

T H E S I S

on

The Tetra-alkyl Ammonium Compounds,
Their Possible Use in Agriculture and Industry

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Edward Cleveland Callaway

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APPROVED:

Redacted for privacy

Professor of Organic Chemistry

In Charge of Major

Redacted for privacy

Head of Department of Chemistry

Redacted for privacy

Chairman of Committee of Graduate Study

UTILITY OF THE TETRA-ALKYL AMMONIUM BASES

Of the chemicals useful to man, none have found a more extensive use than the alkali metals and their compounds. Every day chemists are discovering new uses for these versatile metals.

Apparently, one of the neglected fields of research is the extended investigation of the possible "synthetic alkali metals" as the tetra-alkyl ammonium bases or substituted ammonia compounds are sometimes called. It would appear to be one of the masterpieces of scientific skill that men should discover a method of making a metal-like substance from carbon, nitrogen and hydrogen. But having discovered these new basic substances, the research army has passed on to more enticing fields, and we do not know as yet how these "synthetic metals" can be used.

The first amine discovered was made from ethyl isocyanate by Wurtz in 1848. Hofmann followed with a brilliant research in 1850. His original paper on the tetra-alkyl ammonium bases appeared in *Annalen* (1851, 78, 266). Since Hofmann's method was to treat tetra-methyl ammonium iodide with silver oxide and thus obtain the base, tetra-methyl ammonium hydroxide, it was inferred by chemists everywhere for nearly fifty years, that the cost of making the bases would be too great for them to ever be used commercially. It remained for two English chemists, Walker and Johnston, (1) to revive interest in tetra-alkyl ammonium bases.

bases in 1905. They showed that the use of silver was not necessary in preparing these bases, and investigated the pure crystalline hydroxides. In 1911 (2), McCoy and Moore demonstrated the metallic character of tetra-methyl by making its amalgam.

The Purpose of this Research

This research was undertaken for the purpose of investigating the utility of the tetra-alkyl bases and some of their organic compounds. The work was divided into the following sections.

1. A review of the methods of making the hydroxides with a view of finding a practical manufacturing method.

2. Preparation of the salts of tetra-alkyl ammonium and the organic acids and the investigation of some of their properties.

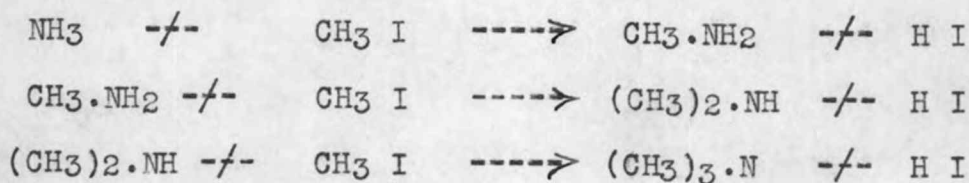
3. Preparation of some of the soaps of the tetra-alkyl bases and an investigation of their properties, for the purpose of discovering some of their industrial uses.

If the alkyl groups from one to ten carbons were to be substituted for hydrogen in ammonia, the tertiary amines formed would have boiling points ranging from 3.5°C to 400°C. The lower members would have strong fishy odors, while the higher members would be odorless and insoluble in water. By uniting these tertiary amines with

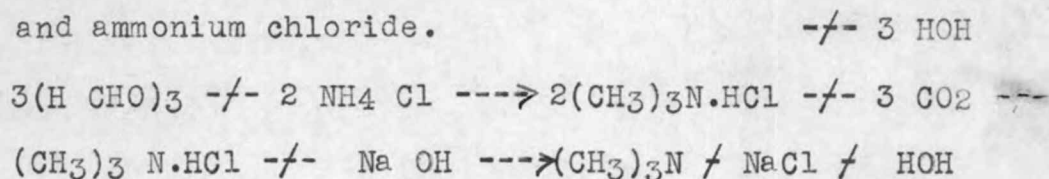
the alkyl halides of the same radicals, the salts of the tetra-alkyl ammonium bases could be made. In alcoholic solutions the hydroxides are readily formed from KOH and and the KCl is precipitated out. The preparation of the bases is just a point of departure. There are just as many salts of any one of these bases as there are of sodium or potassium. The alcohols up to five carbons are now available in quantities that make the manufacture of at least five new bases seem practical.

Synthesis of Tetra-alkyl Ammonium Bases

Hofmann and others reacted ammonia with the alkyl iodide to obtain the tertiary amine:



These reactions take place simultaneously so that the result is a mixture of all three products and is hard to separate. The better way of making trimethyl amine is by the method of R. H. Schmitz (3) as improved by Roger Adams and B. R. Brown (4). This method quickly gives a large yield of the tertiary amine, from paraformaldehyde and ammonium chloride.



Having made the tertiary amines, they may be preserved in the form of the halogen salts until used to prepare the base. These salts are stable at ordinary temperatures.

$$(R)_3N \text{ -/- } RX \text{ ----} \rightarrow (R)_4N^+X^-$$

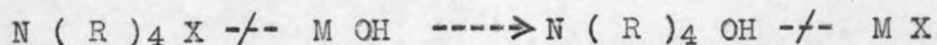
The progress of this reaction may be followed by titration of the excess base until neutrality is reached. The solution should contain about 30% to 35% of the tetra-alkyl salt.

The next step in the manufacture of the base must be under very careful quantitative control, or the final solution of the base will be contaminated with either KOH or the halogen salt. The solution may be carefully assayed

for chlorides by N/10 AgNO₃, and the amount of alcoholic KOH required to just precipitate all the Cl as KCl in the alcoholic solution may be calculated. When the KCl has been filtered off, the alcoholic solution of the tetra-alkyl ammonium base should be from 20% to 30% depending on the conditions.

