

The Direct Gas Chromatographic Analysis of Long Chain Quaternary Ammonium Compounds

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Abstract

Long chain quaternary ammonium compounds are used as germicides, textile softeners and in many other industrial applications. In working with these compounds, it was found desirable to be able to determine their long chain homolog composition. Experiments were carried out attempting to perform this determination using gas chromatography. The first approach was to try and do the Hofmann degradation of the quaternaries on strongly alkaline columns used for amine determination. However, the postulated hydrocarbon peaks were not obtained. Instead, a series of peaks that represented identifiable tertiary amines emerged from the column. Using these peaks, the homolog composition of the original quaternary ammonium compound could be determined. Quaternaries containing up to 38 carbons have been identified. The types of columns and conditions used in this work are described. The quantitative relationship of the composition found was related to that of the actual composition. The apparent unequivalence of various carbon-nitrogen bondings is discussed.

Introduction

LONG CHAIN quaternary compounds have found increasing use as germicides, textile softeners, and industrial chemicals. The commercially available organic salts are generally the alkyltrimethylammonium halides or dialkyldimethyl ammonium halides and similar benzonium compounds. The alkyl groups may be the C-8 to C-18 homologs giving quaternary salts of 11-38 carbons. In our work with the long chain quaternary ammonium compounds, we found it desirable to be able to determine the long chain homolog composition of these materials.

The quaternary ammonium salts do not readily lend themselves to chain length separation by classical methods such as distillation and crystallization. Paper and column chromatography (1-3,5) have found some use in recent years for this task. The paper and column chromatography methods are slow and in our hands did not give reliable qualitative or quantitative results. Recently, gas chromatography was used to separate the tertiary amines formed by hydrogenating alkyl-benzyl dimethyl ammonium chlorides (8). The gas chromatography method cited is limited to quaternaries that contain the benzyl group.

Alkaline columns have long been used for the chromatography of long chain amines (6). It occurred to us that solutions of quaternary ammonium compounds placed directly on these very alkaline gas chromatography columns at relatively high flash temps might undergo a Hofmann degradation (4). The resulting olefins and tertiary amines from the degradation would form the basis for the identification of the long chain homologs of the quaternary. When this experiment was performed the peaks emerged as predicted. However, no peak had a retention time that corresponded to any of the postulated higher olefins (7).

The peaks that emerged had the retention time of the tertiary amines that would result if methyl chloride or benzyl chloride were removed from the quaternary ammonium compound. It was found that the homolog composition could be calculated from the retention time and the areas of these peaks. By varying the gas chromatographic conditions, the amount of column liquid phase, and the column length, various quaternaries could be determined. Trimethylalkyl, dimethylbenzylalkyl and dimethyldialkyl quaternary ammonium halide compounds (Alkyl = C-8-C-18) up to 38 carbons were analyzed for homolog composition directly by gas chromatography.

Experimental

Apparatus. A gas chromatographic instrument of our own design was used in this work. The detection system was a thermoconductivity type employing four Gow-Mac matched tungsten filaments. Any gas chromatographic instrument capable of operating up to 300C should be satisfactory for this work.

Reagents.

1. *Quaternary Salts and Amines*—A series of commercial and also some pure quaternary ammonium compounds and the amines from which they were made were used in this study. The quaternaries were made by reacting the amines with methyl chloride or methyl iodide. The compounds used in these experiments had free amine and amine hydrochloride content of less than 1%.
2. Chromosorb W—acid-washed 60-80 mesh.
3. Apiezon L.
4. Carbowax 6000.
5. Potassium hydroxide, reagent grade.

Column Packing. The packing was made by first coating acid-washed Chromosorb-W, 60-80 mesh, with 10% by wt KOH. The KOH dissolved in methanol and then the Chromosorb W was added to this solution. The solvent was removed on a steam bath with stirring. The last traces of solvent were removed in an oven at 105C. The KOH-Chromosorb was then coated with the liquid phase, 20% or 5% by wt. Apiezon L was dissolved in petroleum ether and the KOH-Chromosorb was added to this solution. If the carbowax was used, it was first dissolved in methanol. The solvent was removed from the coated packing in the same manner as in the KOH treatment of the Chromosorb W.

