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ANALYSIS OF QUATERNARY AMMONIUM COMPOUNDS BY PYROLYSIS GAS CHROMATOGRAPHY

by

Amal Adel Daham

submitted to the

Faculty of the College of Arts and Sciences

of The American University

in Partial Fulfillment of

the Requirements for the Degree

of

Master of Science

in

Chemistry

1995

The American University

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AMAL ADEL DAHAM

ABSTRACT

Quaternary ammonium halides (Quats) are antimicrobial compounds that are used as disinfectants and sanitizers. Promotion of their use as clinical disinfectants on hard surfaces has necessitated a method for the determination of their chemical composition. Not only is the quantity of halogen and nitrogen present in each needed, but also the length of the carbon chains attached to nitrogen.

Gas Chromatography (GC) is a viable technique for separating and detecting these complex mixtures. This method has been used for the separation and identification of commercial quat disinfectants with highly complex composition containing many quaternary ammonium halides with long carbon chains. Quats are stable molecules with an estimated evaporation rate much slower than ethyl ether. They are ionic, non volatile, and they will not pass through the GC. If the injector port of the GC is held at high temperatures (250 deg. C), the long chain quaternary ammonium halide will undergo a Hofmann elimination yielding a tertiary amine. The resulting tertiary amine can then be separated by the GC. Since the Hofmann elimination can give
more than one product, pure quaternary ammonium compounds were injected into the GC and the resulting products were measured. The results of these experiments were then used to determine which quats were present in the commercial preparations. Under these conditions, chromatograms with narrow and sharp peaks were obtained.

Gas Chromatography coupled to mass spectroscopy (GC/MS) was used to confirm the structures of the tertiary amines produced by the Hofmann elimination. Quat standards were injected into the hot injection port of the GC/MS and the mass spectrum of the peaks eluting from the GC were measured. This method gave reproducible spectra using the same chromatographic conditions.
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INTRODUCTION

Quaternary ammonium chlorides

Long chain quaternary ammonium chlorides (Quats) that are used as disinfectants, are complex mixtures of alkylbenzyldimethylammonium chlorides of the general formula, \([\text{C}_6\text{H}_5\text{CH}_2\text{N} (\text{CH}_3)_2 R]\)Cl, in which \(R\) represents a mixture of alkyls groups. These groups begin with \(n\)-\(\text{C}_8\text{H}_{17}\), and extend through higher homologs, with \(n\)-\(\text{C}_{12}\text{H}_{25}\), \(n\)-\(\text{C}_{14}\text{H}_{29}\), \(n\)-\(\text{C}_{16}\text{H}_{33}\), and \(n\)-\(\text{C}_{18}\text{H}_{37}\) comprising the major portion.

Quats are soluble in all proportions in water, methanol, ethanol, isopropanol, glycerol, glycols, and acetone. They are insoluble in non-polar solvents, animal, vegetable, and mineral oils. They are antimicrobials and their typical applications are as hard surface cleaners, disinfectants, and sanitizers. Quaternary ammonium salts are useful in synthetic organic chemistry as phase transfer catalysts. In another, more direct application, quaternary ammonium hydroxides are used as substrates in an elimination reaction to form alkenes. This reaction, known as the Hofmann elimination or Hofmann degradation, is one of the most widely used processes in degradative studies of alkaloids and is also of considerable value in synthetic organic chemistry, produces an olefin and a tertiary amine, generally by pyrolysis (1).
Methods of analysis

High-molecular-weight quaternary ammonium chlorides are prepared commercially by the reaction of a methyl (or other alkyl) chloride and fatty amines in the presence of sodium hydroxide.

Numerous methods are available for the analysis of quaternary ammonium chlorides.

**Argentimetric titration:**

Methods based on the argentimetric titration of halide are used to determine the concentration of quaternary ammonium chloride, amine hydrochloride (or free alkali), amine, and sodium chloride (2).

The scheme of analysis is to determine amine hydrochloride by a titration with standard alkali to a phenolphthalein end-point; or if free alkali is present, it is titrated with standard acid. The sodium chloride is titrated with standard silver nitrate. A total chloride titration after correction for amine hydrochloride and sodium chloride determines the quaternary ammonium chloride. Free amine is titrated with standard acid to a bromocresol green end point. Dichlorofluorescein was chosen as a suitable indicator for the chloride titrations. It functions in a pH range of ca. 4.4 to 10.5. The amine hydrochloride (or free alkali) determination should precede the total chloride and the sodium chloride determinations since the latter two may require acidity adjustments dictated by the results of the former.

Although this method is used to determine the concentration of quaternary
ammonium chloride, it does not differentiate between different quats in the same sample.

The analytical procedures for this method of quat analysis are straightforward and suitable for routine product and process control.

Titration of quaternary halides with dyes to form colored salts:

This procedure is based on an end point detection of certain cationic surface-active agents such as cetyl pyridinium bromide, from stoichiometric salts with anionic surface-active agents such as the alkyl sulfates or other similar surface active-agent (4). Since the chloride of the basic dye-stuff methylene blue is insoluble in chloroform, the alkyl sulfate and related salts are freely soluble and may be extracted quantitatively from aqueous solution provided that the chain length of the organic portion is sufficiently large.

In this titrimetric method, 10 ml of an alkyl sulfate (0.004 M) is pipetted into a 250 ml stoppered reagent bottle. Aqueous indicator solution (25 ml) containing 0.0038 per cent methylene blue (B.P.), 1.2 per cent sulfuric acid, and 5 per cent sodium sulfate are added, followed by 15 ml chloroform. A solution of cetyl pyridinium bromide (0.004 M) is then added from a burette. After each small addition of the latter the mixture is shaken. At first, the blue color concentrates in the chloroform layer, but as the titration proceeds there is a slow transfer of color to the water layer. Later the rate of transfer increases, and eventually the color of the two layers is visually the same. This is found to be the equivalence point. On further addition the chloroform layer lightens in shade, and becomes colorless.
The end point is surprisingly sharp and not affected by the presence of excess inorganic salt, acids, moderate quantities of organic solvents, commonly occurring temperature variations.

Substances with chain-lengths greater than C$_g$ can be determined accurately, but the longer the chain-length the sharper the end point. The limitation of this method is that it is most suitable for dilute solutions and cannot be directly applied in the presence of amines. Again, this method determines the aggregate total concentration of quaternary amines present and does not differentiate between individual components.

**Titration of quats in food and beverages using bromophenol blue method**

The analysis of quaternary ammonium compounds in food and beverages is described in the AOAC, Official Methods of Analysis, 1990 (4) as method 942.13.

The reagents used are: sodium carbonate solution, sodium sulfate, lauryldimethylbenzylammonium chloride, and bromophenol blue solution. The last solution should pass the following test for purity: 50 ml dichloroethane and 5 ml 1% sodium carbonate solution are added to 20 mg bromophenol blue in 125 ml separatory funnel. Mixture is shaken and let stand until mixture separates into two layers. Lower layer is colorless, upper layer is purple. Addition of 10 ml of quat will turn lower layer into clear blue. The lower layer is drained and examined in a spectrophotometer. Absorption peak should be at ca. 608 nm. If test gives yellow or green solution or if absorption curve is different from that of purified sample, bromophenol blue should be purified by placing 2 g bromophenol blue in 400 ml beaker and dissolving in 25 ml 1%
sodium carbonate solution. The compound is then transferred into a 1 L separatory funnel and 500 ml of CH₂ClCH₂Cl is added. Addition of 1 ml solution of quat is followed by shaking until lower layer has greenish tint. Then lower layer is drained and discarded. CH₂ClCH₂Cl and quat are then added to separatory funnel and shaken until lower layer is colorless or only faint blue. Aqueous layer is acidified with HCl and CH₂ClCH₂Cl is added until aqueous solution is faint yellow. Most of CH₂ClCH₂Cl is distilled off and the remainder in beaker is evaporated, and the residual powder is ground. Purity is tested and if suitable, it is to be used as reagent. Sample can be prepared from bottled beverages containing fruit juices, from beer, table syrup, or eggs. For instance, the preparation method for table syrup is to transfer 20 g sample to 100 ml volumetric flask, and to be diluted to volume with water and then mixed thoroughly. An aliquot of solution is pipetted into separator, and 5 ml bromophenol blue solution and 1 ml HCl (1+1) are added. As for sample determination, 50 ml CH₂ClCH₂Cl is pipetted into separator. The lower layer is drained into second separator containing 10 ml 1% Na₂CO₃ solution. If lower layer is blue, quaternary base is present. If color is suitable for reading without dilution, lower layer is dried by draining 2 g of the Na₂SO₄ and let stand for 30 min. The layer is transferred to suitable cell and intensity is read at 610 nm. The amount of quaternary ammonium compound present is determined from the standard curve (4).