A Brief Review of the Literature

The methyl, ethyl, propyl and amyl hydroxides have been made. In 1888, two English chemists, Lamson and Collier (5) worked with these bases by the old methods of Hofmann. They made the observation " that the salts of tetra-alkyl ammonium had been neglected for about 40 years." In 1905, James Walker and John Johnston (6), Carnegie Research Scholars, made the purified bases from alcoholic solutions by the KOH-process. They showed that there was no necessity for using silver in making the bases since KCl was relatively insoluble in absolute alcohol, and precipitated out about as well as AgCl in a water solution. They suggested the general equation:



Walker and Johnston crystallized out the pure methyl ammonium base in the form of the penta-hydrate. It had a strength in saponification of methyl acetate of 92 compared to NaOH taken at 100. This base was very soluble, 220 grams dissolving in 100 grams HOH at 15°C.

It fused at 62°C, and manifested a heat of solution of 2,120 calories per gram-mol.

David C. Crichton (7), another Carnegie Scholar, extended the work of Walker and Johnston in 1907. He made the tetra-ethyl and the tetra-propyl ammonium bases, the former crystallizing out as a tetra-hydrate and the latter as a hepta-hydrate. The tetra-ethyl base melted at 49°C and was extremely soluble in water.

Sixty years had passed since the discovery of these new bases, their inorganic salts had been investigated by many physical chemists; their conductivity and heat of formation was known; yet they found little utility. When physical chemists began to study the conductivity of salts in liquid ammonia, they discovered a curious thing about the tetra-methyl ammonium radical. It gave a blue color at the cathode, like sodium.

In 1902, W. Palmaer (8), electrolysed tetra-methyl ammonium halide salts in liquid ammonia and noticed the blue striae at the cathode. Schulbach and Ballauf extended this research in 1921 (9). Tetra-ethyl ammonium iodide was electrolysed in liquid ammonia at 70°C. A blue solution was formed at the cathode, which was decolorized immediately by iodine to form the iodide. The same blue solution reacted with sulphur to form the sulphide.

It was the opinion of these two chemists that since the

solution became colorless at low temperatures, there must be association: $2 (N (C_2H_5)_4) \text{ ----} \rightarrow N(C_2H_5)_4 \cdot N(C_2H_5)_4$.

By 1910, Franklin and Kraus had developed a whole system of chemistry in liquid ammonia, comparable in many ways with the system in water that is so familiar. The tetra-alkyl ammonium compounds were among the interesting compounds studied by Franklin and Kraus.

It was in 1911 that McCoy and Moore(2) demonstrated the metallic character of tetra-methyl ammonium. They electrolysed a saturated solution of $N (CH_3)_4 Cl$ in absolute alcohol with a Pt. anode and a Hg. cathode. They were astonished to find that after 30 minutes using 18 v. a stiff amalgam appeared on the top of the mercury at the cathode. This amalgam was stable at $20^\circ C$, and manifested a solution tension comparable with potassium. Other investigators have corroborated these results, and the indications are that other metal-like substances will be made. The tetra-methyl amalgam reacted violently with water like sodium amalgam.

In the field of bio-chemistry, an attempt was made to make and use some of the organic salts of the tetra-methyl ammonium as drugs. Tetra-methyl ammonium oxalate was introduced under the trade name: "Albiagen" (10). The dose was 0.005 grams per kilogram of body weight. The physiological action was supposed to be an increase of blood

pressure and a retarded heart beat. It was used to some extent in Europe.

Tetra-methyl ammonium formate was introduced under the name "Forgenin"(11). It was supposed to have a physiological action similar to Digitalis. The dose was 0.01 to 0.02 grams per kilogram of body weight.

The inorganic salts of tetra-methyl ammonium that have been investigated by the physical chemists are the iodide, bromide,, chloride, nitrate, ferrocyanide, perchlorate, chlorate, thiocyanate, and several of the double salts. These are stable at ordinary temperatures and not as hygroscopic as the organic salts. The iodide, for instance, decomposes at 360°C.

THE EXPERIMENTAL PROCEDURE

Trimethyl Amine. This product was made by the method of Roger Adams and B. R. Brown (4). 417 gms. of powdered ammonium chloride and 1000 grams of paraformaldehyde were mixed and introduced into a five liter flask. The flask was heated on an oil bath until the reaction started and then the heat was removed. After an hour, the mixture was heated to 160°C. for four hours. When allowed to cool over night, the dark liquid crystallized into a solid mass of long transparent needles of trimethyl amine hydrochloride.

Tetra-methyl Ammonium Chloride. The flask was warmed to melt the trimethyl amine salt, and strong Na OH was run in to liberate the trimethyl amine as a gas. The gas was dried by passing it through soda-lime tubes; condensed by means of a long spiral condenser packed in ice-salt mixture; and run into absolute methyl alcohol under ice. A second flask was set to absorb the gas not dissolved in the first flask. The gas was troublesome to work with, as the offensive fishy odor saturated the clothing and remained for days.

Methyl chloride was now conducted into the trimethyl amine solution to form the tetra-methyl ammonium chloride. Methyl chloride was made by passing HCl gas into the warm methyl alcohol in the presence of zinc chloride.

