-covered to protect the contents from light during solvent removal. If exposed, the impregnated alumina turns black and loses its ability to adsorb olefins quantitatively. Removal of solvent on a water-pump aspirated rotating evaporator resulted in a light gray product that was free-flowing. It was packed to a 1-in. depth in a $48 \times \frac{1}{4}$ in. column and the rest of the column filled with plain alumina. The column was ready for use after 30 min aging at 300C.

Mixtures to be separated were syringe-injected into the $AgNO_3:Al_2O_3$ precolumn end. Each chromatogram was temperature programmed from 75 to 300+ at 21°/min. Nitrogen was the carrier gas.

All unsaturates, whether cyclic, branched, straight-chain, aromatic or acetylenic, are selectively and quantitatively removed from mixtures with paraffins. Removal of unsaturates is not through irreversible adsorption but, as will be shown later, the result of destruction through oxidative degradation. Work with acetylenes was limited because of dangers inherent in silver acetylides that might be formed in the column.

Figure 2, a chromatogram of C_5 to C_8 n-alkanes and 1-alkenes, illustrates the subtractive properties of $AgNO_3$-impregnated alumina. Part A is the chro-
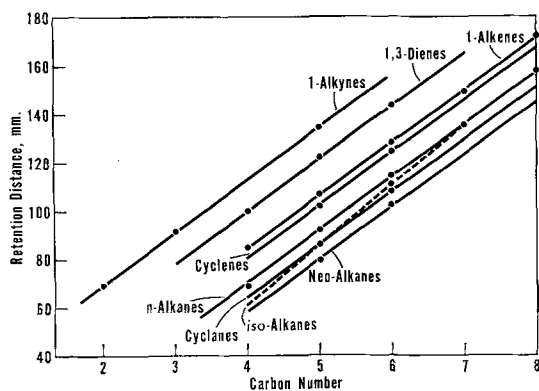

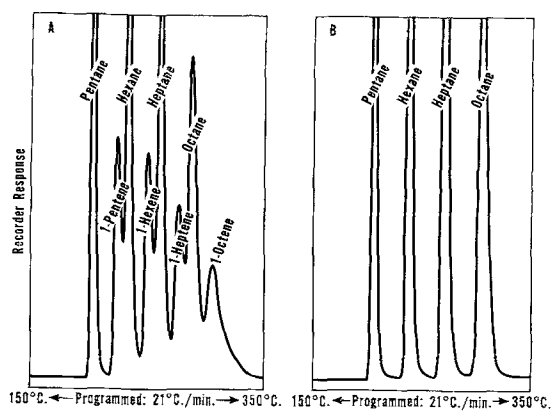FIG. 1. Retention time versus carbon number for eight classes of homologous hydrocarbons.

FIG. 2. Chromatograms illustrating the subtractive properties of $AgNO_3$-impregnated alumina: A, without $AgNO_3$; B, with $AgNO_3:Al_2O_3$ precolumn.
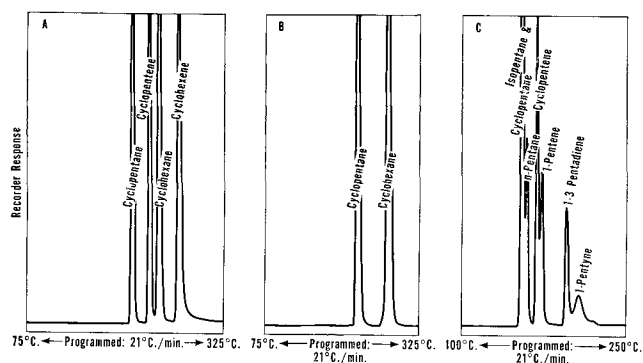
FIG. 3. Subtractive chromatographic technique applied to cyclic hydrocarbons: *A*, without $AgNO_3$; *B*, with $AgNO_3:Al_2O_3$ precolumn; *C*, shows separation of C_5 hydrocarbons on plain alumina.

matogram from this mixture separated on a 48-in. plain alumina column. Part B shows the result when the same mixture is chromatographed under identical conditions but through a 1-in. $AgNO_3:Al_2O_3$ precolumn followed by 47 in. of plain alumina. Removal of all olefins is complete and the paraffins elute unchanged.

Figure 3 illustrates the subtractive technique applied to a mixture of saturated and unsaturated cyclic hydrocarbons. Part A is a chromatogram of mixed cyclanes and cyclenes. Part B shows that cyclopentene and cyclohexene were removed and that cyclopentane and cyclohexane were eluted unaltered. Part C illustrates the resolving power of plain alumina for six C_5 hydrocarbons. Although cyclanes and cyclenes have nearly the same retention time as *n*-alkanes and 1-alkenes of equal carbon content, they are separable on a 4-ft column when temperature is programmed.