Gas Chromatographic Columns and Conditions. All columns were $\frac{1}{4}$ in. copper or stainless steel tubing, vibration packed, with the G. C. packings that were prepared as described. Four types of columns were used at given temps:

1. 4 ft, 20% Carbowax-KOH used at 225C
2. 3 ft, 20% Apiezon L-KOH used at 240C
3. 2 ft, 5% Apiezon L-KOH used at 280C
4. 1 ft, 5% Apiezon L-KOH used at 280C

TABLE I

Some Quaternary Ammonium Compounds Analyzed by Gas Chromatography for Homolog Composition

1. Trimethyldodecylammonium chloride
2. Trimethyloctadecylammonium chloride
3. Trimethyl "coco" ammonium chloride
4. Trimethyl "hydrogenated tallow" ammonium chloride
5. Trimethyloctadecylammonium iodide
6. Dimethyldioctadecylammonium chloride
7. Dimethyl di "coco" ammonium chloride
8. Dimethyl di "hydrogenated tallow" ammonium chloride
9. Trimethyl "soya" ammonium chloride
10. Dimethylbenzyloctadecylammonium chloride
11. Dimethyl "coco" dodecylbenzyl ammonium chloride
12. Dimethylethylododecylammonium chloride
13. Dimethylethylhexadecylammonium bromide

The flash heater was operated at 280C and the helium flow was 50 ml/min with the 3 and 4 ft columns and 70 ml/min with the 1 and 2 ft columns.

Procedure. The quaternary ammonium compounds were dissolved in enough isopropyl alcohol to give approximately 50% solutions. About 4 μ l of this solution were injected into the G. C. instrument. The instrument conditions and columns used varied with the sample type. The trimethylalkyl ammonium halides and alkyl dimethylbenzyl ammonium chloride were analyzed using the 3 and 4 ft, 20% liquid phase columns at 240C. Quaternaries having 20-30 carbons were determined using the 5%, 2 ft column at 280C. Quaternaries having over 30 carbons were determined using the 5%, 1 ft column at 280C. The resulting amines from these very high mol wt quaternaries did not readily emerge from the longer columns.

Results and Discussion

A number of typical long chain quaternaries that were analyzed by the gas chromatographic procedures are listed in Table I. Compounds of various chain lengths and different halide anions are represented.

Sharp symmetrical peaks were obtained when dimethylalkylamine (Alkyl = C-8-C-18) were chromatographed on the alkaline columns. When the trimethylalkylammonium halides were placed on the column similar peaks were obtained. Figure 1 shows a comparison of the peaks and their retention times

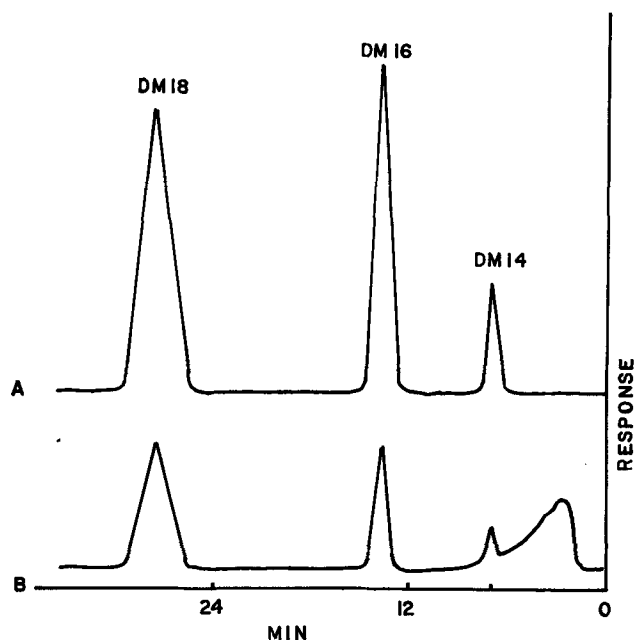


Fig. 1. Synthetic mixture of dimethylalkylamines (A) compared to a trimethylalkyl ammonium chloride from "hydrogenated tallow" (B). 4 ft column 25% Carbowax 6000 on 60-80 mesh Chromosorb W-KOH. Column temp 225C.

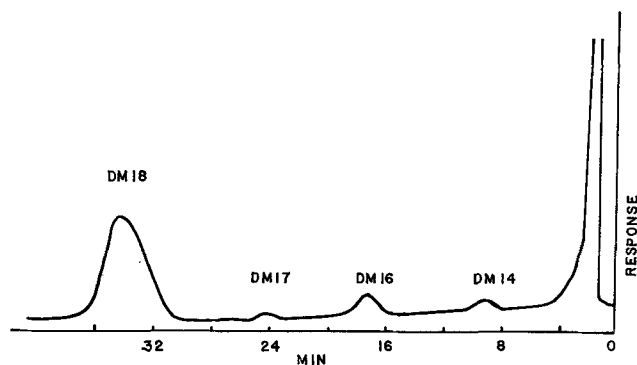


Fig. 2. Chromatogram of dimethyl "hydrogenated tallow" benzyl ammonium chloride. 3 ft column, 20% Apiezon L on 60-80 mesh Chromosorb W-KOH. Column temp 240C.