By titrating samples from the flask from time to time the progress of the reaction was followed until the base was completely neutralized. In passing in the methyl chloride, the gas was led through several soda-lime tubes to remove the excess of HCl . When the reaction was complete there was 852 cc. of a saturated solution in the main flask. The tetra-methyl ammonium chloride crystals separated out in large transparent plates, but easily dissolved on warming the flask. These crystals decomposed on heating to about 350°C . giving the strong odor of trimethyl amine. An assay of the solution showed 76.9% tetra-methyl ammonium chloride. The yield was 711 grams or 83% of the theoretical calculated from the amount of ammonium chloride used.

Tetra-methyl Ammonium Hydroxide. 445.5 cc. of the 852 cc. of tetra-methyl ammonium chloride solution was treated with 752 cc. of alcoholic KOH containing 121.15 grams of potassium. The potassium chloride came down as a heavy white precipitate in the alcoholic solution. The suspension was allowed to stand four hours and then was filtered on a Buchner funnel. The precipitate was washed with a little alcohol. The final filtrate measured 1,197 cc. The solution was a slight amber color and strongly caustic. It assayed 21.18% tetra-methyl ammonium hydroxide giving a yield of 253.6 grams, or

81.71% of the theoretical yield.

Later, the 406.5 cc. remaining of the original solution was run over into the tetra-alkyl base by the same process and gave a yield of 78.56% of theoretical.

The alcoholic KOH should not be red as the resulting solution of the base will be red.

Qualitative Reactions of Tetra-methyl Ammonium

With the following reagents tetra-methyl ammonium hydroxide gives:

Cu SO₄ -- Light blue cupric hydroxide and no complex.

Not soluble in excess. Turns brown on standing.

Ni NO₃ -- Green nickelic hydroxide. No complex.

Hg NO₃ -- Yellowish-gray precipitate, tinged with brown.

Hg Cl₂ -- Yellow precipitate of HgO.

Ag NO₃ -- Brown to black Ag₂O.

Fe Cl₃ -- A reddish brown Fe (OH)₃.

Fe SO₄ -- A greenish flocculent Fe (OH)₂.

Al Cl₃ -- White Al (OH)₃, soluble in excess.

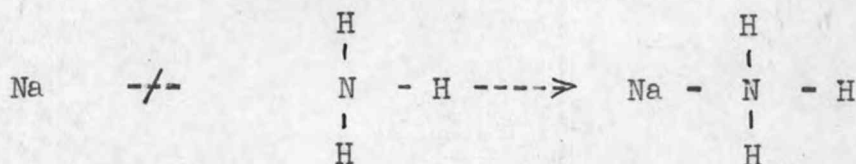
Mn Cl₂ -- White Mn (OH)₂, not soluble in excess.

Zn Cl₂ -- White gelatinous Zn (OH)₂.

The tetra-methyl ion is precipitated by sodium cobaltic nitrate, perchloric acid, and fluosilicic acid. Thus the tetra-methyl ion reacts sometimes like Na and sometimes like K, but never like NH₃.

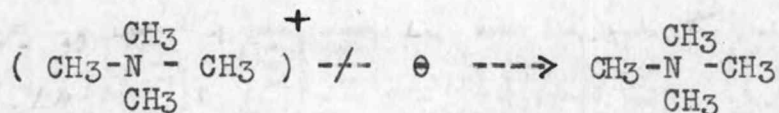
Molecular Constitution of Tetra-alkyl Compounds

this solution would be explained. Sodium would be discharged at the cathode, but would redissolve and re-ionize in the liquid ammonia. The ammonia liberated at the anode would regenerate ammonia molecules. When the conductivity of these solutions was being measured, it was found that solute and solvent reacted to form sodamide and hydrogen: $2 \text{ Na} \xrightarrow{-/-} 2 \text{ NH}_3 \longrightarrow 2 \text{ Na.N H}_2 \xrightarrow{-/-} \text{H}_2$ Fry is of the opinion that some of the sodium ions unite with the negative ammonia to form soda-ammonia, - undissociated and a free radical :



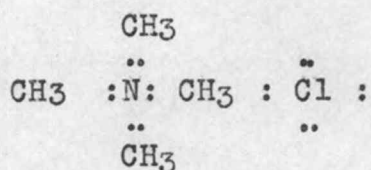
Thus we would have tetra-valent nitrogen as in NO_2 , a free radical and unstable due to the tendency of the N to revert to the normal by the gain or loss of electrons.

This gives a very good analogy for a concept of the constitution of tetra-methyl ammonium compounds, and explains their unstability. McCoy and Moore (2) made their strange amalgams from tetra-methyl ammonium salts in an alcoholic solution. Under these conditions the tetra-methyl ammonium ion loses its positive charge and the nitrogen becomes quadrivalent:



Thus Fry makes a good case for tetra-methyl ammonium being a free radical. This conception fits the observed data very well. The tendency of the tetra-methyl ammonium radical is to lose an electron and become positively charged. When thus charged, it takes on the properties of a metal high in the electromotive series replacing such metals as copper and zinc.

G. N. Lewis (14) indicates the probable structure of tetra-methyl ammonium chloride as follows:



$\text{CH}_3 \text{ Cl}$ is a very weak electrolyte, but when treated with $(\text{CH}_3)_3 \text{ N}$, the resulting solution is a very strong electrolyte. The tetra-methyl ammonium is thus shown to be a compound of tetra-valent nitrogen in which the nitrogen shares two electrons with the four carbons of the methyl groups.