**Hofmann degradation of quats**

The thermal decomposition of quaternary ammonium chlorides can be seen in a hot GC injection port at temperatures ranging from 175 deg. C (initial) to 280
deg. C (final). The main products of such decomposition are alkyldimethylamine (reaction 1) and alkylmethylbenzylamine (reaction 2), in addition to benzylchloride and methyl chloride.

$$\text{RN(CH}_3\text{)}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \quad (1)$$

$$[\text{RN(CH}_3\text{)}_2\text{CH}_2\text{C}_6\text{H}_5]^+ \text{Cl}^- \quad \rightarrow$$

$$\text{RNCH}_3\text{CH}_2\text{C}_6\text{H}_5 + \text{CH}_3\text{Cl} \quad (2)$$

Prior to the advent of the spectroscopic methods, Hofmann elimination reactions were routinely employed in the identification of alkaloid structures. By treating the quaternary ammonium halide with an ion exchange resin, a solid polymeric material that replaces halide ions by hydroxide ions (5). When quaternary ammonium hydroxides are heated, they undergo a $\beta$-elimination reaction to form an alkene and an amine as in the reaction:

$$\text{Cycloheptyltrimethyl ammonium hydroxide} \quad \rightarrow$$

$$\text{Cycloheptene} \quad \text{Trimethylamine} \quad \text{Water}$$

Hofmann was the first to use this reaction as an analytical method (5).

Hofmann elimination was first developed in the mid-nineteenth century and is used both as a synthetic method to prepare alkenes and as a degradative tool for structure determination (5).

The preferred orientation of the atoms in the H-C-C-N unit at the
transition state for a Hofmann elimination reaction has been demonstrated to be anti on the basis of experiments performed with the stereoisomeric quaternary ammonium salts derived from cis- and trans-4-tert-butylcyclohexylamine. The activated complex for elimination from the trans isomer has a significantly higher energy than the cis complex (5).

The number of Hofmann eliminations required to remove nitrogen from the molecule gives the number of points of attachment to the amino function, and the identity of the alkene produced reveals the carbon skeleton.

Hofmann also was the first to realize the potency of the elimination for examining the natural bases. Reported yields for the degradation reaction are usually good to very good (60 - 100%). The mechanism of the Hofmann elimination has received considerable attention in the last two decades and a number of reviews on the mechanism of this and other elimination reactions have appeared. Two facets of the reaction have been studied in particular, the degree of concertedness of the reaction and the orientation of the elimination (6). Ingold examined the elimination and found that it was first order for the quaternary ammonium ion (6). But whether the mechanism is first or second order, elimination is favored by increasing temperature, and the reason is that the activation energies of elimination is high since it has great changes in bonding. Several types of compounds undergo elimination on heating, with no other reagent present. Reactions of this type are often run in the gas phase (7).

With any reaction, a more polar environment enhances the rate of mechanisms that involve ionic intermediates. For neutral leaving groups, it is expected
that elimination mechanisms will be aided by increasing polarity of solvent and by increasing ionic strength (7).

Chromatography

Chromatography is a general technique in which molecules are separated according to their selective absorption. In gas chromatography, the sample is converted to the vapor phase (if it is not already a gas) and the eluent is a gas (the carrier gas). The stationary phase is generally a nonvolatile liquid supported on an inert solid such as firebrick (Chromosorb-P or W) or diatomaceous earth (8). The sample is rapidly injected by means of a hypodermic syringe through a rubber septum into the column. The injection port and detector are kept somewhat warmer than the column to promote rapid vaporization of the injected sample and prevent sample condensation in the detector. Separation occurs as the vapor constituents partition between the gas and the liquid phases. It is a widely used tool for recognizing the presence or absence of component of mixtures containing a limited number of possible species whose identities are known. However, confirmation of identity requires spectral or chemical investigation of the isolated components. On the other hand, positive spectroscopic identification would ordinarily be impossible on some complex samples without a preliminary chromatographic separation. Thus, chromatography is often a vital precursor to qualitative spectroscopic analysis (8).

The nature of the liquid or solid phase will determine the exchange equilibrium with the sample components and this will depend on the solubility or
absorbability of the sample, the polarity of the stationary phase and sample molecules, the degree of hydrogen bonding, and specific chemical interactions (8). The proper choice of stationary phase is vital to the success of a gas-chromatographic separation. Generally, this choice is based upon polarity parameters of the stationary phase relative to those of the sample constituents (9). There are thousands of commercially available column materials, and several attempts have been made to predict the proper selection of liquid immobile phase. These methods attend to group phases according to their retention properties, for example, according to polarity. Retention indexes, Rohrschneider constants, and McReynolds constants are three related measures of polarity (8). The retention index is defined as a parameter for identifying solutes from chromatograms. For a normal paraffin, the retention index is equal to one hundred times the number of carbons in the compound regardless of the column packing, the temperature, or other chromatographic conditions. Within a homologous series (those that differ in the number of carbon atoms in a similar structure), a plot of the logarithm of adjusted retention time $t'_R$ ($t'_R = t_R - t_M$) obtained on a given column at a given temperature versus the number of carbon atoms is linear. If boiling point is substituted for number of carbon atoms, to separate homologs, then, a stationary phase is chosen that will readily dissolve the sample. In either case elution would be expected in the order of boiling point or molecular weight (9). A graphical procedure is not always required in determining retention indexes. Instead adjusted retention data are derived by interpolation from a chromatogram of the solute of interest and two normal paraffin standards with retention times one less and one greater than that of the solute (9).
retention index is ideally suited for substance identification since its only dependence is on the stationary (liquid) phase and temperature not on instrumental parameters. The retention index of a substance can be calculated from the following equation:

\[
I = \frac{\log t'_{R(z)} - \log t'_{R(0)}}{\log t'_{R(z+1)} - \log t'_{R(z)}} \times 100 + 100
\]

where \( z \) is the number of carbon atoms in the smaller alkane, and \( z+1 \) refers to the larger alkane. The retention index of an unknown compound can be compared with catalogued indices on various columns to aid in its identification (10).

The actual relationship between retention index and column temperature can generally be described by a linear relationship equation:

\[
I = a'T + b'
\]

where \( a' \) and \( b' \) are constants. In most cases \( a > 0 \) and thus, the retention index increases with temperature. However, cases where the opposite is true also exists.

The correlation between retention index and molecular structure for a homologous series is that the retention index values of two members of a homologous series differing only by a -CH\(_2\) - group in the main chain will differ by 100 index units. This can be represented by the following equation:

\[
I_{(z+1)} - I_z = 100
\]

where \( I_{(z+1)} \) and \( I_z \) are the retention indices of the two consecutive members of a homologous series (10). This equation is not valid when \( z \) is smaller than 4 or 5 due to the well known curvature of the log \( t'_{R} \) vs. carbon number plots for the first members of a
homologous series. The practical meaning of this equation is that in the chromatogram of a complex mixture, one can find with reasonable accuracy the peaks corresponding to members of certain homologous series even if only limited number of data are available. To compare polarities of the stationary phases, a reference material could be chosen, the least polar for instance, and retention index differences $\Delta I$ can be calculated (9). Rohrschneider constants and McReynolds constants are closely related and are derived from retention indexes. Rohrschneider and McReynolds suggested five different reference compounds differing in the chain length of the alcohol, ketone, and nitro standards would suffice to fully characterize stationary phases for the effects of the various interactions. The five McReynolds constants are symbolized by $X'$, $Y'$, $Z'$, $U'$, and $S'$. Each is related to one type of interaction between a solute and the stationary phase. The magnitude of each of these constants provides a measure of the strength of this type of interaction for a group of compounds represented by the standard (9).

McReynolds constants are simply equal to the $\Delta I$ value of the particular test substance. They are widely used to characterize the multitude of stationary phases that are now available. To obtain the Rohrschneider constants ($X$, $Y$, $Z$, $U$, $S$) of a particular phase, the test substances are to be analyzed on the phase and on a non-polar phase (squalene was selected as such) and the value $\Delta I/100$ is calculated for each (9).