of a commercial quaternary ammonium compound and the tertiary amine to which it is related. The quaternary analyzed was a trimethylalkylammonium chloride and the amine was dimethylalkylamine (Alkyl = C-14, C-16, C-18). The early peak that shows considerable tailing is believed to be methyl chloride. Figure 2 shows a dimethylbenzylalkylammonium chloride (Alkyl = C-14, C-16, C-18) that was analyzed using the 3 ft, Apiezon L-KOH column. Again the only peaks emerging had the retention time of the dimethyl alkylamines. This observation indicates that the benzyl group is preferentially split off over the methyl groups. In one experiment, a benzyl quaternary was made on which long chain alkyl groups were substituted on the benzene ring. When this quaternary was chromatographed, a series of peaks were obtained that represented the usual dimethylalkyl amines and a group of peaks for the alkylbenzyl chlorides that were split off from the quaternary salt.

It was decided to extend the method to very high mol wt quaternaries containing two long chains. Figure 3 indicates the peaks obtained from a commercial dimethyldialkylammonium chloride (Alkyl = C-14-C-18). These peaks represent methyldialkylamines having a total of 31, 33, 35, and 37 carbons, respectively. The peaks obtained from a commercial dimethyl di "coco" ammonium chloride are shown in Figure 4. This analysis indicates the very complicated random reactions obtained when there are many long chain homologs available in the original starting material.

A series of experiments were conducted to determine if the quaternary homolog content could be quantitated and if the homolog ratios were altered in any manner by the gas chromatography conditions. A series of amines were first analyzed by gas

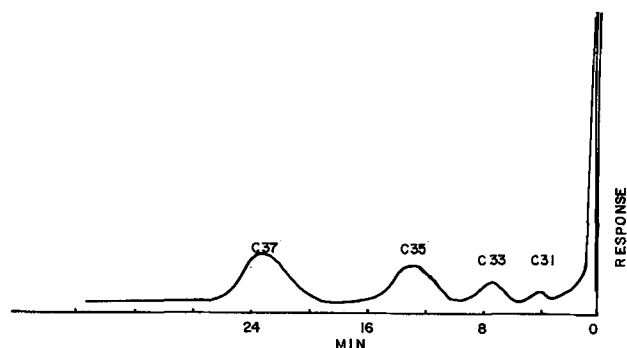


Fig. 3. Chromatogram of dimethyl di "hydrogenated tallow" ammonium chloride. 1 ft column, 5% Apiezon L on 60-80 mesh Chromosorb W-KOH. Column temp 280C.

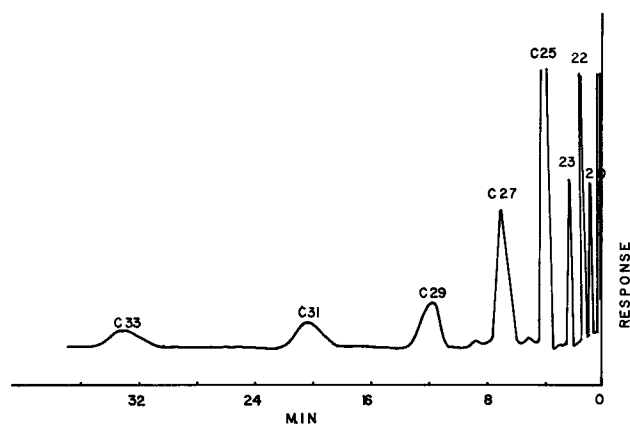


FIG. 4. Chromatogram of dimethyl "di coco" ammonium chloride. 2 ft column, Apiezon L on 60-80 mesh Chromosorb W-KOH. Column temp 285C.

chromatography. These same amines were then converted to quaternary salts using either methyl chloride or methyl iodide. Table II shows a comparison of the homolog analysis of a commercial dimethylalkylamine and its corresponding quaternary ammonium salt. The long chain alkyl groups were 14, 16, and 18 carbons. Table III shows the homolog comparison of a commercial dialkylamine and the quaternary made from it by reaction with methyl chloride. This sample contained amines of 28, 32, and 36 carbons, respectively, and the quaternary salts made from these amines had 30, 34, and 38 carbons. The

TABLE II

Comparison of the Homolog Analysis of a Dimethylalkylamine and Its Corresponding Quaternary Ammonium Compound

Alkyl group	Wt %		
	Amine	Quaternary	Difference
C-14.....	4.7 ± 0.1	5.6 ± 0.35	0.9
C-16.....	36.1 ± 1.3	35.6 ± 2.5	0.5
C-18.....	59.3 ± 1.4	58.8 ± 2.8	0.4

peak areas found by triangulation were used directly to calculate wt per cent. No correction for variation of thermal conductivity response with respect to mol wt was made. Reasonably good agreement between the homologs of the amines and the quaternaries was obtained. However, the greater variation was obtained between the dialkylamine and its quaternary derivative.