MANUFACTURE OF THE TETRA-METHYL AMMONIUM COMPOUNDS

SOAPS

Tetra-methyl Ammonium Linseed Oil Soap. 50 grams of pure linseed oil was saponified with 105 cc. of 21.18% $(\text{CH}_3)_4\text{N OH}$. The resulting soap was yellowish-brown in color and neutral in reaction. There was no odor of trimethyl amine until after it had been stored in a warm place for a while. During the summer months there was a gradual decomposition of the soap on the top of the jar. In twelve months the decomposition had proceeded to a depth of three-fourths of an inch. Apparently a methyl ester and not the fatty acids were liberated in the decomposition. On hydrolysis, the ester gave the fatty acids and methyl alcohol. When the jar was opened there was a strong odor of trimethyl amine. Evidently, this soap would continue to give off trimethyl amine until completely decomposed. It gave a good lather; was a fair emulsifying agent; gave detergent properties comparable with yellow bar laundry soap; and possessed a strong toxicity for insect life. It was apparently non-injurious to plant life. It was soluble in alcohol and water.

Tetra-methyl Ammonium Oleate Soap. 50 grams of pure oleic acid was saponified by 71 cc. of 21.18% $(\text{CH}_3)_4\text{N OH}$. The oleate soap was very much like sodium oleate in ap

appearance. It gave good detergent values and was soluble in both water and gasoline. In its detergent properties in gasoline it resembled ammonium oleate.

Tetra-methyl Ammonium Olive Oil Soap. 40 grams of olive oil was saponified with 62.5 cc. of 16.24% $(\text{CH}_3)_4\text{NOH}$. The resulting soap was more like a potash soap than it was like castile soap. It was a soft brown paste. It was soluble in alcohol and water, and gave good detergent values.

Tetra-methyl Ammonium Tallow Soap. 40 grams of tallow was saponified with 77.4 cc. of 16.24% $(\text{CH}_3)_4\text{N OH}$. The resulting soap was very much like yellow laundry soap. It was soluble in alcohol and water. It gave good average detergent values.

Tetra-methyl Ammonium Palm Oil Soap. 40 grams of palm oil was saponified with 61.6 cc. of 16.24% base. The resulting soap was greenish yellow, and gave good detergent properties. It was soluble in alcohol and water.

The Organic Salts of Tetra-alkyl Ammonium

A survey of the literature revealed that practically all of the work on the tetra-alkyl ammonium compounds was on the inorganic salts. The organic salts appear to have been neglected. It was therefore decided to be of interest to make some of the organic salts and investigate some of their properties.

Tetra-methyl Ammonium Formate. A solution of 40 grams of pure formic acid in water was neutralized with $(\text{CH}_3)_4\text{N OH}$; evaporated to a small volume on a steam bath; decolorized with charcoal; evaporated to a paste on the bath; and then reduced to a solid mass in the vacuum oven after heating for six hours at 110°C . The crystals were transparent, rhombic, and very hygroscopic. The assay for nitrogen showed 9.03% which indicated the formula:
 $(\text{CH}_3)_4\text{N.O.O.C.H} \cdot 2 \text{ HOH}$

Tetra-methyl Ammonium Acetate. A solution of 40 grams of glacial acetic acid was neutralized with the base and evaporated to a small volume; decolorized; and evaporated to a thick syrup on the steam bath. It held water tenaciously so that it required six hours in the vacuum oven at 110°C . to drive off the last trace of water. The crystals were rhombic and very hygroscopic. The dry solid assayed 5.4% nitrogen, which indicated the formula: $\text{CH}_3.\text{CO.O. N} (\text{CH}_3)_4 \cdot 7 \text{ HOH}$

Tetra-methyl Ammonium Propionate. A solution of 20 grams of propionic acid was neutralized with the base; evaporated to a small volume; decolorized; reduced to a syrup on the steam bath; and when allowed to cool it formed a stiff jelly. Under the microscope the jelly was found to be composed of long threads or filaments similar to the potassium soap jellies. It required eight hours in the vacuum oven at 110°C to reduce the jelly to a dry mass. It assayed 3.9% nitrogen.

Tetra-methyl Ammonium Butyrate. A solution of 20 grams of syrupy butyric acid was neutralized by the base. After purifying and evaporating the residue was a firm jelly. A microscopic examination revealed the presence of filaments. After 8 hours in the vacuum oven at 110°C the residue still contained water. The temperature was raised to 120°C . which slightly browned the mass. The salt crystallized from alcohol in fan-like bunches of sharp needles. The brown pasty mass was dry but very hygroscopic. It seems that these salts, like the bases crystallized by Crichton (7), crystallize with varying amounts of water of hydration. When heated in vacuum, as the temperature is elevated they keep giving up more and more of their water of hydration. This salt began to decompose at 140°C . It was soluble in alcohol, water and acetic acid. The assay for nitrogen gave 2.96%.

Tetra-methyl Ammonium Valeriate. A solution of 20 grams of pure valeric acid was neutralized with the base. It also gave a jelly when evaporated to a syrupy residue on a steam bath. It was reduced to a friable mass after heating for eight hours in the vacuum oven at 115°C. Under the microscope the jelly showed long filaments similar to the filaments of potassium soap jelly. The salt began to decompose at 140°C. It was soluble in alcohol, water and acetic acid. The assay for nitrogen gave 6.1%.

Tetra-methyl Ammonium Oxalate. A solution of 50 grams of oxalic acid was neutralized with the base. When purified and evaporated down the resulting product was a white hygroscopic crystalline mass. This salt crystallized from alcohol in thin plates, rectangular, with sharp corners and square ends. After six hours in the vacuum oven at 110°C a fine white powder was produced. The salt decomposed at 180°C. It was soluble in alcohol and water. The assay for nitrogen gave 4.7%.