The Rohrschneider constants are usually calculated from retention index measurements at 100-120 deg. C. The effect of temperature on the Rohrschneider constants is negligible. Rohrschneider-McReynolds constants can be applied to select a liquid phase for a given separation or to classify liquid phases how similar or different they are, and
even to establish the sequence of a phase among other similar phases (10).

High molecular weight quaternary ammonium chlorides are compounds with low volatility. The degradation of long chain quaternary ammonium chloride upon injection in the GC injection port into tertiary amines has resulted in a broad boiling range for the degradation products. In this case, it is often desirable to employ temperature programming whereby the column temperature is increased either continuously or in steps as the separation proceeds. A thermal conductivity, or hot wire detector, was used and it allows detection of the degradation products and consequently their determination.

The second method of analysis used in this experiment is the hyphenated technique of gas chromatography-mass spectrometry. Mass spectrometry is a sophisticated instrumental technique that produces, separates, and detects ions in the gas phase (8). This very powerful tool is a very useful method that permits exploiting the unique capabilities of mass spectrometers to enhance the specificity of gas chromatographies.

The experiments follow can be divided into two parts: those that present the instrumental techniques used to confirm and identify the degradation products. In the second part of the thesis, those that present a review of all available data from samples and standards obtained using GC and GC/MS instrumental techniques. These data will help in the determination of the carbon chain distribution of the quaternary ammonium chloride samples used in this experiment. In this order, the analysis will be based on similarities and possible structures of the target degradation products and on MS data that confirms the analysis.
EXPERIMENTAL

The quaternary ammonium chloride analytes studied are BTC samples which are registered trademarks ( Stepan Company, Northfield, IL ).

The standards are quaternary ammonium halides ( Aldrich Chemical Co., Milwaukee, WI ).

The solvent used is Ethyl Alcohol USP Absolute 200-proof ( AAPER Alcohol and Chemical co., Shelbyville, KY )

Reagents

BTC 50 USP is the product name of the first sample studied. It has the following:

Chemical description: n-Alkyl(dimethyldimethylbenzylammonium Chloride.

\[
\text{Chemical structure: } [R - N - CH}_2\text{C}_6\text{H}_3^* + \text{Cl} \\
\text{CH}_3
\]

\[R = 50\% \text{C}_{12}, 30\% \text{C}_{14}, 17\% \text{C}_{16}, 3\% \text{C}_{18}\]

Composition: Active ingredients:

n-Alkyl (50% C_{12}, 30% C_{14}, 17% C_{16}, 3% C_{18})

dimethylbenzylammoniumChloride..................50%

Inert ingredients..................................................50%

100%
BTC 65 is the product name of the second sample studied.

Description: n-alkyldimethylammonium chloride

\[
\text{Structure: } \left[ \begin{array}{c} R \\
\text{CH}_3 \end{array} \right] + \text{Cl}^- \]

\[
R = 67\% \text{C}_{12}, 25\% \text{C}_{14}, 7\% \text{C}_{16}, 1\% \text{C}_{8}, \text{C}_{10}, \text{C}_{18}
\]

Composition: Active ingredient:

- n-Alkyl (67\% \text{C}_{12}, 25\% \text{C}_{14}, 7\% \text{C}_{16}, 1\% \text{C}_{8}, \text{C}_{10}, \text{C}_{18}) \quad \text{dimethylbenzylammonium Chloride} \quad 50\%

- Inert Ingredients \quad 50\% \quad 100\%

BTC 835 and BTC 8358 are the product names of the remaining two samples studied.

Both have the same chemical description and chemical structure, they differ by their composition.

Description: n-Alkyldimethylbenzylammonium Chloride

\[
\text{Structure: } \left[ \begin{array}{c} R \\
\text{CH}_3 \end{array} \right] + \text{Cl}^- \]

\[
R = 50\% \text{C}_{14}, 40\% \text{C}_{12}, 10\% \text{C}_{16}
\]

Composition: Active ingredient:

- n-Alkyl (50\% \text{C}_{14}, 40\% \text{C}_{12}, 10\% \text{C}_{16}) \quad \text{dimethylbenzylammonium Chloride} \quad \text{BTC 835} \quad 50\% \quad 80\%

\text{BTC 8358} \quad \text{BTC 8358}
BTC 50 USP and BTC 65 are light straw colored liquids. BTC 835 and BTC 8358 are light straw colored, free-flowing liquids.

Cetylecide (Cetylite Industries Inc, Pennsauken, NJ)

Active ingredients: Cetyldimethylammonium Bromide (or Bretol).............................. 6.5%
Alkyl (50%C_{12}, 30%C_{14}, 17%C_{16}, 3%C_{18}) .................................................. 6.5%
Dimethylbenzylammonium Chloride ........................................................................ 6.5%
Isopropyl alcohol .................................................................................... 13.0%
Inert ingredients: .......................................................................................................................74%

The BTC products were too viscous to draw into the syringe, so solutions of these products were prepared by diluting them with a small amount of ethyl alcohol in a vial and then injecting the samples onto the gas chromatograph. A top loader was used for preparing sample solutions.

The amount injected in each run is 1 ul. For each sample, the analysis on the gas chromatograph is considered complete when three reproducible runs were obtained.

**Standards**

**Dodecylethyltrimethylammonium Bromide, 99%**

Molecular structure: $\text{CH}_3(\text{CH}_2)_{11}\text{N(C}_2\text{H}_5)\text{(CH}_3)_{2}\text{Br}$

Physical form: Fine white powder

F.W. 322.38

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Benzylidimethylstearylammonium Chloride monohydrate, 90% (remainder cetyl compound)

Molecular structure: \( \text{C}_6\text{H}_5\text{CH}_2\text{N}[(\text{CH}_2)_{17}\text{CH}_3](\text{CH}_3)_2\text{Cl}.\text{H}_2\text{O} \)

Physical form: Fine white powder

F.W. 322.38

Benzylidimethyltetradecylammonium Chloride

Molecular structure: \( \text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_2\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{Cl}.2\text{H}_2\text{O} \)

Physical form: Fine white powder

F.W. 404.08

Phenyltrimethylammonium Chloride, 98+%

Molecular structure: \( \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{Cl} \)

Physical form: Crystalline white powder

F.W. 171.67

Benzyltriethylammonium Chloride, 99%

Molecular structure: \( \text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3\text{Cl} \)

Physical form: Fine crystalline white powder

F.W. 227.78

Benzylidimethyldodecylammonium Bromide, 97%

Molecular structure: \( \text{C}_6\text{H}_5\text{CH}_2\text{N}[(\text{CH}_2)_{11}\text{CH}_3](\text{CH}_3)_2\text{Br} \)

Physical form: Fine white powder

F.W. 384.45
Benzyltributylammonium Chloride, 98+%
Molecular structure: $C_6H_5CH_2N[(CH_2)_3CH_3)_3Cl$
Physical form: Fine white powder
F.W. 311.94

Benzyltrimethylammonium Chloride
Molecular structure: $C_6H_5CH_2N(CH_3)_3Cl$
Physical form: Fine white powder
F.W. 185.70

Benzylcetyltrimethylammonium Chloride, Monohydrate
Molecular structure: $C_6H_5CH_2N[(CH_2)_{15}CH_3]N(CH_3)_3Cl\cdot H_2O$
Physical form: Fine white powder
F.W. 414.12

Cetyltrimethylammonium Chloride, 25 wt.% solution in water
Molecular structure: $[(CH_2)_{15}CH_3]N(CH_3)_3Cl$
F.W. 320.01

Cetyldimethylethylammonium Bromide
Product name: Bretol
Molecular structure: $CH_3(CH_2)_{15}N(CH_3)_2C_2H_5Br$
Physical form: White powder

Benzalkonium Chloride (Cetylite Industries, Inc., Pennsauken, NJ)
Molecular structure: $[C_6H_5CH_2N(CH_3)_2R]Cl$
$R$ (20% $C_{12}H_{25}$, 40% $C_{14}H_{29}$)
Physical form: White powder

F.W. 360

In terms of some typical properties, all standards are hygroscopic, irritant, corrosive, toxic, and cause eye and skin damage.