The preferential splitting off of the benzyl group over the methyl group and the methyl group over the longer chain groups indicates an apparent non-equivalence of the carbon-nitrogen bonds under the conditions imposed on these compounds. The gas chromatographic method suggests a convenient way of studying the apparent non-equivalence of this bond. This observation is undoubtedly related to Hofmann's rule which states that quaternary ammo-

TABLE III

Comparison of the Homolog Analysis of a Dialkylamine and Corresponding Dimethyldialkylammonium Chloride

Secondary amine		Quaternary		
Total carbons	Wt %	Total carbons	Wt %	Difference
C-28	0.7 ± 0.1	C-30	0.3 ± 0.0	0.4
C-30	4.0 ± 0.45	C-32	2.1 ± 0.0	1.9
C-32	15.4 ± 1.3	C-34	13.0 ± 0.05	2.4
C-34	36.1 ± 0.3	C-36	39.4 ± 0.05	3.3
C-36	43.7 ± 2.0	C-38	45.2 ± 0.1	1.5

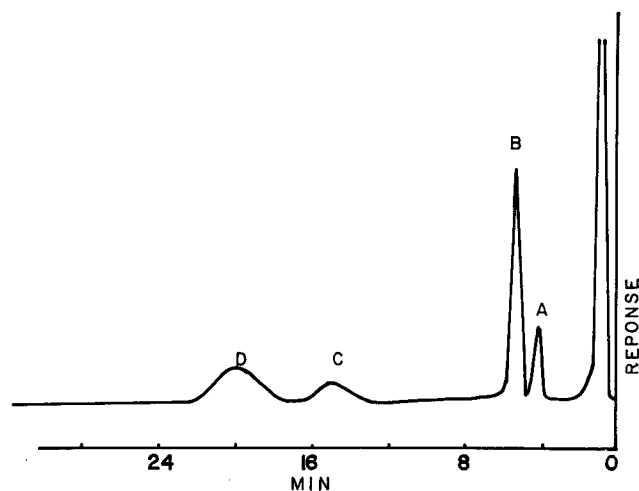


FIG. 5. Combined chromatograms of pure dimethylethyldecyl ammonium chloride and dimethylethylhexadecyl ammonium bromide: A) dimethyldodecylamine, 22.6%; B) methylethyldecylamine, 78.4%; C) dimethylhexadecylamine, 28.4%; D) methylethylhexadecylamine, 71.6%.

nium compounds with several different constituents attached to the nitrogen atom will decompose to yield a tertiary amine and an olefin which has the smallest number of alkyl groups attached to it.

A further study was made on the effect of different groups attached to the nitrogen atom on the decomposition of quaternaries. A purified dimethylethyldecylammonium chloride was analyzed on the 3 ft Apiezon L-KOH column. Two tertiary amines were observed in the chromatogram: dimethyldodecylamine (22.6% ± 1.0%) and methylethyldecylamine (77.4% ± 1.0%). A similar experiment was performed with purified dimethylethylhexadecylammonium chloride. Again, two tertiary amines were observed: dimethylhexadecylamine (28.4% ± 1.5%) and methylethylhexadecylamine (71.6% ± 1.5%). Figure 5 shows the combined chromatograms of the two quaternaries used in this experiment. From these limited experiments it was observed that the long chain alkyl group has a profound effect on the manner in which a quaternary having mixed alkyl groups on the nitrogen atom will decompose.

A method has been described by which the homolog composition of a great variety of long chain quaternary ammonium compounds can be determined by gas chromatography. The method should prove useful as a qualitative tool for identifying quaternary ammonium compounds. Its use as a quantitative method has yet to be explored. However, it should be applicable to chemical residue analysis in foods and other substances by using sensitive ionization detectors. Using this procedure with an internal standard, the amount of trimethyldialkylammonium salt (one long chain) in commercial dimethyldialkylammonium salts (two long chains) may also be estimated.

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[Received July 13, 1962]