Tetra-methyl Ammonium Tartrate. A solution of 40 grams of crystalline tartaric acid was neutralized by the base. It was very difficult to free from water. After being evaporated on the bath, and two six hour periods in the vacuum oven at 110°C. a friable crystalline mass resulted. It decomposed at 175°C. It dissolved in water and alcohol. The assay for nitrogen gave 8.8%.

Tetra-methyl Ammonium Citrate. This salt was made in the same way as the other salts, but it gave so much trouble in trying to reduce it to a dry powder free from moisture that it was not assayed. It was soluble in water and alcohol, and decomposed at 150°C.

Tetra-methyl Ammonium Benzoate. An alcoholic solution of 30 grams of benzoic acid was neutralized by the base. When evaporated at 100°C a hygroscopic mass of white crystals resulted. The salt was dried at 110°C in the vacuum oven. It was a white crystalline powder, soluble in water and alcohol containing 7.3% nitrogen.

Tetra-methyl Ammonium Cinnamate. An alcoholic solution of 30 grams of pure cinnamic acid was neutralized by the base. It gave up water with difficulty. The temperature of the vacuum oven was raised to 120°C when it came out of the oven a brown mass. It was hygroscopic, soluble in water and alcohol, and showed a nitrogen content of 5.1%.

Tetra-methyl Ammonium Gallate. An alcoholic solution of gallic acid was neutralized with the base. After evaporating and drying in the vacuum oven at 110°C. for six hours a dark crystalline powder resulted. It was hygroscopic and dissolved in water and alcohol with deep brown solutions.

Analysis of Tetra-methyl Compounds.

After a few preliminary experiments, it was determined to assay these compounds for nitrogen by the Gunning-modification of the Kjeldahl method. The salts were so hygroscopic that samples had to be weighed in the absence of air. Four percent boric acid was used in the receiving flasks, and the absorbed ammonia was titrated with N/10 HCl. The following are the tabulations:

<u>Salt</u>	<u>Weight Sample</u>	<u>Cc. of N/10 HCl</u>	<u>Percent Nitrogen</u>
H.CO.O. (CH ₃) ₄ N. 2. HOH	1.4765	95.6	9.07
, ,	2.3640	152.20	9.03
, ,	1.8492	118.0	8.94
, ,	1.5660	101.7	9.19
CH ₃ .CO.O.(CH ₃) ₄ N. 7 HOH	2.4190	93.4	5.41
, ,	2.4365	94.4	5.39
CH ₃ .CH ₂ .CO.O.(CH ₃) ₄ N. ? HOH	1.0980	30.1	3.92
, ,	0.7688	22.5	4.10
CH ₃ .(CH ₂) ₂ .CO.O.(CH ₃) ₄ N - ? HOH	1.1720	26.6	2.76
, ,	0.7130	16.1	2.16
CH ₃ .(CH ₂) ₃ .CO.O.(CH ₃) ₄ N - ? HOH	0.5000	21.5	6.02
, ,	0.4940	21.2	6.15
(CO.O) ₂ ((CH ₃) ₄ N) ₂ . 10 HOH	1.7880	60.7	4.69
, ,	1.8515	62.4	4.78
, ,	0.6400	22.3	4.88

Analysis of Tetra-methyl Compounds Continued

<u>Salt</u>	<u>Weight Sample</u>	<u>Cc. of N/10 HCl</u>	<u>Percent Nitrogen</u>
$(CO.O)_2 \cdot ((CH_3)_4N)_2 \cdot 10 HOH$	1.6540	55.4	4.65
$(CHOH.CO.O.(CH_3)_4N)_2 \cdot 2 HOH$	0.6875	43.7	8.89
, ,	0.9200	59.8	9.10
$CH_2.CO.O.(CH_3)_4N$	0.5927	30.1	7.98
$C(OH).CO.O.(CH_3)_4N \cdot 10 HOH$	0.3110	15.4	8.11
$CH_2.CO.O.(CH_3)_4N$	1.1050	39.3	4.98
$C_6 H_5.CH:CH.CO.O.(CH_3)_4N$	0.7700	28.8	5.24
, ,	0.7565	39.8	7.26
$C_6 H_5.CO.O.(CH_3)_4 N.$	0.5010	26.4	7.35
, ,			

Tabulation of Tetra-methyl Ammonium Salts.

<u>Salt</u>	<u>Solu- bility Gms.in 100 HOH</u>	<u>Temp. of De- comp. C.</u>	<u>Percent of Nitrogen Calc. Found</u>	<u>Solvent for Crystallization</u>
Tet.Me.Am.Formate	195.2	180°	9.03 9.1	Alc. Benz.
Tet.Me.Am.Acetate	296.7	190°	5.4 5.45	,, ,,
Tet.Me.Am.Propionate	190.3	140°	9.8 4.0	,, ,,
Tet.Me.Am.Butyrate	232.7	140°	8.7 2.96	,, ,,
Tet.Me.Am.Valeriate	193.	140°	8.0 6.1	,, ,,
Tet.Me.Am.Oxalate	165.	180°	4.7 4.8	,, ,,
Tet.Me.Am.Tartrate	376.	175°	8.8 9.0	,, ,,
Tet.Me.Am.Cinnamate	61.6	130°	5.0 4.9	,, ,,
Tet.Me.Am.Benzoate	206.8	140°	7.3 7.4	,,
Tet.Me.Am.Gallate	140.7	130	- -	,,

Conductivity of Tetra-methyl Ammonium Salt Solutions

The formate, acetate and oxalate were selected as examples of this series of compounds. Eight-normal solutions were made of each of the salts. From these the solutions of uniform dilutions up to N/512 were made, and the conductivity of each of these solutions was taken by means of a potentiometer. In determining the conductivity at infinite dilution, $1/\Lambda$ was plotted against $(C\Lambda)^{0.5}$ and the best straight line extrapolated to the line of infinite dilution. Degree of ionization = Λ/Λ_0 .