Precolumn length and $AgNO_3$ concentration are critical to subtractive separations. For example, C_1 to C_8 *n*-alkanes and C_2 to C_8 1-alkenes were injected into a 48-in. column containing 17% $AgNO_3:Al_2O_3$ throughout. Original liquid components from C_5 to C_8 had a 1:1 v/v ratio which give essentially equal peak areas. Although their chromatogram (Fig. 4) shows complete removal of all olefins, it also depicts a marked reduction in *n*-alkane peak area as carbon number increases. When silver nitrate-impregnated alumina is used to pack the entire column, it has a degradative effect on even saturated hydrocarbons.
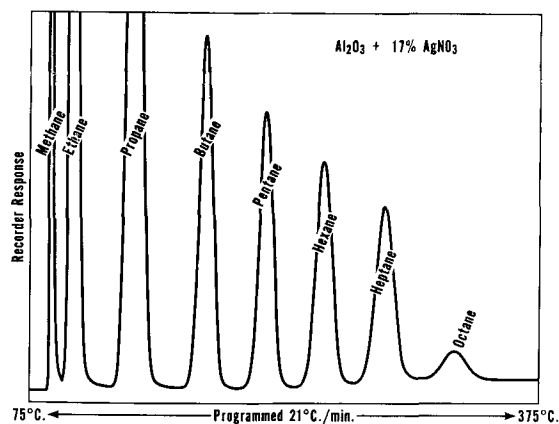

FIG. 4. Chromatogram illustrating decreased recovery of paraffins and removal of olefins at a high concentration of $AgNO_3$.

Temperature programming does not move the less volatile saturates through the reaction zone before sample components are exposed to the oxidative effects of high temperature and $AgNO_3$, whereas when the length of the precolumn is limited to only 1 in. of impregnated alumina, saturates are moved beyond the $AgNO_3$ zone before they are degraded.
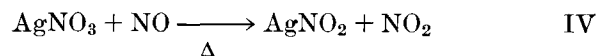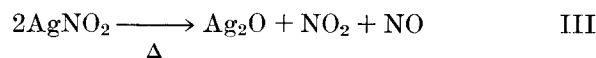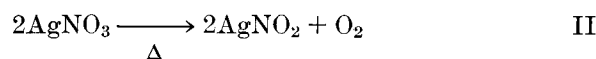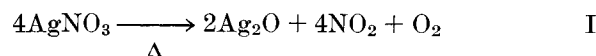
Although olefin removal is independent of starting temperature, column temperature must be increased to elute the adsorbed longer chain paraffins. Ethylene can be removed from any mixture with ethane when the precolumn and column are at room temperature. Observations at room temperature and above indicate that the chemisorption of olefins is not temperature dependent. If the column is operated isothermally at temperatures above 200C, both olefins and paraffins are consumed whether applied to a full-length $AgNO_3:Al_2O_3$ column or to a 1-in. precolumn of this same packing. Therefore, programming is essential and must begin at a temperature as far below 200C as is practicable.

Precolumn life depends on the temperature at which it is operated and on the olefin concentration of chromatographed samples. Failure to remove olefins from standard mixtures known to contain them signal precolumn exhaustion.

Fate of Adsorbed Olefins

1-Heptene was repeatedly injected, until no more was adsorbed, into a $12 \times \frac{1}{4}$ in. column filled with 17% $AgNO_3:Al_2O_3$ and held at 300C. Column packing was removed and exhaustively extracted with purified pentane. The residue left after evaporation of the pentane was identified by infrared spectroscopy to be primarily *n*-hexanoic acid containing a trace of aldehyde. The silver nitrate alumina both before and after pentane extraction was black, whereas before exposure to olefins it is light gray.

Silver nitrate melts at 212C. As temperature is increased, slow decomposition occurs until, at its boiling point (444C), the nitrate rapidly liberates O_2 and NO_2. Mellors' treatise (7) lists the following explanatory reactions:

$$4AgNO_3 \xrightarrow{\Delta} 2Ag_2O + 4NO_2 + O_2 \qquad \text{I}$$

$$2AgNO_3 \xrightarrow{\Delta} 2AgNO_2 + O_2 \qquad \text{II}$$

$$2AgNO_2 \xrightarrow{\Delta} Ag_2O + NO_2 + NO \qquad \text{III}$$

$$AgNO_3 + NO \xrightarrow{\Delta} AgNO_2 + NO_2 \qquad \text{IV}$$

Reaction III produces NO that autocatalytically decomposes still more $AgNO_3$ by Reaction IV. This reaction occurs well below the melting point of $AgNO_3$.

Thermolysis of silver nitrate impregnated within the alumina will yield finely divided Ag_2O and Ag metal. Both of these are powerful surface-active catalysts which in the presence of O_2 could effect oxidative cleavage of olefins. Since $AgNO_3$ itself is a powerful oxidizing agent (7), it may act directly upon the olefin as a primary oxidant, aided by the surface catalytic effects of Ag and Ag_2O and by the oxidizing atmosphere from decomposed $AgNO_3$. Effluent from an unused 17% $AgNO_3:Al_2O_3$ column heated to 300C quickly bleached a diluted sample of Fieser's solution (1) indicating the presence of oxidizing gases.

At low temperatures, electron-rich olefins are probably retained on the $AgNO_3:Al_2O_3$ by weak π-complex bonds. As column temperature increases, paraffins move through the short precolumn unchanged and escape oxidative effects of $AgNO_3$ before the temperature becomes excessive. In the presence of O_2 liberated by decomposing $AgNO_3$, a silver complex of a 1-olefin thermally cleaves at the double bond to an acid containing one less carbon atom. Polar-oxygenated materials, such as aldehydes and acids, are bound to alumina even in the absence of $AgNO_3$ (4).

Activated alumina is an unusual chromatographic substrate of particular value for qualitative separation of C_1 to C_{10} hydrocarbons. When alumina is properly treated with $AgNO_3$ and is used as a precolumn to one of plain alumina, olefins and acetylenes are selectively and quantitatively removed from mixtures with paraffins.

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