**Gas Chromatography (GC)**

All sample and standard solutions prepared were analyzed by gas chromatography-thermal conductivity detector. The instrument used was a Hewlett-Packard Model 5890 A Gas chromatograph (HP Co., Palo Alto, CA) equipped with an HP 3392A integrator (HP Co., Palo Alto, CA). The degradation products were separated by a DB5 type column, 30 meters, 0.32 mm I.D. (wide bore), film thickness 0.25 micron, (5%-Phenyl)-Methylpolysiloxane, non-polar, high temperature limit (-60 to 325/350 deg.C), (J&W Scientific, Folsom, CA).

**Operating parameters:**

- (5%-Phenyl)-Methylpolysiloxane DB5 Column
- Carrier Gas: Helium, 4.0 ml / min
- Injector Port Temperature: 250 °C
- Detector Temperature: 300 °C.
- Oven program: 175 °C for 8 minutes, initial 
  280 °C for 0.00 minutes, final 
  6 °C per minute, rate
- Injection Volume: 1µl
Samples:

Test solutions were prepared by weighing 1.5 grams of sample into a vial and then diluting with 2 ml ethyl alcohol.

Standards were prepared by accurately weighing 5 grams of the standard into a tared 100 ml volumetric flask and then diluting to volume with ethyl alcohol.

Mass Spectroscopy (MS)

A Hewlett-Packard 5995A option 098 Gas Chromatograph-Mass Spectrometer (HP Co., Palo Alto, CA) was used to study the mass spectra of the unknown degradation products. Samples and standard solutions were injected into the GC splitless injector and were separated by a DB5 capillary column of 30 meters and 0.25 micron I.D. (J&W Scientific, Folsom, CA). After entry into the ion source for electron impact (1800 eV) by an open capillary split interface located between the capillary column and mass spectrometer, the analyte is bombarded with electrons and radical cations are formed. The fused silica capillary column meets an uncoated fused silica restrictor which limits the flow into the mass spectrometer. The restrictor isolates the column from the presence of the high vacuum system.

The spectra of the standards and unknowns were recorded by an HP 59970C MS ChemStation having an operating flexible disc software and a ChemStation hardware that consists of the following: computer, monochrome monitor, disc drive, keyboard, knob, and printer (HP Co., Palo Alto, CA).
Operating parameters:

Carrier Gas: Helium, 1.4 ml / min
Injection Port Temperature: 250 °C
Detector temperatures: Transfer Line 280 °C
Ion Source 180 °C
Mass Analyzer 220 °C
Oven Program: 175 °C for 8 min, initial
280 °C for 0.00 min, final
6 °C per minute, rate
Volume injected: 1μl

Samples:

Solutions of standards (5% by weight) were prepared with ethyl alcohol.

Each sample solution was prepared by diluting 1.5 grams of sample with 2 ml ethyl alcohol in a vial.
RESULTS AND DISCUSSION

Similarities and possible structures of breakdown products from quat samples and standards

Gas Chromatography:

Gas Chromatography (GC) is an excellent technique for separating small, volatile organic molecules. Solutes into the gas phase, are separated at high temperatures according to their selectivity for the stationary phase, and are eluted by the flow of the inert gaseous mobile phase (Helium).

BTC compounds (Stepan company, Northfield, Illinois), Quats, of the general formula: n-alkylbenzyldimethylammonium chloride (containing different alkyl groups), were analyzed by a Hewlett Packard model 5890 A gas chromatograph equipped with a DB5 type capillary column with a thermal conductivity type detector. Standard Quats of the type quaternary ammonium halides (Aldrich Chemical Co., Milwaukee, WI) were injected using the same conditions.

Although Quats are not volatile enough to be separated by GC, the breakdown products can be easily separated by GC. If the injection port of the GC is hot enough, the Quats will undergo a Hofmann degradation in the injector and the breakdown products will be swept by the carrier gas into the separation column. Temperature programming permitted the separation of the degradation products of quats.
according to their affinity for the stationary phase

Highly reproducible chromatograms with sharp and narrow peaks, such as those shown in figures 1, 2, and 3 for compound BTC 50 USP, were obtained for each sample as well as for standards while operating under the same chromatographic conditions. Figures 4 through 19 are the GC chromatograms for all reagents and standards previously listed.

Highly pure quaternary ammonium compounds were used as standards (97 to 99% pure) for the identification of BTC samples. They were analyzed and separated using the same chromatographic conditions.
Figure 1

Gas chromatographic separation of BTC 50 USP (run # 1)
Figure 2

Gas chromatographic separation of BTC 50 USP (run # 2)
Figure 3

Gas chromatographic separation of BTC 50 USP (run #3)
Figure 4

Gas chromatographic separation of BTC 65

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Figure 5

Gas chromatographic separation of BTC 835

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Figure 6

Gas chromatographic separation of BTC 8358
Figure 7

Gas chromatographic separation of Cetylide
Figure 8

Gas chromatographic separation of Dodecylethylidimethylammonium bromide, 99%

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Figure 9

Gas chromatographic separation of Benzyldimethylstearylammonium chloride, 90%
Figure 10

Gas chromatographic separation of Benzyltrimethyltetradecylammonium chloride
Figure 11

Gas chromatographic separation of Phenytrimethylammonium chloride, 98%
Figure 12

Gas chromatographic separation of Benzyltriethylammonium chloride, 99%
Gas chromatographic separation of Benzyldimethyldecylammonium bromide, 97%
Figure 14

Gas chromatographic separation of Benzyltributylammonium chloride, 98%

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Figure 15

Gas chromatographic separation of Benzyltrimethylammonium chloride, 97%
Figure 16

Gas chromatographic separation of Benzylcetyltrimethylammonium chloride, monohydrate

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Figure 17

Gas chromatographic separation of Cetyltrimethylammonium chloride, 25 wt % solution in water

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Figure 18

Gas chromatographic separation of Benzalkonium chloride

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Figure 19

Gas chromatographic separation of Bretol

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The retention time of a given sample component under a standard set of conditions was compared to the retention times of highly pure standards. Retention time data from both BTC samples and standards are listed in tables in order to discuss similarities and common peaks occurring in BTC mixtures and quat standards. Tables 1 and 2 list the retention times of the peaks in the BTCs and Quat standards respectively. Peaks are labeled A through U in order of their elution from the GC.

As table 1 shows, several peaks are present in all BTC samples. For instance, peaks A(2.13), C(3.70), D(3.86), E(4.00), H(6.35), I(6.62), and M(11.86) appear in all the BTC chromatograms. Other peaks are present in some BTC samples and not in others. For instance, peaks K(6.98) and R(16.45) are present in three of the BTC samples (50 USP, 65, and 835 for peak K(6.98), and 50 USP, 65, and 8358 for peak R(16.45). In fact, a close look at the BTC chromatograms show all four to be very similar with little or no difference. This can be attributed to the fact that all BTC samples contain n-alkyldimethylbenzylammonium chlorides that differ only in the composition of the alkyl group.

The main degradation products of BTC compounds are alkylamines, alkylmethylammonium, and benzylamines. It is the distribution of the carbon chain of the resulting tertiary amines that helps determine the composition of the quaternary ammonium chloride compound present in the BTC. Methyl chlorides, benzyl chlorides and alkyl chlorides are also degradation products of the BTC samples.
**TABLE I**

Gas Chromatographic representation of BTCs and Cetylcide samples versus the retention times (RT) of their pertinent peaks

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</table>

| I | Dodecylethylidimethylammonium Bromide |
| II | Benzyldimethylstearylammonium Chloride Monohydrate, 90% |
| III | Benzyldimethyltetradecylammonium Chloride dihydrate, 99+%
| IV | Phenyltrimethylammonium Chloride, 98+%
| V | Benzyltriethylammonium Chloride, 99%
| VI | Benzyldimethyldodecylammonium Bromide, 97%
| VII | Benzyllributylammonium Chloride, 98+%
| VIII | Benzylltrimethylammonium Chloride, 97%
| IX | Benzylicetidyldimethylammonium Chloride monohydrate |
| X | Cetyltrimethylammonium Chloride 25 wt % solution in water |
| XI | Benzalkonium Chloride |
| XII | Bretol |
In order to identify, if possible, the pertinent peaks of interest from the complex chromatograms of the BTC samples, BTC 65 was chosen for comparison because it contains the most components and all BTC samples have peaks with similar peak patterns.

Table 2 is a representation of the retention times of peaks from all chromatograms of both BTC compounds and standards versus the standards, which are labeled from I to XII. In addition, table 2 lists those retention times (A→U) which are common to samples and standards.