Ionization of Tetra-methyl Ammonium Salts.

<u>Salt.</u>	<u>Concen</u> <u>tration</u>	<u>Specific</u> <u>Conduc-</u> <u>tance</u>	<u>Equiv.</u> <u>Conduc-</u> <u>tance</u>	<u>$1/\Lambda \times$</u> <u>10^{-3}</u>	<u>$(C\Lambda)^{0.5}$</u>	<u>Degree</u> <u>Ioniz-</u> <u>ation.</u>
Tetra-	N/8	0.0139	111.1	9.002	3.727	63.34
methyl-	N/16	0.0075	119.5	8.376	2.732	68.05
ammonium-	N/32	0.0041	130.6	7.655	2.023	74.45
formate	N/64	0.0022	141.5	7.064	1.487	81.70
	N/128	0.0012	147.5	6.782	0.944	84.83
$\Lambda_0 = 175.4$	N/256	0.0006	155.7	6.424	0.780	88.75
	N/512	0.0003	160.3	6.240	0.559	91.12
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Tetra-	N/8	0.0153	122.3	8.176	3.911	58.96
meth-	N/16	0.0086	137.8	7.257	2.931	66.41
ammonium-	N/32	0.0047	151.2	6.660	2.166	72.36
acetate.	N/64	0.0025	162.1	6.171	1.592	78.11
	N/128	0.0013	170.5	5.865	1.015	82.18
$\Lambda_0 = 207.5$	N/256	0.0007	181.5	5.510	0.831	87.48
	N/512	0.0004	192.0	5.209	0.612	93.17
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Tetra-	N/8	0.0232	197.6	5.060	3.852	52.57
methyl-	N/16	0.0135	215.8	4.634	3.672	57.40
ammonium-	N/32	0.0074	237.1	4.205	2.726	63.26
oxalate.	N/64	0.0041	266.1	3.773	2.035	70.51
	N/128	0.0022	286.6	3.488	1.477	76.25
$\Lambda_0 = 376.0$	N/256	0.0012	305.0	3.277	1.091	81.17
	N/512	0.0006	326.7	3.071	0.797	86.62

Physical Properties of the Tetra-methyl Ammonium Salts

The tetra-methyl ammonium salts are characterized by great affinity for water. When exposed to the air, the salts of the organic acids soon liquify. They are very soluble in water and alcohol, and soluble in benzol. They are relatively insoluble in chloroform, ether, petroleum ether, and carbon disulphide. Most of these salts are stable at ordinary temperatures when stored in dry bottles. Some slowly decompose liberating trimethyl amine.

The salts of the fatty acids are soaps, and give gels like the potassium soaps. The soaps have average but not exceptional emulsifying and detergent properties.

Possible Utility of Tetra-alkyl Ammonium Salts

The tetra-methyl ammonium salts of organic acids are similar to the potassium and sodium salts in many double decompositions and reactions, yet they have their own peculiar characteristics. All are extremely hygroscopic. They absorb water from the air faster than calcium chloride and some use might be made of this property.

All reports of the biological action of these salts on the animal body indicate that they are powerful in their action on the heart and on blood pressure. Tetra-methyl ammonium formate has an action similar to Digitalis in that it stimulates the vascular nervous system causing contraction of the arterioles, and thus increasing arterial tension. Tetra-methyl ammonium oxalate is much more toxic than the formate. It retards the heart beat and increases blood pressure. The pharmacology of the other salts has not been published. The indications are that in the case of vascular stimulants for instance, where a salt of some organic compound is used, the tetra-methyl ammonium compound might be substituted for sodium; the resulting compound would probably be more soluble and the dosage would be reduced by reason of the enhanced physiological action. In general, the tetra-alkyl ammonium salts could be substituted for potassium or sodium salts

in any compound where the specific physiological action of the tetra-alkyl compound would be helpful.

Since the sodium ~~flu~~osilicate has been substituted for sodium flouride as an insecticide, the use of tetra-alkyl ammonium ~~flu~~osilicate is here indicated. It would be more toxic than the sodium salt and yet not so toxic as to make it dangerous for large animals in the amounts used to kill bugs and beetles. The toxicity of the tetra-alkyl ammonium is about equal to that of bismuth.

Tetra-methyl Ammonium Soaps

The soaps manufactured from the tetra-methyl ammonium base were linseed oil, oleic acid, stearic acid, olive oil, tallow, and palm oil. soaps. They were bland neutral soaps, not unpleasant in odor when fresh, and most of them stable at ordinary temperatures when fresh. Age, exposure to air, and elevated temperatures appear to start a decomposition in which trimethyl amine gas is liberated. This was noticeable to some extent with all the soaps, but the linseed oil soap decomposed the fastest. This of course eliminates these soaps from consideration in the field of cosmetics because of the offensive odor of the trimethyl amine. But it also very definitely indicates the possible use of tetra-methyl ammonium soaps as repellant sprays. These soaps showed just average emulsifying values.