In table 2, Dodecylethyldimethylammonium Bromide (standard I), with the molecular structure \( \text{C}_{12}\text{H}_{25}\text{NC}_{2}\text{H}_5\text{CH}_3 \) has 2 pertinent peaks: E(4.00) and G(4.82). The possible degradation products are: \( \text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_2 \) (Dodecyldimethylamine), \( \text{C}_{12}\text{H}_{25}\text{NC}_2\text{H}_5\text{CH}_3 \) (Dodecylethylmethylamine), and \( \text{C}_2\text{H}_5\text{N}(\text{CH}_3)_2 \) (Ethyldimethylamine). \( \text{C}_2\text{H}_5\text{Br} \) (Ethyl Bromide), \( \text{CH}_3\text{Br} \) (Methyl Bromide), and \( \text{C}_{12}\text{H}_{25}\text{Br} \) (Dodecyl Bromide) are possible alkyl bromides. Referring to table 1, we find E is common to BTC samples. Only one degradation product is similar to both BTC and the standard in question and that is \( \text{C}_{12}\text{H}_{25}(\text{CH}_3)_2\text{N} \), which is the most probable structure for peak E(4.00).

Benzyldimethylstearylammonium Chloride Monohydrate (standard II), in table 2, with the molecular structure \( \text{C}_6\text{H}_5\text{CH}_2\text{N}[\text{CH}_2\text{C}_{17}\text{H}_{33}]\text{(CH}_3)_2\text{Cl}.\text{H}_2\text{O} \), gives peaks A(2.13) and Q(16.31). The Benzyldimethylstearylammonium chloride has possibly degraded upon injection in GC into one or more of these tertiary amine products: Benzyldimethylamine \( \text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_2 \), stearylmethylbenzylamine

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C\textsubscript{18}H\textsubscript{37}CH\textsubscript{3}NC\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}, and stearyldimethylamine C\textsubscript{18}H\textsubscript{37}N(CH\textsubscript{3})\textsubscript{2}. The possible alkyl chloride products are: benzyl chloride C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}Cl, methyl chloride CH\textsubscript{3}Cl, and stearyl chloride C\textsubscript{18}H\textsubscript{37}Cl. On the other hand, table 1 shows that peak A(2.13) is common to all BTCs, while peak Q(16.31) is common to BTC 835 and Cetylcide. As a result, any of the previous degradation products can refer to any of the latter two peaks.

The benzyldimethyltetradecylammonium chloride with the molecular structure CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{13}N(CH\textsubscript{2}C\textsubscript{6}H\textsubscript{5})(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}H\textsubscript{2}O (standard III) gives peaks: A(2.13), H(6.35), K(6.98), and T(20.11) which can be seen in table 2. Peak H at 6.35 is small and barely detected with an area % of 0.029 and will be considered to be unimportant.

The degradation of benzyldimethyltetradecylammonium chloride in the GC injection chamber may have given one of the following tertiary amines: C\textsubscript{14}H\textsubscript{29}CH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}N (tetradecylmethylbenzylamine), C\textsubscript{14}H\textsubscript{29}(CH\textsubscript{3})\textsubscript{2}N (tetradecyldimethylamine), and C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}N (Benzyldimethylamine). One or more of the following alkyl chlorides could have also been produced: C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}Cl (benzyl chloride), CH\textsubscript{3}Cl (methyl chloride), and CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{13}Cl (tetradecyl chloride). Three peaks A, K, and T are common to all BTC compounds. Further analysis will identify these peaks.

Phenyltrimethylammonium chloride with the molecular structure C\textsubscript{6}H\textsubscript{5}N(CH\textsubscript{3})\textsubscript{3}Cl (standard IV), which can be seen in table 2, gives only one peak: B(2.34). The possible tertiary amines resulting from the degradation of the phenyltrimethylammonium chloride are: trimethylamine N(CH\textsubscript{3})\textsubscript{3}, and phenyldimethylamine C\textsubscript{6}H\textsubscript{5}N(CH\textsubscript{3})\textsubscript{2}. Phenyl chloride C\textsubscript{6}H\textsubcript{5}Cl and methyl chloride CH\textsubscript{3}Cl are the only possible alkyl chlorides produced by the degradation of this standard.
None of these possible structures are of any interest because they do not match breakdown BTC products except for methyl chloride. Further analysis will be needed to identify the B peak.

The GC trace of benzyltriethylammonium chloride \( \text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2\text{Cl} \) (standard V) shows only one pertinent peak, A(2.13). The benzyltriethylammonium chloride can be degraded in the GC injection port to give one or more of these tertiary amine products: benzyl-diethylamine \( \text{C}_6\text{H}_5\text{CH}_2\text{N(\text{C}_2\text{H}_5}_2\) and triethylamine \( \text{N(\text{C}_2\text{H}_5})_3\), benzyl chloride \( \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \) and ethyl chloride \( \text{C}_2\text{H}_5\text{Cl} \) as possible alkyl chlorides. Table 1 shows that peak A(2.13) is present in all BTC samples, and since ethyl chloride is not a possible product resulting from the BTC degradation, we can conclude that peak A(2.13) is Benzyl chloride.

Standard VI, benzyldimethyldodecylammonium bromide with the molecular structure \( \text{C}_6\text{H}_5\text{CH}_2\text{N[\text{(CH}_2\text{)11CH}_3\text{]}(\text{CH}_3}_2\text{Br, has four pertinent peaks, B(2.34), F(4.29), G(4.82), and R(16.45). The benzyldimethyldodecylammonium bromide can possibly give one or more of the following tertiary amine products: dodecylmethylbenzylamine C_{12}\text{H}_{25}\text{C}_6\text{H}_5\text{CH}_2\text{NCH}_3, dodecyldimethylamine C_{12}\text{H}_{23}\text{N(\text{CH}_3}_2, and benzyldimethylamine C}_6\text{H}_5\text{CH}_2\text{N(\text{CH}_3}_2. \) It may also breakdown to one or more of these alkyl bromides: benzyl bromide \( \text{C}_6\text{H}_5\text{CH}_2\text{Br}, \) methyl bromide \( \text{CH}_3\text{Br}, \) and dodecyl bromide \( \text{C}_{12}\text{H}_{25}\text{Br. All bromide products are eliminated because BTCs give alkyl chlorides. F and G peaks are absent from all BTC sample spectra which leave peaks B(2.34) and R(16.45) being the only tertiary amines mentioned earlier (with the exception of dodecylmethyldiethyamine) as possible structures. It was shown earlier that

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dodecyldimethylamine is the most probable structure for peak E(4.00).

Benzyltributylammonium chloride $C_6H_5CH_2N[(CH_2)_3CH_3]_2Cl$ (standard VII) shows two peaks at A(2.13), and B(2.34) as can be seen in table 2. Benzyl chloride was shown to be the structure for peak A(2.13). The benzyltributylammonium chloride degraded in the GC injection chamber to give one or more of the following tertiary amines: benzyl dibutylamine $C_6H_5CH_2N[(CH_2)_3CH_3]_2$, and tributylamine $N[(CH_2)_3CH_3]_3$. In addition, benzyl chloride $C_6H_5CH_2Cl$, and butyl chloride $[(CH_2)_3CH_3]_2Cl$ are possible alkyl chloride products. Peak B(2.34) could be any of those products except for benzyl chloride. Table 1 shows two of the BTCs giving the B(2.34) peak.

The benzyltrimethylammonium chloride $C_6H_5CH_2N(CH_3)_3Cl$ (standard VIII) shows only one peak at A(2.13). Benzyl chloride $C_6H_5CH_2Cl$ is one of the possible breakdown products for this compound. The A(2.13) peak was shown to be this possible structure since it is common to both reagents and standards.

The benzylcetyldimethylammonium chloride $C_6H_5CH_2N[(CH_2)_15CH_3](CH_3)_2Cl.H_2O$ (standard IX) gives three pertinent peaks: A(2.13), N(12.12), and U(23.20) as can be seen in table 2. None of the BTC samples gave the N(12.12) peak. However, the U(23.20) peak is common to all BTCs. The benzylcetyldimethylammonium chloride monohydrate may have given upon degradation one or more of the following tertiary amines: cetylmethylbenzylamine $C_{16}H_{33}C_6H_5CH_2NCH_3$, cetyldimethylamine $C_{16}H_{33}N(CH_3)_2$, and benzyltrimethylamine $C_6H_5CH_2N(CH_3)_2$. Also this compound could have degraded into one or more of the following alkyl chlorides: benzyl chloride $C_6H_5CH_2Cl$, cetyl chloride $[(CH_2)_{15}CH_3]Cl$, and
methyl chloride CH$_3$Cl. The U(23.20) peak could represent one of these except for benzyl chloride since it was shown to be the A peak.