Detergent Values of Tetra-methyl Ammonium Soaps

The method used in testing the detergent values of the soaps was that of Paul H. Fall (15). Fall begins with 2% solutions of the soaps and tests the suspension power of different dilutions down to 0.05%. The tests are made in 100 cc. oil-sample bottles. Instead of dirt, manganese dioxide of a uniform degree of fineness (No. 100) is used. One gram of the manganese dioxide is weighed into each oil-sample bottle, and 50 cc. of the dilution of soap is poured in. The bottles are shaken for fifteen seconds, and set at temperature for four hours. With the pipette exactly 43 mm. below the surface, 25 cc. of the suspension is drawn off into 25 cc. of a solution of ferrous ammonium sulphate containing 40 grams in a liter of 6 N. H_2SO_4 . In this solution the manganese dioxide is reduced to manganese sulphate and the ferrous iron is oxidized to ferric iron. The excess of ferrous iron is then titrated with N/10 Permanganate in the usual way. The difference between the number of ccs. of permanganate used and a blank indicates the amount of manganese dioxide in suspension in 25 cc. of the soap solution. The amount per kilogram is then computed and this is taken as the "MnO₂ Value" of the soap solution.

While the difference in values is not very wide by this method, the results do have practical significance.

"MnO₂ Value" of Tetra-methyl Ammonium Soaps

<u>Soap</u>	Dilution of <u>Soap</u>	<u>Cc. of KMnO₄</u>		<u>MnO₂ Value</u>	
		<u>Samples</u>		<u>Samples</u>	
		<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
Tetra-methyl	2.0%	23.8	23.7	50.2	52.1
Ammonium	1.4%	21.5	21.4	90.5	92.1
Tallow Soap	0.8%	21.4	21.2	92.1	95.9
	0.4%	21.3	21.2	94.1	95.9
	0.2%	19.3	19.4	127.6	126.8
	0.1%	21.7	21.6	86.9	88.7
Tetra-methyl	2.0%	24.8	24.9	33.0	31.2
Ammonium	1.4%	22.0	22.2	90.5	92.1
Olive Oil Soap	0.8%	21.6	21.7	92.1	95.9
	0.4%	21.5	21.5	90.5	90.5
	0.2%	20.4	20.5	105.0	107.9
	0.1%	21.0	21.2	99.5	95.9
Tetra-methyl	2.0%	22.8	22.8	69.5	69.5
Ammonium	1.4%	20.6	20.4	105.1	109.3
Palm Oil Soap	0.8%	19.4	19.3	126.8	127.6
	0.4%	19.6	19.0	134.3	134.3
	0.2%	18.3	18.2	146.2	147.0
	0.1%	19.7	19.8	121.7	119.2

"MnO₂ Value" of Tetra-methyl Ammonium Soaps

	Dilution of Soap	Cc. of KMnO ₄		MnO ₂ Value	
		Sample		Sample	
		A	B	A	B
Castile Soap	2.0%	23.5	23.3	55.7	59.3
(Sodium Olive	1.4%	21.5	21.4	90.5	92.0
Oil Soap)	0.8%	19.5	19.5	125.1	125.1
	0.4%	18.8	18.6	139.7	140.8
	0.2%	18.1	18.3	149.8	146.2
	0.1%	18.6	18.8	140.8	139.7

Comparison of Detergent Values of Soaps

<u>Soap</u>	<u>Optimum Dilution</u>	(A) <u>Mn O₂ Values</u>	(B) <u>Mn O₂ Values</u>
Castile Soap	2.0%	149.8	146.2
Tet.Me.Palm Oil Soap	2.0%	146.2	147.0
Tet.Me.Tallow Soap	2.0%	127.6	126.8
Tet.Me.Olive Oil Soap	2.0%	105.0	107.9

This comparison indicates that the tetra-methyl ammonium salts have about the same detergent value as the sodium soaps. The detergent values by the Fall method are slightly lower than Castile Soap on average, but in drying the samples for the test there was a slight

decomposition of the tetra-methyl ammonium soaps. The actual detergent values undoubtedly compare very well with the sodium soaps. However, the tetra-methyl base will perhaps never compete with sodium and potassium in the field of commercial laundry and cosmetic soaps. The increased cost of the synthetic base, and the offensive odor of its decomposition products preclude this. But the indications are very good that there will be a very practical use for these soaps as insect repellants.

Tetra-methyl Ammonium Linseed Oil Spray

The linseed oil soap was selected as the most promising as a spray material to be used as an insecticide and an insect repellant. It continually gives off the odor of trimethyl amine, which should be repulsive to all forms of insect life that feeds on fresh tender shoots and green leaves. It might not be to the forms of insect life that live on decaying animal and vegetable matter. Trimethyl amine belongs to the series of compounds that result from the decomposition of animal matter and carry the repulsive odor of putrid things. Hence any compound that would continue to give off the odor of a triamine for a long period of time should be a good repellant. Since linseed tetra-methyl ammonium soap promised to be a repellant, a 2% solution in water was used as a spray.

Practical Test of the Soap Spray

In the following tests rose bushes were sprayed that were badly infested with aphids. The tender shoots and buds of the bushes sprayed were well covered with the insects.

April 2. Sprayed one-half of rose bush that was covered with aphids. Left the other half unsprayed for a comparison of results. Contact killed the aphids. A 2% solution in water was used.

April 4. No aphids to be found on the sprayed half of the rose bush. The unsprayed side was still covered with the insects.

April 6. Still there are no aphids on the sprayed half of the bush. Unsprayed half still infested. A slight odor of trimethyl amine could be detected on the foliage.