The cetyltrimethylammonium chloride [(CH$_2$)$_{15}$CH$_3$]N(CH$_3$)$_3$Cl, 25 wt. % solution in water (standard X) gave only one pertinent peak: M(11.86). Referring to the BTC data in Table 2, we notice that all sample solutions contained this peak in their chromatograms. The breakdown of this compound in the GC injection chamber could have given one cetyldimethylamine C$_{16}$H$_{33}$N(CH$_3$)$_2$, or trimethylamine N(CH$_3$)$_3$. Also possible alkyl chlorides are: cetyl chloride C$_{16}$H$_{33}$Cl and methyl chloride CH$_3$Cl.

Cetyldimethylamine, methyl chloride, and cetyl chloride are three common structures for BTCs and standards. As a result, the M(11.86) peak could be one of the 3 possibilities: C$_{16}$H$_{33}$N(CH$_3$)$_2$, C$_{16}$H$_{33}$Cl, or CH$_3$Cl.

Bretol or Cetyldimethylethylammonium bromide

CH$_3$(CH$_2$)$_{15}$N(CH$_3$)$_2$C$_2$H$_5$Br (standard XII) degraded and gave two pertinent peaks: M(11.86), and O(13.74). While the first peak is common to all BTCs, the second peak is not. Possible tertiary amine products resulting from the degradation are: cetyldimethylamine C$_{16}$H$_{33}$N(CH$_3$)$_2$, cetylmethylethylamine C$_{16}$H$_{33}$NCH$_3$C$_2$H$_5$, and dimethylethylamine N(CH$_3$)$_2$C$_2$H$_5$. Possible alkyl bromide products are: cetyl bromide C$_{16}$H$_{33}$Br, methyl bromide CH$_3$Br, and ethyl bromide C$_2$H$_5$Br. C$_{16}$H$_{33}$N(CH$_3$)$_2$ is the only common structure for BTCs and Bretol. The M peak could then only be:

cetyldimethylamine.

Benzalkonium chloride (std XI) give more peaks because this Quats contains alkyl groups (C$_{12}$, C$_{14}$, C$_{16}$, and C$_{18}$), with compositions like those found in
BTC compounds. Benzalkonium chloride is a mixture of alkylbenzyldimethylammonium chlorides of the general formula, 

\[ \text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_2\text{R}\text{Cl} \], in which \( R \) represents a mixture of alkyls (C\(_a\) through higher homologs). The degradation of this product (standard XI) have resulted in many peaks as table 2 shows: A(2.13), C(3.70), D(3.86), E(4.00), J(6.85), M(11.86), Q(16.31), S(20.00), and U(23.20). Except for peak J(6.85), almost all other peaks are common to BTC compounds. BTCs and Benzalkonium chloride differ only by their alkyl group compositions.

Cetylcide has all benzalkonium chloride peaks in addition to those of Bretol because its formula is a mixture of both.

The previous discussion can be summarized by the following:

<table>
<thead>
<tr>
<th>Standards</th>
<th>Peaks</th>
<th>Possible product structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>E(4.00), G(4.82)</td>
<td>Dodecyldimethylamine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dodecylethylmethylamine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dimethylethylamine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methyl bromide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ethyl bromide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dodecyl bromide</td>
</tr>
<tr>
<td></td>
<td>A(2.13), O(13.74),</td>
<td>Stearylalkylbenzylation</td>
</tr>
<tr>
<td>II</td>
<td>Q(16.31)</td>
<td>Stearylalkylamine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Benzyldimethylamine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Benzyl chloride</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Section</th>
<th>Compound 1</th>
<th>Compound 2</th>
<th>Compound 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>Methyl chloride</td>
<td>Stearyl chloride</td>
<td>Tetradecylmethylbenzylamine</td>
</tr>
<tr>
<td></td>
<td>H(6.35), K(6.98), T(20.11)</td>
<td></td>
<td>Benzyldimethylamine</td>
</tr>
<tr>
<td>IV</td>
<td>IV B(2.34)</td>
<td>Trimethylamine</td>
<td>Phenyl dimethylamine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Phenyl chloride</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Methyl chloride</td>
</tr>
<tr>
<td>V</td>
<td>V A(2.13)</td>
<td>Benzyldiethylamine</td>
<td>Triethylamine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Benzylic chloride</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ethyl chloride</td>
</tr>
<tr>
<td>VI</td>
<td>VI B(2.34), F(4.29), G(4.82), R(16.45)</td>
<td>Dodecylmethylbenzylamine</td>
<td>Dodecyl dimethylamine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Benzyldimethylamine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Benzylic bromide</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Methyl bromide</td>
</tr>
</tbody>
</table>
VII A(2.13), B(2.34).
- Benzyldibutylamine
- Tributylamine
- Benzyl chloride
- Butyl chloride

VIII A(2.13)
- Benzyldimethylamine
- Trimethylamine
- Benzyl chloride
- Methyl chloride

IX A(2.13), N(12.12), U(23.20)
- Cetyl methyl benzylamine
- Cetylethylbenzylamine
- Benzyl chloride
- Methyl chloride
- Cetyl chloride

X M(11.86)
- Cetylethylbenzylamine
- Cetyl chloride
- Methyl chloride

XII M(11.86), O(13.74)
- Cetyldimethylamine
- Cetyl methyl ethylamine
- Dimethylethylamine
- Methyl bromide
- Ethyl bromide
Only peaks that appear in the BTC chromatograms will be discussed. The following discussion will help identify the most common peaks in BTCs and standards. Yet, GC/MS spectra will be further evidence for what was previously discussed.

The first peak E(4.00) in standard I is common to all BTCs. This eliminates, as a possible structure, alkyl bromide and other tertiary amines that are not present in BTC products. As a result, dodecyldimethylamine is the only possible structure for the E peak.

Peak A(2.13) is common to all BTCs and common to most of the standards having benzyl chloride in their formulas. Most probably, A(2.13) is benzyl chloride.

Peak Q(16.31) has one of the following possible structures: stearylmethylbenzylamine, stearyldimethylamine, benzylidimethylamine, methyl chloride, or stearyl chloride.

Peaks H(6.35)(barely detected), K(6.98), and T(20.11) are common to all BTCs and appear in the GC spectrum of standard III (benzylidimethyltetradecylammonium dihydrate, 99+%). As a result, they can be either tetradecylmethylbenzylamine, tetradecyldimethylamine, tetradecyl chloride, benzylidimethylamine, or methyl chloride.

Peak U(23.20), is present in all BTC spectra. However, except for standard IX, and benzalkonium chloride, all other standards do not exhibit the U peak. This means the U(23.20) peak has one of the possible following structures:
cetylmethylbenzylamine, cetyltrimethylamine, cetyl chloride, benzyldimethylamine, and methyl chloride.

M(11.86) is common to all BTC chromatograms. It appears only in standards X, XII, cetylecide, and benzalkonium chloride. The structure of peak M(11.86) can only be cetyltrimethylamine.

Peak R (16.45) is present in three of the BTC chromatograms: BTC 50 USP, BTC 65, and BTC 8358. R can be one of several possibilities: dodecylmethylbenzylamine, dodecyltrimethylamine, benzyldimethylamine, methyl chloride, or dodecyl chloride.

To summarize:

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Possible structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(2.13)</td>
<td>Benzyl chloride</td>
</tr>
<tr>
<td>E(4.00)</td>
<td>Dodecyltrimethylamine</td>
</tr>
<tr>
<td>Q(16.31)</td>
<td>Stearyltrimethylamine</td>
</tr>
<tr>
<td></td>
<td>Stearyldimethylamine</td>
</tr>
<tr>
<td></td>
<td>Benzyldimethylamine</td>
</tr>
<tr>
<td></td>
<td>Methyl chloride</td>
</tr>
<tr>
<td></td>
<td>Stearyl Chloride</td>
</tr>
<tr>
<td>H(6.35), K(6.98), T(20.11)</td>
<td>Tetradecyltrimethylamine</td>
</tr>
<tr>
<td></td>
<td>Tetradecyl chloride</td>
</tr>
<tr>
<td></td>
<td>Benzyldimethylamine</td>
</tr>
<tr>
<td>Compound</td>
<td>Mass</td>
</tr>
<tr>
<td>-------------------</td>
<td>--------</td>
</tr>
<tr>
<td>Methyl chloride</td>
<td>U(23.20)</td>
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<tr>
<td>M(11.86)</td>
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<tr>
<td></td>
<td>R(16.45)</td>
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</table>

**Mass Spectroscopy:**

Gas Chromatography coupled with Mass Spectroscopy is an excellent technique for the separation and identification of organic compounds. This method exploits the unique capabilities of the Mass Spectrometer to identify organic molecules which have been separated by chromatography.

The chromatographic separation was carried out on a capillary column and the samples were introduced into the ionization source by a restrictor interface which effectively isolated the column from the vacuum while providing a natural pressure drop. The samples and standards were subsequently analyzed by MS and fragmentation patterns.
were recorded.

Gas Chromatograms for sample and standard solutions obtained using the GC method, have the same pattern as those obtained with the GC/MS technique even though peaks do not appear at exactly the same retention times, since some of the GC/MS conditions do not match those of the GC which were previously used. A solvent delay of 2 minutes permitted only the fragmentation of the compounds of interest in the ionization chamber.

Figure 20 shows the mass spectrum of the peaks eluting at 2.919 minutes in the Gas Chromatogram of Standard I. It correlates well with the GC/MS spectra of all BTC samples: BTC 50 USP, BTC 65, BTC 835, and BTC 8358, and standard VI for peaks at 2.926, 2.921, 2.909, and 2.878 respectively. These peaks correspond to the E(4.00) peak in the GC chromatograms. The E peak was most likely to be the tertiary amine: dodecyldimethylamine. The mass spectrum, figure 20, gives a parent peak at m/e = 213 an odd number mass, which proves the presence of a nitrogen atom. Furthermore, the base peak at m/e = 58 corresponds to the loss of the long carbon chain that results from the C-C cleavage next to the nitrogen atom:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\left(\text{CH}_2\right)_{10} & \quad \left(\text{CH}_2\right)_{10} \\
\text{CH}_2 - N^+ - \text{CH}_3 & \quad \text{CH}_2 - N^+ - \text{CH}_3 \\
\rightarrow & \quad + \\
\text{CH}_3 - (\text{CH}_2)_{10} & \quad \left(\text{CH}_3\right)_2 \\
\end{align*}
\]

As a result, the E(4.00) peak is confirmed to be C_{12}H_{25}N(CH_3)_2.
Figure 20

Mass Spectrum of Dodecylethyl(dimethylammonium bromide (std 1) at 2.919 min in its total ion chromatogram.
Figure 21 shows the mass spectra of peaks 2.926 and 2.921 minutes in BTC 50 and BTC 65 respectively.

Figure 22 is the mass spectrum of the 13.742 peak of standard II. This peak matches the Q(16.31) peak in the GC chromatogram of benzyldimethylstearylammonium chloride, monohydrate 90%. Among the many possible structures previously listed for the Q(16.31) peak, stearyldimethylamine is the most probable structure. Figure 22 confirms this assignment. First, no m/e peaks indicate the presence of a benzyl substituent such as m/e = 77 or m/e = 91 for the tropyllium ion fragment. Second, the parent peak at m/e = 297 is the formula weight of stearyldimethylamine, and the base peak at m/e = 58 represents the loss of C_{17}H_{35}^+ by the following mechanism:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3-(\text{CH}_2)_{16}-\text{CH}_2-\text{N}^+\text{-CH}_3 & \quad \text{m/e} = 297 \\
\text{m/e} = 58
\end{align*}
\]

The structure of peak Q(16.31) is stearyldimethylamine.
Figure 21-(a)

Figure 21-(b)

Mass Spectra of (a): BTC 50 USP and (b): BTC 65 at 2.926 and 2.921 min. respectively in their total ion chromatograms.

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Figure 22

Mass Spectrum of Benzylidimethylstearylammonium chloride (std II) at 13.742 min in its total ion chromatogram.
The mass spectrum in figure 23 is from standard VI at 13.800 min. This peak matches the R peak at 16.45 min. in the total ion chromatogram of standard VI. Figure 24 shows the spectra from BTC 50 USP, BTC 65, BTC 835, and BTC 8358 of peaks at 13.834, 13.845, 13.842, and 13.879 min. respectively. Mass spectra in figures 23 and 24 have m/e = 134 as their base peak and m/e = 91, as the tropyllium ion peak with a very high percent abundance (76%). The parent peak at m/e = 289 is the molecular weight of dodecylmethylbenzylamine (the possible breakdown product of standard VI). The reaction of degradation at m/e = 289 is:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 - (\text{CH}_2)_10 - \text{CH}_2 - \text{N}^+ - \text{CH}_2 - \text{C}_6 \text{H}_5 & \quad \rightarrow (\text{CH}_3)_2 - (\text{CH}_2)_10 + \cdot \text{CH}_2 - \text{N}^+ - \text{CH}_2 - \text{C}_6 \text{H}_5 \\
\text{m/e} = 289 & \quad \text{m/e} = 134
\end{align*}
\]

Consequently, the R(16.45) peak is proven to be C_{12}H_{25}NCH_3CH_2C_6H_5.

Figure 25 shows the mass spectrum of the peak at 17.434 minutes in the total ion chromatogram of standard III (benzyldimethyltetradecylammonium chloride, dihydrate 99+%). This GC/MS peak refers to the peak T(20.11) in the GC spectra of standard III. The mass spectrum in figure 25 matches those in figure 26 for BTC 50 USP, BTC 65, BTC 835, and BTC 8358 at 17.511, 17.547, 17.547, and 17.585 minutes respectively. The peaks at m/e = 77 and m/e = 91 proves the presence of a benzyl substituent in the molecular formula of the compound related to that mass spectrum. Although the parent peak m/e = 317 is undetectable in two of the BTCs and exist in BTC 835 and BTC 8358 where it appears at a very low percent abundance (0.03%), it shows that the tertiary amine related to that peak is tetradecylmethylbenzylamine.
Figure 23

Mass Spectrum of Benzyldimethyldodecylammonium bromide, 97% at 13.800 min in its total ion chromatogram.

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Figure 25

Mass Spectrum of Benzyldimethyltetradecylammonium chloride (std III) at 17.434 min in its total ion chromatogram

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Figure 26

Mass Spectra of (a): BTC 50 USP, (b): BTC 65, (c): BTC 835, and (d): BTC 8358 at 17.511, 17.547, 17.547, and 17.585 min. respectively in their total ion chromatograms.
with the molecular formula C_{14}H_{29}N(CH_3)CH_2C_6H_5. The base peak at m/e = 134 is the
fragment that corresponds to the loss of the long carbon chain by cleavage at the C–C
bond next to the nitrogen atom. The fragmentation can be demonstrated by the following
reaction:

\[
\begin{align*}
\text{CH}_3 & \quad \text{m/e} = 317 \\
\text{CH}_3-(\text{CH}_2)_{12}-\text{CH}_2-N^+\text{CH}_2-C_6H_5 & \rightarrow \text{CH}_3-(\text{CH}_2)_{12} + \text{CH}_2-N^+\text{CH}_2-C_6H_5 \\
\text{m/e} & = 134
\end{align*}
\]

Then spectrum 25 confirms peak T(20.11) to be tetradecylmethylbenzylamine.