April 11. Still no aphids on the sprayed twigs.

April 13. Diluted the spray one-half with water making a 1% solution and sprayed the infested half of the bush. The other half had been free from aphids for eleven days as a result of the spray treatment. Sprayed other rose bushes with the 1% solution.

April 15. No aphids on any of the sprayed bushes.

April 18. No aphids on the sprayed bushes. Still slight odor of trimethyl amine on the foliage of the

original bush. The spray apparently did not retard or injure the plant growth in any way. Some tender house plants sprayed with the 1% solution showed no ill effects.

April 20. No aphids on the sprayed bushes. Other bushes were sprayed with the 1% solution. The 1% solution killed the aphids on contact as well as the 2%.

April 22. All the rose bushes sprayed with the soap are free from aphids. Most of the rose bushes in the neighborhood were badly infected. On one bush, the spray had been effective for twenty days.

May 1 The sprayed bushes are still free from aphids with the exceptions of two twigs which might have escaped the spray. Several rains have washed the leaves since the tests began. Still a thin film of the spray seems to cling to the foliage. A dust storm which persisted for three days and some dry weather has not dissipated the repellant action of the spray.

May 10. The sprayed bushes are still free from aphids though many of them stand by the side of bushes that have been infested continually during the past thirty days. Apparently the spray has proven to be a repellant for aphids that will persist for more than thirty days. The odor of trimethyl amine could be detected on the foliage for twenty days. Tetra-methyl ammonium linseed oil soap is evidently an aphid repellant.

How the Spray Works

The efficiency of the tetra-methyl ammonium linseed oil soap as an aphicide is probably due in part to the fatty acid mixture and in part to the tetra-methyl ammonium. Whale oil sodium and potassium soaps will destroy aphids but it is always necessary to spray again in a very few days to keep plants free from aphids. Hence the soap prepared from linseed oil and this synthetic base has strong repellant properties. The fact that this soap continues to give off the trimethyl amine gives it a decided repellant value.

The decomposition that takes place in this soap is a splitting of the soap into the methyl ester of the fatty acids and the gas trimethyl amine. These esters probably undergo a certain amount of hydrolysis, the fatty acids are set free and begin to oxidize like linseed paint, or the esters may themselves form an insoluble film which holds the soap on the leaves and prevents the rain from washing it off. The soap continues to give off the trimethyl amine gas. Thus the spray persists and is an effective repellant until completely decomposed. The gas trimethyl amine persists on any absorbent material for ten to twenty days. It seems to be easily adsorbed on the surface of almost anything. This in part accounts for the persistence of the offensive odor.

Method of Manufacture of Soap

If the linseed and the fish oil soaps of tetramethyl ammonium are found to be practically useful as repellants, then an economical method of manufacture becomes an immediate problem. The base made from ammonium chloride and paraformaldehyde would be expensive., though the alcohol and potassium chloride might be recovered as by products.

Perhaps the most economical method would be to make the trialkyl amines^{by} an electrical method direct from the alcohols; united with the alkyl halides; converted to the base and then made into soap. Some work has already been done in this direction and the problem offers no unusual difficulties.

Further Research Problems

If trimethyl amine proves to be an effective repellent and commercially practical; what would be the action of the triethyl, tripropyl, tributyl, triamyl, and so on up the list of trialkyl compounds. These compounds and their respective tetra-alkyl ammonium soaps gives a very interesting and promising field for further research. Also there are probably tetra-compounds of arsenic, antimony and phosphorus that may have value in this field of insecticides, fungicides and repellants.

SUMMARY

1. The tetra-alkyl ammonium bases have been known for more than seventy years, yet no good use of any commercial or industrial importance has been found for these interesting compounds.

2. The impression that existed for more than fifty years, that these bases could not be made without the use of silver oxide is proven erroneous.

3. The tetra-methyl and tetra-ethyl ammonium radicals act like free radicals of tetra-valent nitrogen. They form amalgams with mercury like sodium and potassium.

4. The tetra-methyl ammonium radical has a strong physiological effect in that it increases blood pressure.

5. The tetra-methyl ammonium halide is made by uniting the alkyl halide with the corresponding trialkyl amine. Then the base is made by treating with alcoholic KOH in an alcohol solution.

6. The amount of potassium as an impurity in the solution when made by this process is practically nil.

7. The tetra-methyl ammonium salts of the common organic acids were made and all were very hygroscopic. When reduced to dry powders they were white and crystalline. They were very soluble in water, and highly ionized.

Summary Continued

8. Most of the qualitative reactions of the tetramethyl ammonium radical ~~are~~ like potassium and sodium. Notable exceptions are its reactions with mercurous ions and with potassium and sodium precipitants. In some reactions this radical seems more chemically active than either potassium or sodium.

9. The tetra-methyl ammonium soaps are stable when fresh and at low temperatures, but begin to decompose at elevated temperatures. They have about the same detergent value as the sodium soaps.

10. The tetra-methyl ammonium linseed oil soap has exceptional value as a repellant for aphids. The reason for this seems to be that the soap slowly decomposes on the plant leaves and stems forming a paint like film over a layer of soap which continues to decompose giving off the offensive odor of trimethyl amine. Thus the bushes are continually in a fog of the gas until the soap has completely decomposed. Using a 1% solution of this soap as a spray for aphids has revealed that a re-spraying is not necessary for more than twenty days, and perhaps for the season.

11. Further research is indicated in the field of the other alkyl salts of the organic acids; the other alkyl ammonium soaps; and in the soap manufacture.

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