Figure 27 shows the mass spectrum of the peak at 4.884 minutes in the
total ion chromatogram of standard III (benzyldimethyltetradecylammonium chloride,
dihydrate 99+%). This peak can be referred to peak K(6.98) in the GC chromatogram of
this standard. Also the peak K(6.98) appears in the GC chromatograms of all BTC
samples. The mass spectra that correspond to that peak for BTC 50 USP, BTC 65, BTC
835, and BTC 8358 appear at 4.936, 4.923, 4.975, and 5.054 respectively as can be seen
in figure 28. The parent peak at m/e = 241 corresponds to the tetradecyldimethylamine
with the molecular formula C_{14}H_{29}N(CH_3)_2. The odd number of the parent peak proves
the presence of a nitrogen atom in the molecular structure of standard III. The base peak
at m/e = 58 is the fragment that corresponds to the loss of the long carbon chain at the
C–C bond next to the nitrogen atom. This fragmentation can be shown in this equation:

\[
\begin{align*}
\text{CH}_3 & \quad \text{m/e} = 241 \\
\text{CH}_3-(\text{CH}_2)_{12}-\text{CH}_2-N^+\text{CH}_2-\text{CH}_3 & \rightarrow \text{CH}_3-(\text{CH}_2)_{12} + \text{CH}_2-N^+\text{CH}_3 \\
\text{m/e} & = 58
\end{align*}
\]

As a result, this spectrum confirms peak K(6.98) to be tetradecyldimethylamine.
Figure 27

Mass Spectrum of Benzyldimethyltetradecylammonium chloride (std III) at 4.884 min in its total ion chromatogram.
Mass Spectra of (a): BTC 50 USP, (b): BTC 65, (c): BTC 835, and (d): BTC 8358 at 4.938, 4.923, 4.975, and 5.054 min. respectively in their total ion chromatograms.
Figure 29 shows the mass spectrum of the 20.661 minutes peak in the total ion chromatogram of standard IX (benzylcetyldimethylammonium chloride, monohydrate). It matches the peak U(23.20) in the gas chromatogram of standard IX. This peak is detectable in the mass spectrum of BTC 50 USP only at 20.724 minutes as can be seen in figure 29. This can be attributed to the fact that the U(23.20) peak in the gas chromatographic spectra of all other BTCs is at a very low concentration (area % = 0.199). The parent peak is not observed. The base peak at m/e = 77 indicates the presence of a monosubstituted benzene ring. Also the prominent peak at m/e = 91 with a percent abundance of 49.87% confirms the presence of the tropylium ion C<sub>7</sub>H<sub>7</sub>+.

The GC results suggested the U(23.20) peak could be one of three possible structures: cetylmethylbenzylamine, cetyldimethylamine, and cetylchloride. Figure 29 shows the presence of a benzene ring which only cetylmethylbenzylamine contains the molecular weight of 345 confirms the structure C<sub>16</sub>H<sub>33</sub>NCH<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>. The peak at m/e = 134 is due to the fragmentation of the tertiary amine at the C — C bond next to the nitrogen atom. This is shown in the following equation:

\[
\begin{align*}
\text{CH}_3\left(\text{CH}_2\right)_{14}-\text{CH}_2-\text{N}^+-\text{CH}_2-\text{C}_6\text{H}_5 & \rightarrow \text{CH}_3-\left(\text{CH}_2\right)_{14}+ \text{CH}_2-\text{N}^+-\text{CH}_2-\text{C}_6\text{H}_5 \\
m/e = 345 & \quad m/e = 134
\end{align*}
\]

This confirms peak U(23.20) to be cetylmethylbenzylamine.

The total ion chromatogram of standard IX also gives a peak at 9.289 minutes whose spectrum is shown in figure 30. This spectrum is similar to the mass spectra of minutes respectively as shown in figure 31. These peaks have been referred to
Mass Spectra of (a): BTC 50 USP and (b): BTC 65 at 20.661 and 20.724 min. respectively in their total ion chromatograms.
Figure 30

Mass Spectrum of Benzylcetyldimethylammonium chloride (std IX) at 9.289 min in its total ion chromatogram.
as the N(12.12) peak in standard IX that is near to the M(11.86) peak in standard X (cetyltrimethylammonium chloride) and all other BTC sample solutions. Figure 30 shows a parent peak at m/e = 269 which is the same as that for cetyldimethylamine, \( \text{C}_{16}\text{H}_{33}\text{N(CH}_3\text{)}_2 \). A base peak at m/e = 58 indicates that the following fragmentation took place:

\[
\text{CH}_3\text{I} \rightarrow \text{CH}_3 - \text{(CH}_2\text{)}_{14} - \text{CH}_2 - \text{N}^+ - \text{CH}_3 \rightarrow \text{CH}_3 - \text{(CH}_2\text{)}_{14} + \text{CH}_2 - \text{N}^+ - \text{CH}_3
\]

This confirms for peak M(11.86) to be cetyldimethylamine. Peak H(6.35) is then confirmed to be tetradecyl chloride with the molecular formula: \( \text{C}_{14}\text{H}_{29}\text{Cl} \).

The GC / MS spectra of both standards and samples can be summarized by the following:

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Structures confirmed by GC /MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(2.13)</td>
<td>Benzyl chloride</td>
</tr>
<tr>
<td>E(4.00)</td>
<td>Dodecyldimethylamine ([\text{C}<em>{12}\text{H}</em>{25}\text{N(CH}_3\text{)}_2])</td>
</tr>
<tr>
<td>H(6.35)</td>
<td>Tetradecyl chloride</td>
</tr>
<tr>
<td>K(6.98)</td>
<td>Tetradecyldimethylamine ((\text{C}<em>{14}\text{H}</em>{29}\text{N(CH}_3\text{)}_2))</td>
</tr>
<tr>
<td>M(11.86) or N(12.12)</td>
<td>Cetyldimethylamine ((\text{C}<em>{16}\text{H}</em>{33}\text{N(CH}_3\text{)}_2))</td>
</tr>
<tr>
<td>Q(16.31)</td>
<td>Stearyldimethylamine ((\text{C}<em>{18}\text{H}</em>{37}\text{N(CH}_3\text{)}_2))</td>
</tr>
<tr>
<td>R(16.45)</td>
<td>Dodecylmethylbenzylamine ((\text{C}<em>{12}\text{H}</em>{25}\text{NCH}_2\text{C}_6\text{H}_5\text{CH}_3))</td>
</tr>
<tr>
<td>T(20.11)</td>
<td>Tetradecylmethylbenzylamine ((\text{C}<em>{14}\text{H}</em>{29}\text{NCH}_2\text{C}_6\text{H}_5\text{CH}_3))</td>
</tr>
</tbody>
</table>
Table 3 lists the molecular structures of the previously identified peaks that appear in the gas chromatograms of most of the BTCs and Cetylceide compounds.
TABLE 3

Gas Chromatographic representation of BTC samples versus the retention times (RT) of their pertinent peaks and the molecular structures of some of the identified peaks.

<table>
<thead>
<tr>
<th>RT</th>
<th>Degradation products</th>
<th>BTC 50 USP</th>
<th>BTC 65</th>
<th>BTC 835</th>
<th>BTC 8358</th>
<th>Cetylcide</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.13</td>
<td>C₆H₄Cl</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>2.34</td>
<td>B</td>
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<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>3.70</td>
<td>C</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>3.86</td>
<td>D</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>4.00</td>
<td>C₁₂H₂₅N(CH₃)₂</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>4.29</td>
<td>F</td>
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<tr>
<td>4.82</td>
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<tr>
<td>6.35</td>
<td>C₁₄H₂₉Cl</td>
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<tr>
<td>6.98</td>
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<tr>
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<td>-</td>
</tr>
<tr>
<td>11.86</td>
<td>C₁₈H₃₃N(CH₃)₂</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>12.12</td>
<td>N₁₈H₃₃N(CH₃)₂</td>
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<td>-</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>16.20</td>
<td>P</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16.31</td>
<td>Q₁₈H₃₇N(CH₃)₂</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>16.45</td>
<td>R₁₆H₃₂NCH₃C₆H₃CH₃</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>20.00</td>
<td>S</td>
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<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>20.11</td>
<td>T₁₆H₃₂NCH₃C₆H₃CH₃</td>
<td>+</td>
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</tr>
<tr>
<td>23.20</td>
<td>U</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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</table>
CONCLUSION

A simple scheme of analysis was used to analyze and identify the high molecular weight quaternary ammonium compounds in an aqueous solution upon their degradation in a hot GC injection port into tertiary amine and alkyl chlorides. A capillary gas chromatographic instrument was used to separate the degradation products which were produced.

The very low volatility and ionic nature of quaternary ammonium compounds has made their separation by GC impossible. Operating at high temperatures, a Hofmann elimination occurs producing compounds that can be separated by GC. Highly reproducible GC chromatograms were obtained for all BTC samples as figure 1, 2, and 3 show for BTC 50 USP compound.

The decomposition of long chain quaternary ammonium compounds, the BTC samples and the standards are given in tables 1 and 2. Using pattern recognition, the structure of individual components of these mixtures were resolved. The identity of some of the degradation products were determined by GC / MS.
REFERENCES


